Coordination Chemistry of Thioethers, Selenoethers, and Telluroethers in Transition-Metal Complexes

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I. Introduction

Although the coordination chemistry of group 6B donor ligands is not as prolific as that of the group 5B[1,2] or group 7B[3] donor ligands, there are many reviews on the various types of chalcogen containing ligands (see Table I). Much of the recent work has centered on the so-called "non-innocent" ligands,[4-7] and the last review dealing with all types of group 6B ligand complexes was published in 1965.[15] There is no review in the literature dealing specifically with the coordination chemistry of thioethers, selenoethers, and telluroethers, an area neglected compared to other donor types, reflecting the much poorer coordinating ability of thioethers, selenoethers, and telluroethers compared with the charged group 6B and 7B ligands or the uncharged group 5B ligands.

Telluroethers and to a lesser extent selenoethers suffer from an inherent instability of the ligands themselves. It is difficult to prepare all but the simplest organotellurium ligands, and at the present time only monodentate telluroethers are known. The organic chemistry required to prepare the organo-group 5B ligands is well understood, but that required in the preparation of similar types of ligand with selenium and tellurium is at the very least obscure. This discrepancy has recently been somewhat remedied by the appearance of two books, one discussing selenium chemistry[16] and the other the chemistry of tellurium.[13]

To avoid ambiguity we will use the term thioether for R_2S and not sulfide, which has also been used for this group. Sulfide more correctly describes S^{2-} and will be used as such if required. Mercaptide or thiolo will describe the group RS^-. The appropriate terms for selenium and tellurium species are analogous to those for sulfur as above.

II. Scope of the Review

The literature to the middle of 1980 is fully covered. Structure and bonding, alkylation and dealkylation at the coordinate donor, and inversion at coordinated sulfur and selenium are discussed, and a general literature survey is included. Schiff bases and amino acids containing a thioether donor will not be covered. We consider the transition metals to be the d-block elements and will thus include the subgroups scandium to zinc.

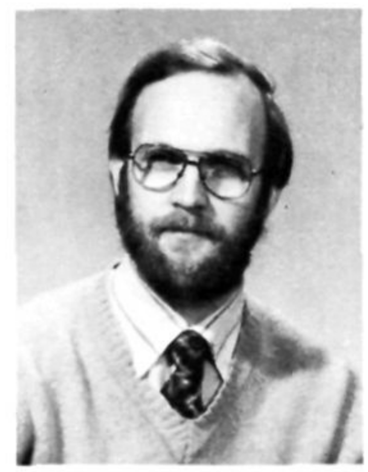
III. Structure and Bonding

A. Structure

Before turning to the question of the nature of the bonding in thioether, selenoether, and telluroether complexes, we shall examine the structural data available for these complexes, since any theory of bonding that is to have any chance of success must be able to explain all the known structural features.

1. X-ray Diffraction Studies

The structural data available from X-ray diffraction studies for thioether, selenoether, and telluroether



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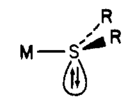
0009-2665/81/0781-0365$06.00/0

Table I. Reviews on Chalcogen-Containing Ligands

author(s)	subject	ref
Schrauzer	1,2-dithiolene complexes	4
McCleverty	1,2-dithiolene complexes	5
Coucouvanis	dithio acid and 1,1-dithiolene complexes	6
Eisenberg	dithiolato complexes	7
Ali and Livingstone	S-N chelate complexes	8
Lindoy	S-ligand complex reactions	9
McAuliffe and Murray	S-amino acid complexes	10
Jorgensen	Electronic spectra of S-ligand complexes	11
Jensen and Jorgensen	organic Se and Te complexes	12
Irgolic	organic Te complexes	13a
Livingstone	monothio-β-diketone complexes	14
Livingstone	S, Se, and Te complexes	15

complexes is listed in Tables II and III. We have been able to find only one report of an X-ray diffraction study of a telluroether complex. In order to determine whether the M–E bond is "normal" in length, approximate values for the sums of the covalent radii are given. These estimated sums of covalent radii are, in general, taken from Pauling's data,[79] using radii appropriate to the coordination number and oxidation state of the central metal ion. For niobium(III), tantalum(III), molybdenum(II), molybdenum(IV), cobalt(III), rhodium(III), and nickel(II), the observed bond lengths are about what would be expected. For the other metal ions studied, with the exception of rhenium(II) and copper(II) in some complexes, the observed bond lengths are shorter than the calculated sum of the covalent radii. Thus for chromium(0) in both $[Cr(EtS(CH_2)_2SEt)(CO)_4]$ and $[Cr(MeS)_2C{=}C(SMe)_2)(CO)_4]$ the chromium–sulfur bonds are significantly shorter than the calculated sum of the covalent radii.[20,21] In addition the chromium–carbon bonds to the carbonyl groups trans to sulfur are significantly shorter than to the cis carbonyls. Both observations are consistent with the presence of chromium(0) to sulfur π back-donation. By comparison of the bond lengths in these thioether complexes and in $[Cr(Ph_2PCH_2CH_2PPh_2)(CO)_2]$, it is suggested that the thioether sulfur atoms are both poorer σ donors and poorer π acceptors than phosphorus in 1,2-bis(diphenylphosphino)ethane. For palladium(II), platinum(II), copper(I), and gold(I), the observed bond lengths are shorter than expected on the basis of the sums of the covalent radii, an observation that has often led to the suggestion that these M–S bonds, together with the Pd–Se bond where the same is also found (Table III), involve some π back-donation from metal to sulfur or selenium (see Bonding, section IIIC). The only Pd–Te bond length so far determined (Table III) is only slightly shorter than the sum of the covalent radii, suggesting little or no π bonding in this bond. In three of the five copper(II) complexes studied, the Cu–S bonds are significantly longer than the calculated sum of the covalent radii; this is consistent with the weakness of copper(II)–thioether bonds. Mercury(II) is rather variable, some Hg–S bonds being shorter, some about the same, and some longer than the calculated sum of covalent radii.

In all the complexes the bond angles about sulfur, selenium, and tellurium are approximately tetrahedral, consistent with the presence of one lone pair of electrons in an orbital that can be roughly described as sp^3.



Distortions from the ideal tetrahedral angle would be expected and are indeed found where the metal and sulfur or selenium atoms form part of a ring. Most M–S–C angles lie below rather than above the tetrahedral angle, an observation that can be attributed, according to personal prejudice, either to the large steric effect of a lone pair (Gillespie–Nyholm approach) or to a less than complete involvement of the s orbital in any orbital hybridization. The only important exception to this generalization is the diethyl sulfide bridged platinum(II) dimer, $[Br_2Pt(SEt_2)_2PtBr_2]$, where the Pt–S–C bond angles open up to a mean value of about 117°. This is a consequence of a bridging sulfur carrying no nonbonding lone pairs of electrons, so that the geometry about sulfur is dominated by the geometric requirements of the PtS_2Pt 4-membered ring (Pt–S–Pt = 98.1 (5)°).[42]

The trans influence of ligands can be determined by analyzing the influence of a series of ligands on the bond length of a given metal–ligand bond. For square-planar complexes, the metal–chlorine bond is frequently used as a probe, and accordingly the relevant data have been collected in Table IV. The magnitude of the observed effects is small compared to the precision with which they can be measured, but it is clear from Table IV that thioethers and selenoethers lie low in the trans-influence series, above oxygen and comparable to chloride. With platinum(II), thioethers appear to have a trans influence comparable to that of primary amines, but when the central metal is palladium(II) the trans influence of thioethers is slightly larger than that of primary amines. There are insufficient data to place thioethers into a trans-influence series for octahedral complexes, although it is interesting to note the Co^{III}–Cl trans to a thioether group in $[Co(H_2N(CH_2)_2S(CH_2)_3S(CH_2)_2NH_2)Cl(NO_2)]Cl$ is significantly longer (2.27 Å)[29] than Co^{III}–Cl trans to ammonia (1.91 Å)[90] in $[Co(NH_3)_5Cl]Cl_2$. In contrast, the trans influence of thioethers on Co^{III}–N bonds appears to be negligible.[30] The higher trans influence of the thioether ligand than of a nitrogen ligand also parallels the trans effects of these two ligands since the cation $[Co(H_2N(CH_2)_2S(CH_2)_3S(CH_2)_2NH_2]Cl(NO_2)]^+$ was prepared by treating the dinitro complex with hydrochloric acid. It was the nitro group trans to the thioether rather than that trans to NH_2 that was replaced.[91] For linear gold(I), the variation of the Au–Cl bond length trans to a thioether (2.29 (1) or 2.33 (1) Å)[69] is greater than the variation observed on changing the ligand trans to Cl from Cl (Au–Cl in $AuCl_2^-$ = 2.31 Å)[92] to PCl_3 (Au–Cl in Cl_3PAuCl = 2.33 Å)[93] so that it is impossible to construct a trans-influence series.

X-ray diffraction studies of the palladium(II) and platinum(II) complexes $[L_2M_2X_4]$ (X = Br; M = Pd, L = Me_2S; M = Pt, L = Et_2S) confirmed the suggestion made on the basis of infrared spectroscopy[94] that in the palladium(II) complex the dimethyl thioether ligands are terminal whereas in the platinum(II) complex the diethyl thioether ligands are bridging.[42] When the thioether is in a bridging situation, the metal–sulfur bond is significantly shorter (2.21–2.25 Å) than when it is terminal (2.30 Å) due to the absence of repulsion between a nonbonding lone pair of electrons when the sulfur is bridging. However the total number of repulsions between the ligand nonbonding lone pairs and the metal nonbonding d electrons is not altered on transferring a bromide from terminal to bridging since a terminal bromide has three nonbonding lone pairs whereas a bridging bromide has only two. Accordingly the reason the palladium(II) and platinum(II) complexes differ so much in structure is far from clear, although it may well be due to the spatial dissimilarity of the 4d and 5d orbitals. The situation in the palladium(II) and platinum(II) complexes is paralleled in the tantalum(III) and niobium(III) complexes of tetrahydrothiophene where the bridging M–S bonds are shorter than the terminal M–S bonds, whereas the reverse is true for M–Br bonds.[17] It is also paralleled in molybdenum(II) thioether complexes[22] whereas for copper(I) the structure of $[(Et_2S)_3Cu_4I_4]$ shows bridging thioether bonds to copper(I) to be longer (2.337 and 2.331 Å) than terminal bonds (2.297 and 2.298 Å).[57]

The structure of $[Pt(CF_3SCH(CH_3)CH_2SCF_3)Cl_2]$ is of interest since substitution of CH_3 by the strongly electronegative CF_3 might well be expected to reduce the σ-donor ability of sulfur but could also facilitate π back-donation to the sulfur. In fact the effect is marginal; the Pt–S distances in $[Pt(CF_3SCH(CH_3)CH_2SCF_3)Cl_2]$ are only slightly shorter than in *cis*-$[Pt(S(C_6H_4Cl)_2)_2Cl_2]$ and *cis*-[Pt(L-methionine)Cl_2] (see Table II) and the Pt–Cl bond lengths trans to sulfur in all three compounds are virtually identical. Thus the presence of CF_3 on sulfur has only a minor effect on the Pt^{II}–S bonding, in contrast to the influence of CF_3 on phosphorus, where a CF_3 substituent results in a very short Pt–P bond that has a very weak trans influence.[95] This difference is consistent with (i) the Pt^{II}–S bond being weaker than the Pt^{II}–P bond as a consequence of the much weaker donor ability of thioethers as compared to tertiary phosphines, (ii) the π back-donation present in a Pt^{II}–S bond being much less than in a Pt^{II}–P bond, and (iii) the already low trans influence of thioethers as measured by bond length data which cannot be reduced much further by an electronegative group.

The two complexes *trans*-$[PtBr_2(OCH_2CH_2ECH_2CH_2)]$ where E is S or Se show a marked difference in their thermodynamic properties for site inversion. Investigation of the solid-state structures of these complexes by X-ray diffraction shows that the Pt–S bond lies equatorial to the six-membered ring whereas the Pt–Se bond is in the axial conformation.[52] This difference cannot be explained by intermolecular packing forces, since packing is significantly less efficient in the selenium than the sulfur complex. It has been suggested that axial bonding, as observed in the selenium complex, is the preferred mode of bonding, but in cases where the substituent (here platinum) would interact sterically with the β-methylene groups, equatorial bonding may be preferred, as observed here for the smaller sulfur ligand. In support of this, cyclic ether ligands always link equatorially and cyclic selenoether ligands always link axially whereas examples of both equatorial and axial linkage are known for cyclic thioether ligands.

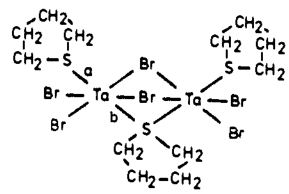
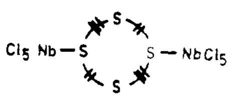
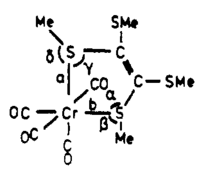
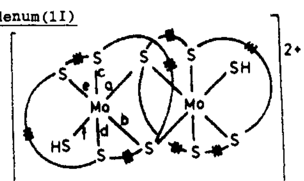
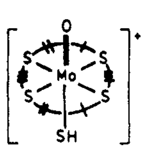
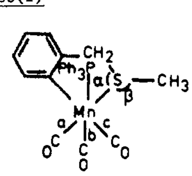
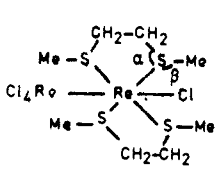
2. Vibrational Spectroscopy

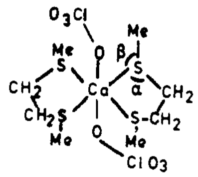
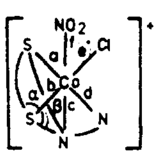
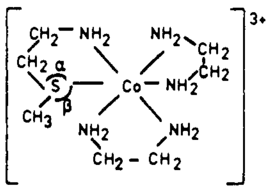
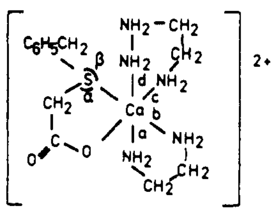
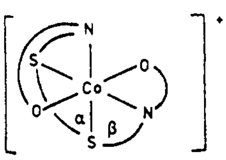
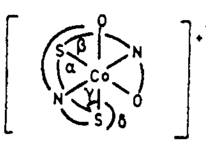
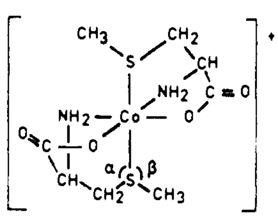
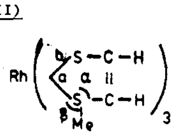
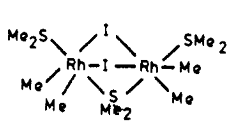
The use of infrared and Raman spectroscopy as techniques for determining structure is not as straightforward as X-ray diffraction. This arises for two reasons: (i) For complex polyatomic molecules of relatively low symmetry, more than one fundamental mode often contributes to a given band in the spectrum. Thus the statement that "a band at x cm^{-1} is due to an A–B vibration" is incorrect, although in some cases the statement "the band at x cm^{-1} is largely due to an A–B vibration" may well be close to the truth. (ii) In order to investigate the bonding between metals and ligands it is generally necessary to carry out a detailed force field analysis, and this requires data from many isotopically substituted species.

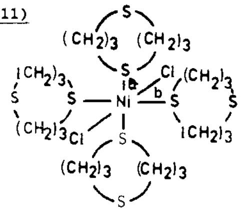
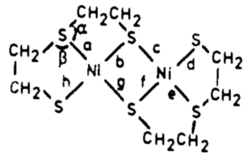
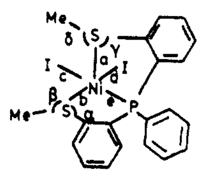
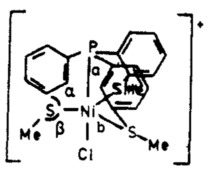
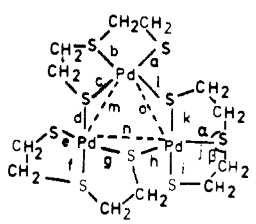
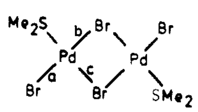
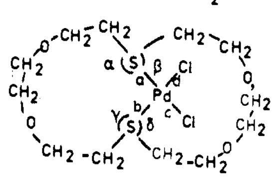
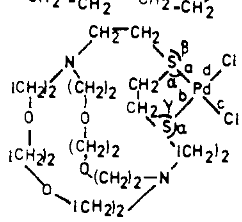
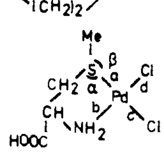
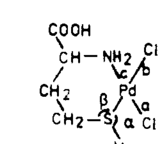
Most of the more detailed spectral studies have been carried out on palladium(II), platinum(II), platinum(IV), copper(II), gold(I), and mercury(I), the results for which are summarized in Table V. Metal–sulfur, –selenium, and –tellurium bands are often weak in intensity and occur in a region of the spectrum similar to that of the metal–halogen band of the halogen in the same period of the periodic table. Thus metal–sulfur vibrations occur around 320 ± 20 cm^{-1} (cf. metal–chlorine), metal–selenium vibrations around 220 ± 20 cm^{-1} (cf. metal–bromine), and metal–tellurium around 200 ± 30 cm^{-1} (cf. metal–iodine). There are, as inspection of Table V shows, some major exceptions to these generalizations. If the correctness of these exceptions is confirmed, then they serve to emphasize the importance of vibrational interactions in these complexes. The most important exceptions to the above generalizations are the thioether-bridged platinum(II) complexes $[(R_2S)_2Pt_2X_4]$ where the metal–sulfur stretching vibration around 400 ± 20 cm^{-1} reflects the much stronger metal–sulfur bond when thioethers are bridging rather than terminal[109]—a result confirmed by X-ray diffraction.[42]

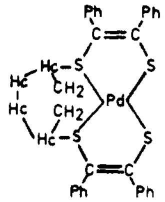
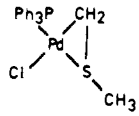
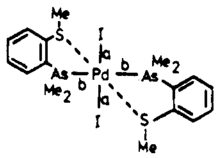
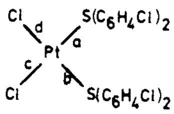
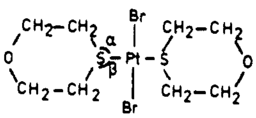
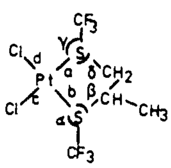
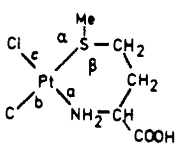
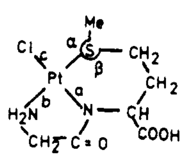
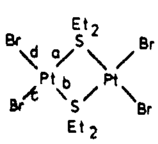
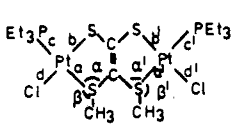
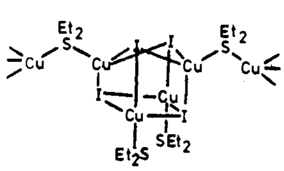
In spite of the problem of vibrational interactions, some attempts have been made to use infrared spectroscopy as a source of information concerning the nature of the metal–thioether link. Studies of the C–O stretching frequencies in $[MoL_3(CO)_3]$ and $[ML(CO)_5]$ where M = Cr, Mo, and W have shown the ν_{CO} increases as L is varied in the order dien $\sim$ pyr $<$ R_2S $<$ PPh_3 $<$ $AsPh_3$ $<$ PCl_3,[114-116] suggesting that thioethers have a greater π-acceptor capacity than nitrogen donor ligands such as pyridine, but rather less than tertiary phosphines or arsines. Another often used source of data concerning the nature of metal–ligand bonding is the influence of a ligand on the metal–ligand bond in the trans position (often M–Cl). Although a great deal of data of this type has been recorded for platinum(II) in particular, its interpretation can be complicated by at least four factors: (i) intermolecular and intramolecular hydrogen bonding involving the Cl ligand being influenced; (ii) vibrational coupling, which will be particularly important when the influencing and influenced groups have similar metal–ligand stretching frequencies; (iii) the effect of the masses of heavy donors such as Te will be to lower the frequency of the trans M–Cl bond; (iv) organochalcogen complexes exhibit an

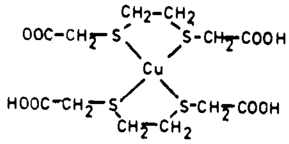
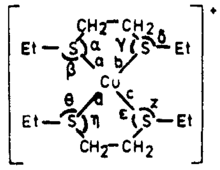
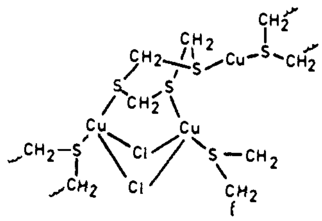
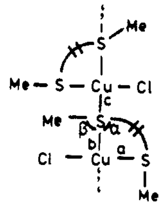
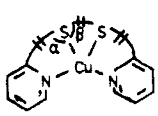
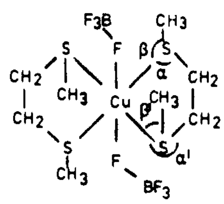
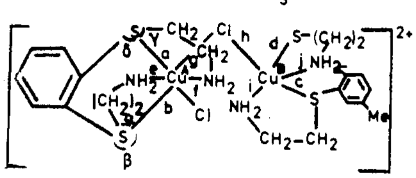
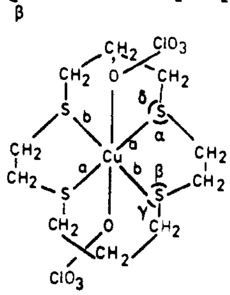
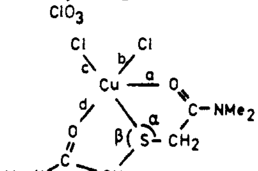
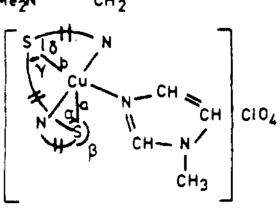
Table II. X-Ray Diffraction Data for Metal-Thioether Complexes

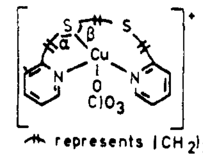
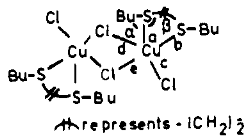
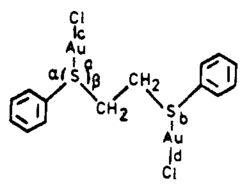
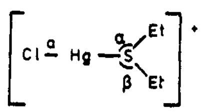
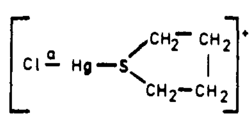
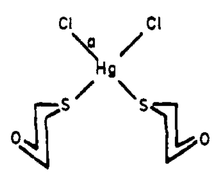
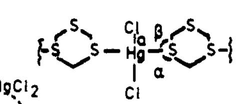
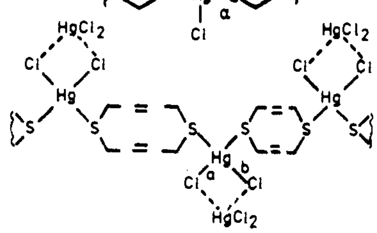
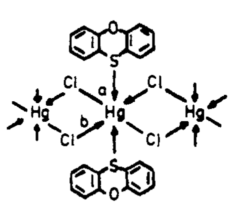
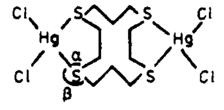
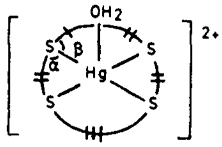
Complex	Observed M-S bond length (Å)	Sum of M and S covalent radii (Å)	∠M-S-C(°)	Further Remarks	Ref.
Tantalum(III) 	a 2.624(10)(mean) b 2.393(10)(mean)	2.42	Not reported	Ta-Ta = 2.710(2)Å consistent with a formal metal-metal double-bond	17
Niobium(III) Complex analogous to Ta^{III} above	a 2.632(14)(mean) b 2.487(13)(mean)	2.43	Not reported	Nb-Nb = 2.728(5)Å consistent with a formal metal-metal double-bond	17
Niobium(V)  represents $(CH_2)_2$ represents $(CH_2)_3$	2.71(1)	2.43	Not reported	Nb is six coordinate with Nb-Cl trans to S 0.05Å less than the other four Nb-Cl which average 2.31(1)Å	18,19
Chromium(0) 	a 2.425(1)	2.52[a]	α 111.0(0) β 104.7(1) γ 103.4(1) δ 113.0(1)	c 1.832(3)Å d 1.831(3)Å e 1.883(3)Å 1.892(3)Å	20
	a 2.370(2) b 2.385(2)	2.52[a]	α 106.1(2) β 113.0(3) γ 106.6(2) δ 113.1(3)	Cr-CO trans to S = 1.886(9)av. Cr-CO trans to CO = 1.833(7)av.	21
Molybdenum(II)  represents $-(CH_2)_3$	a 2.320(1) b 2.380(1) c 2.461(2) d 2.483(2) e 2.537(2) f 2.471(2)	-[b]	Not reported	Mo-Mo = 2.823(1)	22
Molybdenum(IV)  represents $-(CH_2)_3-$	2.476-2.484(2)	-[b]	Not reported		23
Manganese(I) 	2.310(4)	2.43	α 101.2(2) β 112.0(2)	5-membered chelate ring is not planar a 1.802(6)Å b 1.780(6)Å c 1.799(6)Å	24,25
Rhenium(II) 	2.439(8)	∿ 2.35[c]	α 103.8(1.0)(mean) β 113.2(1.2)(mean)	Re-Re = 2.293(2)Å From magnetic data best formulated as zwitterionic $Cl(C_4H_{10}S_2)_2Re^{+III}Re^{-III}Cl_4$	26,27

Cobalt(II)					
	2.290(8)	2.36Å	α 98(1) β 108(1)	Co lies at crystallographic centre of inversion	28
Cobalt(III)					
	a 2.24 b 2.22	2.26	α 109.5(2)(in a 6-membered ring) β 97.7(2)(in a 5-membered ring)	c 1.99Å d 1.99Å e 2.27Å f 2.09Å	29
	2.267(10)	2.26	α 97.9(3) β 114.2(2)	Co-N trans to thioether is within range of the other Co-N bond lengths (1.927(7) - 2.025(7))	30
	2.274(1)	2.26	α 94.4(1) β 111.6(1)	a 1.955(3) b 1.980(3) c 1.949(3) d 1.977(3) trans-influence of thioether is very small (0.02(2)Å)	30
	2.243(5)	2.26	α 101.2(6) β 104.1(5)		31
	2.253(3)	2.26	α 104.8(6) β 110.1(4) γ 102.6(5) δ 112.3(3)		31
	2.270(2) 2.273(2)	2.26	α 96.1(3), 95.5(4) β 104.9(3), 104.4(4)		32
Rhodium(III)					
	a 2.369(3) b 2.322(3)	2.36	α 103.6(4) β 114.0(4)		33
	Not given	2.36	Not given	Rh-Rh = 3.38Å	34

Nickel(II)					
	a 2.478(3) b 2.497(3)	2.43[d]	107.9(4), 112.6(4) 111.2(5), 108.3(5)	Ni-Cl = 2.358(3)Å, which is shorter than usual possibly due to weak bonding of thioether ligand	35
	Refs 26, 27 Ref 28 a 2.15 2.14 b 2.22 2.21 c 2.18 2.18 d 2.16 2.16 e 2.15 2.15 f 2.22 2.22 g 2.18 2.18 h 2.16 2.17	2.22[e]	α 96.6(6) β 102.9(6)	Both Ni atoms are close to square-planar. The two halves of the molecule are folded at a dihedral angle of 82°18' (refs 26, 27) 75.6° (ref 28)	36-38
	a 2.789 b 2.189	2.22[e]	α 107.1(8) β 106.3(14) γ 98.3(8) δ 108.9(15)	Square pyramidal with Ni only slightly (0.09Å) above basal plane. The long apical Ni-S bond is typical of the prolate spheroid electron density distribution of square pyramidal Ni^{II}. c 2.567Å d 2.514Å e 2.120Å Ni-I *trans* to P is longer than *trans* to S.	39
	2.267 (mean) 2.269(6) 2.290(7) 2.242(8)	2.22[e]	α 105.5(6)(mean) β 1.07.7(mean)	Trigonal bipyramidal with Ni 0.061(2)Å out of plane towards Cl a 2.113(7) b 2.227(7)	40
Palladium(II)					
	Mean 2.32 a 2.30 b 2.34 c 2.29 d 2.31 e 2.40 f 2.23 g 2.41 h 2.30 i 2.30 j 2.31 k 2.31 l 2.36	2.35	α 96.8(3.1) β 97.6(3.2)	Each Pd is in a distorted sq. planar environment. PdS_4 planes are inclined at 136°, 126° and 137° to Pd_3 plane. Pd-Pd 3.41(m) 3.66(n) 3.49(o)	41
	2.30(2)	2.35	113.4(25) 95.6(24)	a 2.404(4)Å b 2.429(4)Å c 2.447(11)Å	42
	a 2.302(2) b 2.305(2)	2.35	α 106.1(3) β 106.1(3) γ 108.4(3) δ 105.2(3)	c 2.313(2) d 2.316(3)	43
	a 2.264(1) b 2.265(1)	2.35	α 101.4(2) β 104.9(2) γ 101.7(2) δ 105.4(2)	c 2.305(1)Å d 2.301(1)Å	44
	Molecule 1 2.261(4) Molecule 2 2.230(4)	2.35	α 98.3(7) β 107.2(9)	Crystal contains 2 crystallographically independent molecules. b 2.044(10)Å c 2.312(7)Å d 2.305(4)Å Molecule 2 b 2.050(9)Å c 2.324(3)Å d 2.307(4)Å Pd-Cl *trans* to S is longer than *trans* to $-NH_2$	45
	2.265(4)	2.35	α 104.55(85) β 110.20(53)	a 2.308(4)Å b 2.332(4)Å c 2.061(14)Å Pd-Cl *trans* to S is longer than *trans* to $-NH_2$	46,47

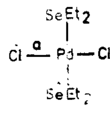
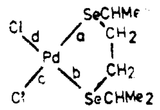
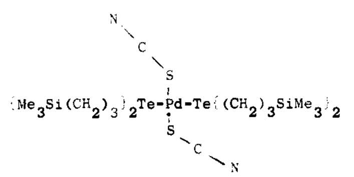
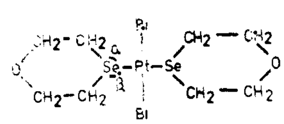
	a 2.300(3)	2.35	α 103.5(3) β 105.8(3)	b 2.278(3)Å	48
	-	2.35	-	CH_2-S = 1.76Å	49
	3.84(1)	2.35 (Sum of Van der Waals radii = 3.92)	-	Pd-S is non-bonded a 2.576(13)Å b 2.392(14)Å	50
Platinum(II)					
	a 2.278(7) b 2.292(6)	2.35	109.1(6)	c 2.301(6)Å d 2.298(6)Å	51
	2.281(3)	2.35	α 113.2(5) β 104.0(4)	Pt-Br = 2.420(1)(Å) Pt-S bond is equatorial to the ring	52
	a 2.239(3) b 2.260(4)	2.35	α 106.2(5) β 105.0(4) γ 106.6(5) δ 102.9(4)	c 2.290(4)Å d 2.295(3)Å	53,54
	2.26	2.35	α 105° β 112°	a 2.03Å b 2.32Å c 2.31Å	55
	2.25	2.35	α 104° β 108°	Loss of H on peptide N shown by a combination of X-ray and neutron diffraction. a 1.98Å b 2.07Å c 2.30Å	55
	a 2.21(1) b 2.25(5)	2.35	117.5(13) 120.5(18) 113.4(21) 115.6(26)	c 2.400(7)Å d 2.384(4)Å	42
	a 2.311(9) a' 2.335(10)	2.35[f]	α 103(1) α' 104(1) β 108(1) β' 106(2)	b 2.253(10) b' 2.253(10) c 2.267(10) c' 2.249(10) d 2.340(11) d' 2.334(11)	56
Copper(I)					
	bridging 2.337 and 2.331 terminal 2.297 and 2.298	2.39	108.9(1.2) 110.7(1.1)	An infinite chain of S bridged Cu_4I_4 cores whose geometry resembles a distorted cube	57

	2.30(twice) 2.34(twice)	2.39	-	Cu is tetrahedral	58
	a 2.310(5) b 2.280(4) c 2.303(5) d 2.318(5)	2.39	α 97.0(6) β 102.6(6) γ 96.1(5) δ 103.0(6) ε 97.1(6) ζ 101.1(6) η 93.3(5) θ 102.1(6)	Cu is approximately tetrahedral	59
	2.25-2.41	2.39	-	Cu-Cl 2.30-2.43Å	60
 ⟊ represents $(CH_2)_2$	a 2.342(2) b 2.336(1) c 2.315(1)	2.39	α 101.0(1) β 105.8(1)	Polymeric, bridged through S Cu-Cl = 2.239(1)Å	61
	2.345(1)	2.39	α 102.3(2) β 100.2(2)	Cu atom is approximately tetrahedral	63
Copper(II)					
	2.317(2)(mean)	2.34[g]	α 99.2(3) α' 102.8(3) β 108.7(2) β' 106.8(3)	Cu is at centre of a distorted octahedral with 4 short Cu-S bonds and 2 long Cu-F bonds (2.579(5)Å)	59
	a 2.445(6) equatorial c 2.431(6) equatorial b 2.609(6) axial d 2.565(6) axial	2.34[g]	α 90.7(6) β 103.0(6) γ 92.4(8) δ 106.0(7)	Cu^A is distorted square-planar; Cu^B is distorted square-pyramidal e 1.991(14) f 2.021(16) g 2.966(6) h 2.304(6) i 1.984(15) j 1.976(16)	64
	a 2.308(1) b 2.297(1)	2.34[g]	α 100.8(2) β 99.1(2) γ 104.2(2) δ 104.7(2)		65
	2.410(5)	2.34[g]	α 99.0(2) β 98.8(2)	a 2.284(3)-apical oxygen b 2.277(4) c 2.267(4) d 2.031(3) Cu is square pyramidal with 2xCl, S and 1xO in a plane and 1xO apical	66
 ⟊ represents $-(CH_2)_2-$	a 2.560(2) b 2.414(2)	2.34[g]	α 99.7(2) β 92.6(2) γ 105.6(2) δ 96.1(2)	The Cu atom is approximately square pyramidal with the sixth site occupied by a perchlorate counterion (Cu-O = 2.845(5))	67

	2.311(2) 2.316(2)	2.34[g]	α 103.3(3) β 98.2(4)	The Cu atom is essentially square pyramidal with a apical perchlorate Cu-N = 2.010(5)Å average Cu-O = 2.264(5)Å	63
	a 2.369(2) b 2.308(2)	2.34[g]	α 105.2(2) β 101.6(2)	Cu is either square pyramidal with a bridging Cl as apical ligand, or trigonal bipyramidal with apical Cl and S c 2.242(2) d 2.825(2) e 2.266(2)	68
Gold(I)					
	a 2.258(11) b 2.260(12)	2.36	α 105.9(11) β 106.0(12)	c 2.329(8)Å d 2.293(10)Å ∠Cl-Au-S = 177.8(4)° and 173.5(4)°	69
Mercury(II)					
	2.41	2.52	α 99.8 β 105.5	a 2.35Å ∠Cl-Hg-S = 158°	70
	2.40	2.52	α 99.9 β 102.6	a 2.30Å ∠Cl-Hg-S = 142.8°	71
	2.57(mean)	2.52	100.5(31)(mean)	a 2.48Å (mean) Coord. about Hg is distorted tetrahedral, ∠S-Hg-S = 115° Hg-S bonds are equatorial with respect to the chair conformation of 1,4-thioxan	72
	2.61	2.52	α 104(1.6) β 102(1.4)	a 2.44Å Coord. about Hg is distorted tetrahedral, ∠S-Hg-S = 113°. Hg-S bonds are axial with respect to the chair conformation of trithian	73
	2.53	2.52	Not reported	a 2.50 b 2.51 Coord. about Hg is distorted tetrahedral	74
	3.12 (described as 'charge-transfer type' interaction since bond length is very long, but interaction does lead to an extra bond in the electronic spectrum	2.52[h]	113.0(1.0) and 109.5(1.0)	a 2.33Å b 3.08Å	75
	2.580(2) 2.699(2)	2.52[h]	α 103.3(3) β 110.9(3)	Coordination about Hg^{II} is approximately tetrahedral Hg-Cl = 2.407(3) and 2.419(3)Å	76
	2.58(4) 2.51(5) 2.60(5) 2.71(4)	2.52[h]	α 108(3) β 105(3)	Coordination about Hg^{II} is approximately square pyramidal with an apical oxygen (Hg-O = 2.35(4)Å)	76

[a] On the basis of 1.48 Å for Cr^0 (F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 5, 1851 (1966)). [b] No values are given because the macrocyclic nature of the ligand limits the validity of any deductions that might be drawn. [c] Based on a typical Re-Cl bond length of approximately 2.30 Å (F. A. Cotton and C. H. Harris *Inorg. Chem.*, 4, 330 (1965); M. J. Bennett, F. A. Cotton, B. M. Foxman, and P. F. Stokely, *J. Am. Chem. Soc.*, 89, 2759 (1967)). [d] Based on a radius of 1.39 Å for octahedral Ni^{II} (A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963)). [e] Based on a radius of 1.18 Å for square-planar Ni^{II} (A. Lopez-Castro and M. R. Truter, *ibid*, 1309 (1963)). [f] Based on radii of 1.31 Å for square-planar Pd^{II} and Pt^{II} (F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science, London, 1973, p 8). [g] Based on a radius of 1.30 Å for Cu^{II} (B. S. Hathaway and D. F. Billing, *Coord. Chem. Rev.*, 5, 143 (1970)). [h] Based on tetrahedral Hg^{II}.

Table III. X-Ray Diffraction Data for Metal-Selenoether and -Telluroether Complexes

Complex	Observed M-E[a] bond length (Å)	Sum of M and E covalent radii (Å)[a]	∠M-E-C (°)[a]	Further Remarks	Ref.
Palladium(II)					
	2.424(7)	2.45[b]	100.8, 109.5	a 2.266(9)Å	77
	a 2.40(1) b 2.36(1)	2.45[b]	105.5(1.7) 103.7(1.6) 107.4(1.4) 104.2(1.6)	c 2.31(2) d 2.32(2)	78
	2.606(1)	2.63[b]	102.3(3) 101.6(3)		78a
Platinum(II)					
	2.430(2)	2.45[b]	α 110.5(7) β 107.2(10)	Pt-Br 2.442(3) Pt-Se bond is axial to ring	52

[a] E = Se or Te. [b] Based on radii of 1.31 Å for square-planar Pd^{II} and Pt^{II} (F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science, London, 1973, p 8).

appreciable substituent effect—thus in *cis*-$[PtCl_2L_2]$ complexes dimethylchalcogens show a trans influence order of S < Se < Te whereas the diethylchalcogens show an order of Se < S < Te.[99] Clearly these complications preclude any precise analysis of the trans-influence results. However it can be stated that organochalcogen ligands generally show greater trans influences than nitrogen donors and smaller trans influences than tertiary phosphines or arsines. For detailed results the reader is referred to ref 117.

3. Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy is an extremely valuable technique for determining the structure of species in solution. It does, of course, depend on having nuclei that possess a nuclear spin. This means that not only can the protons present in thioether, selenoether, and telluroether ligands be studied but so also can selenium (^{77}Se, natural abundance 7.5%, has $I = ^1/_2$) and tellurium (^{125}Te, natural abundance 7.03%, has $I = ^1/_2$); ^{33}S has a nuclear spin of $^3/_2$ and a natural abundance of only 0.74%, making it much less useful. The use of NMR as a structural technique in solution is demonstrated by the use of ^1H NMR, ^{19}F NMR, ^{103}Rh NMR to study the interconversion of isomers formed by chelate rings in such complexes as $[MX_2(RSC_6H_4SR)]$, where M = Pd, Pt, X = Cl, Br, and I, and R = alkyl group, $[PtCl_2(CF_3SCH(Me)CH_2SCF_3)]$, and *trans*-$[RhCl_2(CH_3SCH_2CH_2SCH_3)]Cl$ which results from ring fluxion due to inversion at sulfur.[53,118,119] This and the general problem of inversion at sulfur, selenium, and tellurium are taken up in more detail in section V. Recently a detailed analysis of the ^{195}Pt chemical shifts of a range of complexes, including those of thioether, selenoether, and telluroether ligands, has shown that the study of such shifts can be of value in structure determination.[120]

NMR yields two major parameters, chemical shifts and coupling constants, that may be of use in obtaining

Table IV. M-Cl Bond Lengths Trans to Various Ligands in Square-Planar Pt^{II} and Pd^{II} Complexes

Compound	trans-atom or ligand	M-Cl bond length Å)	Ref.
Platinum			
trans-[$(PPhMe_2)_2(SiPh_2Me)PtCl$]	Si	2.45(1)	80
trans-[$(PPh_2Et)_2PtHCl$]	H	2.42(1)	81
cis-[$(PMe_3)_2PtCl_2$]	P	2.37(1)	82
cis-[$(PEt_3)Pt(C(OEt)NHC_6H_5)Cl$]	C of Carbene	2.365(5)	83
cis-[$Pt(NH_3)_2Cl_2$]	NH_3	2.33(1)	84
K^+[$Pt(C_2H_4)Cl_3$]$^-$.H_2O	$CH_2 = CH_2$	2.327(7)	85
[$Pt(L\text{-}MeSCH_2CH_2CH(COOH)NH_2)Cl_2$]	S $-NH_2$	2.32 2.31	55
K_2[$PtCl_4$]	Cl	2.308(2)	86
cis-[$PtCl_2\{S(C_6H_4Cl)_2\}_2$]	S	2.300(4)	51
K[$Pt(acac)_2Cl$]	O of acac	2.276(5)	87
Palladium			
[$(\pi\text{-}C_4H_7)PdCl(PPh_3)$]	π-allyl	2.38	88
[$Pd(DL\text{-}MeSCH_2CH_2CH(COOH)NH_2)Cl_2$]	S $-NH_2$	2.332(4) 2.308(4)	47
[$(Me_2CHSeCH_2CH_2SeCHMe_2)PdCl_2$]	Se	2.315(20)	78
[$Pd(L\text{-}MeSCH_2CH(COOH)NH_2)Cl_2$].$H_2O$	S $-NH_2$	2.312(7) 2.305(4)	45
$(NH_4)_2$[$PdCl_4$]	Cl	2.299(4)	89

an understanding of the nature of metal–ligand bonding. In general the latter type of data has been more widely used in bonding studies, although an analysis of ^{195}Pt chemical shifts in a range of complexes according to Ramsey's equation has led to the suggestion that the covalency of platinum(II)–ligand bonds increased in the order $NMe_3 << Cl^- < C_2H_4 < Me_2SO \sim SMe_2 < PMe_3 < SeMe_2 < AsMe_3 < SbMe_3 < TeMe_2 < I^-$.[120]

The use of coupling constants to obtain data concerning the nature of metal–ligand bonding, and in particular to study the vexed question of whether or not π bonding is present, is never easy. Thus coupling constants can only give direct information about σ bonding. However if π bonding has the usually assumed synergic effect on the σ bonds, then coupling constants will also be sensitive to π bonding. The use of J_{M-E} (E = chalcogen) coupling constants and in particular ratios of coupling constants for cis and trans isomers as a basis for bonding information[121] is somewhat dangerous, because the observed coupling constants, which result from competition between terms of opposite sign, are small. These small coupling constants have been shown[122] to be related to the presence of a lone pair on the chalcogen by comparing the J_{Pt-Te} coupling constants in $(Bu_4N)_2[X_3Pt(TeMe_2)PtX_3]$ where the bridging telluroether has no residual lone pairs (J_{Pt-Te} = 5923 Hz (Cl) and 5088 Hz (Br)) with $(Bu_4N)[PtX_3(TeMe_2)]$ where a lone pair is present on the tellurium (J_{Pt-Te} = −1553 Hz (Cl) and −1092 Hz (Br)).

$^3J_{Pt-H}$ coupling constants have been studied. The ratios $^3J_{Pt-H}$ for *cis*-$[PtCl_2L_2]$:$[PtCl_3L]^-$:*trans*-$[PtCl_2L_2]$ are much closer when L = SMe_2 (1:0.96:0.84) than when L = PMe_3 (1:0.86:0.60), consistent with the lower trans influence of SMe_2 than of PMe_3. These ratios also imply that the trans influence of SMe_2 is greater than that of chloride.[123] An attempt to use a Parshall-type of approach to analyze the ^1H chemical shifts at the meta and para positions of pyridine in a series of *trans*-$[PtCl_2(pyr)L]$ complexes to obtain a measure of the σ-donor/π-acceptor ability of the ligand L was frustrated by the very small variations in the chemical shifts as a function of L.[124]

4. Ultraviolet and Visible Spectra

The ultraviolet and visible spectra have not been widely studied, although some data for Cr^0, Mo^0, W^0, Ru^{III}, Os^{III}, Rh^{III}, Ir^{III}, Ni^{II}, Pd^{II}, Pt^{II}, and Cu^{II} complexes has been analyzed.[8,94,108,112,117-128] This shows that thioether, selenoether, and telluroether ligands give rise to rather similar crystal field splittings. Although in *trans*-$[PtCl_2(piperidine)L]$ complex the $d_{xy} \rightarrow d_{x^2-y^2}$ transition increases in energy in the order $Et_2Te < Et_2Se < Et_2S$,[128] the crystal field splittings are sufficiently similar for this ligand order not to be universally true.[120] The chain length of the alkyl group can have a significant effect on the crystal field splitting; thus the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in *trans*-$[PdCl_2(R_2S)_2]$ varies with R in the order R = Et (22 600 cm^{-1}) < *n*-Pr (23 200 cm^{-1}) < *sec*-Bu (23 300 cm^{-1}) < *i*-Bu (23 700 cm^{-1}) < *n*-Bu (24 300 cm^{-1}).[102] These ligands fall below tertiary arsines and phosphines but above halides in the spectrochemical series.

An analysis of the ultraviolet and visible spectra of $[ML(CO)_5]$, where M = Cr, Mo, and W, suggests that the lowest energy absorption band provides a sensitive

Table V. Vibrational Spectra of Metal-Thioether-Selenoether and -Telluroether Complexes

Complex	E	X	Range (cm^{-1}) reported for[a] M-S	M-Se	M-Te	Ref.
Palladium(II)						
$[(R_2E)PdX_3]^-$	S	Cl	320-321	-	-	96
	S	Cl, Br	313-322	-	-	97
trans-$[(R_2E)_2PdX_2]$	S	Cl	Not observed	-	-	98
	S, Se, Te	Cl, Br, I	313-322(s) 307-316(a)	B 219(a)	B <227(a)	99
	S	Cl	309-314(a)	-	-	100
	S	Cl, Br, I	300-330(s)[c] 292-327(a)	-	-	101
	S, Se	Cl, Br	295-325.5(a)	220-223(a)	-	102
	S	Cl, Br, I	313-323(s) 307-315(a)	-	-	97
	S	Cl, Br, I	276-337(a)	-	-	103
	Te	Cl, Br	-	-	199-200(a)	104
$[(E\frown E)PdX_2]$	S, Se	Cl, Br	308-331	296-314.5	-	105
	S	Cl	345-398	-	-	106
$[(R_2E)_2Pd_2X_4]$	Se, Te	Cl, Br	-	224-243	183[d]	99
	S	Cl	340	-	-	107
	S	Cl	317	-	-	94
	S, Se	Cl	327-358	282-290	-	108
	S	Cl, Br	336-340	-	-	97
Platinum(II)						
$[(R_2E)PtX_3]^-$	S	Cl	~330-345[b]	-	-	96
	S	Cl, Br	334-349	-	-	97
cis-$[(R_2E)_2PtX_2]$	S	Cl	342, 347	-	-	108
	S, Se, Te	Cl, Br	317-320(s) 305-310(a)	193(s) 152(a)[b]	187(s) 156(a)	99
	S	Cl	349-353(s) 336-339(a)	-	-	97
	S	Cl, Br	287-348(s) 268-360(a)	-	-	103
trans-$[(R_2E)_2PtX_2]$	S, Se, Te	Cl, Br, I	322-345(s) 311-315(a)	208-242(s) 220-233(a)	169(s) <245(a)[b]	99
	S	Br, I	315-318(a)	-	-	108
	S, Se	Cl, Br	301-325(a)	215(a)	-	102
	S	Cl, Br, I	335-343(s) 303-315(a)	-	-	97
	S	Cl, Br, I	286-343(a)			103
$[(E\frown E)PtX_2]$	S, Se	Cl, Br	324-350	283-296	-	105
	S	Cl	359-434	-	-	106
$[(R_2E)_2Pt_2X_4]$	S	Cl, Br	~420	-	-	94
	S, Te	Cl, Br	411-422 380-401	-	185 ± 10	108
	S	Cl, Br	354-374(s) 322-422(a)	-	-	109
$[(R_2E)_3PtX]^+$	S	Cl, Br	348-353[e] 323-329(s) 323-329(a)	-	-	97
$[X_3Pt(R_2E)PtX_3]^-$	S	Cl, Br	316-330(s) 394-408(a)	-	-	109
$[Pt(R_2E)_4]^{2+}$	S	-	317 322 328	-	-	108
Platinum(IV)						
trans-$[(R_2E)_2PtX_4]$	S	Cl, Br	324-335(s) 316-319(a)	-	-	110
cis-$[(R_2E)_2PtX_4]$	S	Cl	343(s)			110
$[(R_2E)PtX_5]^-$	S	Cl, Br	322-323	-	-	110
$[Cu^{II}$(cyclictetrathioether)$]$	S	-	247-282	-	-	111
Gold(I)						
$[(R_2E)AuX]$	S	Cl, Br	344	-	-	98
	S	C, Br	329-345	-	-	

Complex	E	X	Range (cm^{-1}) reported for[a] M-S	M-Se	M-Te	Ref.
Mercury(II)						
$[(R_2E)HgCH_3]NO_3$	S	-	302	-	-	112
$[(PhEC_3H_6EPh)(HgX_2)_x]$	S, Se	Cl, Br	314-327.5	305-334		105
$[(Ph_2Te)HgX_2]$	Te	Cl, Br, I	-	-	95 or 118-133[f]	113

[a] (s) = symmetric; (a) = asymmetric. [b] Assignment not completely certain (see original reference). [c] Bands tentatively assigned as low as 270 cm^{-1}. [d] The Pd-Te stretching frequency in $(Me_2Te)_2Pd_2Br_4$ occurs at either 158 or 228 cm^{-1}. [e] Pd-S trans to X. [f] $(Ph_2Te)HgI_2$ showed bands at 95 and 118 cm^{-1}, one of which is assigned to Hg-Te and the other to Hg-I; which is which is uncertain.

indication of the nature and strength of the M–L interaction.[131-133] On this basis thioethers bond in a manner intermediate between that of amines and phosphines.[116]

5. Other Spectroscopic Methods

Sulfur, selenium, and tellurium do not have nuclei that are suitable for nuclear quadrupole resonance studies,[134] and therefore the only NQR results reported have used other nuclei present in the complex. A study of chloromercury(II) complexes showed that the ^{35}Cl nuclear quadrupole resonances in complexes involving thioethers fell below that in complexes involving nitrogen and oxygen donor ligands.[35] This is consistent with the stronger donor ability of thioethers toward mercury(II).

Of the chalcogens, only ^{125}Te exhibits a Mössbauer effect.[136] The ^{125}Te Mössbauer parameters for several $[(R_2Te)HgX_2]$ complexes indicate that the tellurium atom is in an environment similar to that in $Ph_3Te^+Cl^-$.[113]

B. Further Experimental Results Pertinent to Bonding

1. Equilibrium Studies

There is a paucity of equilibrium data for R_2E (E = chalcogen) complexes. This is especially true at the left-hand side of the transition series, where only thioether and ether complexes of Zr^{IV}, Mo^{IV}, Nb^V, and Ta^V have been studied. The fact that Et_2S and n-Pr_2S replace their oxygen analogues from $[MCl_5\text{-}OR_2]$, M = Nb, Ta, is thought to be largely due to the fact that the sulfur ligands not only have higher dipole moments but are also more polarizable than their oxygen counterparts, thus making them better donors in these high oxidation state complexes.[137] More quantitative data for the reaction

$$MCl_4(cryst) + 2L(l) \rightarrow MCl_4{\cdot}2L(cryst) \quad (1)$$

suggests that some sulfur to metal π bonding may be present. Thus analysis of the enthalpies of reaction 1 (M = Zr, L = pyr, −41.3 kcal/mol, tetrahydrofuran (THF), −33.6 kcal/mol, tetrahydrothiophene (THT), −29.8 kcal/mol; M = Mo, L = pyr, −53.9 kcal/mol, THF, −40.4 kcal/mol, THT, −31.3 kcal/mol) show that the heats of formation of the Mo^{IV} complexes are greater than those of the corresponding Zr^{IV} complexes.[138,139] This is expected since the acceptor ability of M increases on going to the right in the transition series. However adduct formation with tetrahydrothiophene is only slightly more favorable for Mo^{IV} than for Zr^{IV}, in contrast to the situation with pyridine and tetrahydrofuran. The greater difference between Mo^{IV} and Zr^{IV} for pyridine than THF is ascribed to the greater polarizability of the former, so that a larger difference between Mo^{IV} and Zr^{IV} would be expected for rather polarizable THT as opposed to THF. The fact that the reverse is observed is consistent with the presence of sulfur (p_π) to zirconium (d_π) π bonding which increases the stability of the zirconium complex. In Mo^{IV} two of the three t_{2g} orbitals are half-occupied; this will reduce the value of any sulfur (p_π) to molybdenum (d_π) π bonding.

Equilibrium constants for the equilibrium

$$[PdI_2(RS(CH_2)_nSR)] + 2I^- \underset{25\,°C}{\overset{MeOH}{\rightleftharpoons}} [PdI_4]^{2-} + RS(CH_2)_nSR \quad (2)$$

show that 5-membered rings (n = 2) are more stable than 6- (n = 3) and that increasing the electron withdrawing ability of R decreases the stability of the thioether complex, suggesting that the sulfur functions essentially as an electron donor.[140]

A number of papers have reported equilibrium studies of ether, thioether, and selenoether complexes of manganese(II),[141,142] cobalt(II),[141,143] nickel(II),[141,143-145] copper(II),[141,142,145] zinc(II),[141,143,145] and cadmium(II).[141,145] Cobalt(II), nickel(II), and copper(II) show class b character in forming more stable complexes with thioether than ether ligands, whereas zinc(II) shows the opposite trends. For $RECH_2COOH$ the equilibrium constants decreased in the order $Ag^+ >> Cu^{2+} >> Cd^{2+} \sim Co^{2+} > Mn^{2+} \sim Zn^{2+} > Ni^{2+}$, in which nickel(II) has a most unusual position;[141] with $E(CH_2COOH)_2$ the position of nickel(II) is more typical (i.e., $Cu^{2+} > Ni^{2+} > Co^{2+}$).[143] The relative stabilities of the thioether and selenoether complexes are variable, depending on both the metal and the other ligands present.

A considerable number of papers have reported data for silver(I).[141,146-153a] These show the following:

(i) Plots of log K against Hammett σ functions or Taft σ^* functions for alkyl-, alkenyl-, and (substituted-phenyl)thioacetic acids are linear, suggesting that the strength of the Ag–S bond is largely determined by its σ component.[147,149] It has been pointed out[154] that strictly speaking such linearity does not necessarily indicate the absence of π back-donation but that if π back-donation is present, it varies linearly with inductive effects.

(ii) A comparison of analogous oxygen, sulfur, selenium, and tellurium ligands such as $E(CH_2CH_2COOH)_2$ shows that the stabilities decrease in the order E = Te > Se > S >> O, that is, that silver(I) is a class b metal ion.[148,150,153] Analysis of the thermodynamic functions further supports this conclusion since complex formation is enthalpy favored and entropy opposed.[150,153]

(iii) ρ values for log K_1 against Hammett σ-function plots for $XC_6H_4ECH_2COOH$ are less negative for Se than for S complexes. This suggests that there is more π back-donation from silver(I) to selenium than to sulfur. When considering K_2, the change in the ρ value on replacing S by Se is much less than found for K_1, which would be expected since when there are two selenoether groups present they must compete for the π back-donation from silver(I).[147,148]

A study of the influence of the trans ligand on the acid dissociation constants of platinum(II) aquo complexes showed that the trans effect of diethyl thioether was less than that of thiourea, dialkyl sulfoxide, and ethylene but greater than that of pyridine and ammonia.[155,156] The observation that *cis*-$[(R_2S)_2PtX_2]$ complexes isomerize to the trans isomers on heating suggests that any sulfur to platinum π back-bonding cannot be very strong.[157]

2. Kinetic Studies

The kinetics of displacement of amine and halide ligands from square-planar palladium(II), platinum(II), and gold(III) complexes have been studied in some detail.[158-163] Plots of log k_2 (k_2 = second-order rate constant) against the sum of the Taft σ^* values for the entering thioether in reactions 3 and 4 were all straight

$$trans\text{-}[Pd(amine)_2Cl_2] + RSR' \xrightarrow[25\,°C;\ R,\ R' = \text{alkyl or aryl}]{\text{1,2-dimethoxyethane}} trans\text{-}[Pd(amine)(RSR')Cl_2] + amine \quad (3)$$

$$[Pt(bipyr)XY] = RSR' \xrightarrow[R,\ R' = \text{alkyl or aryl}]{\text{MeOH, 25 °C}} [Pt(bipyr)Y(RSR')]^+ + X^-$$

$$X, Y = Cl, Cl;\ Cl, N_3;\ Cl, NO_2;\ NO_2, NO_2;\ N_3, NO_2 \quad (4)$$

lines with alkyl and aryl thioethers lying on the same straight line.[159-161] This suggests that d_π–d_π bonding is either nonexistent or minimal in these metal–sulfur bonds since the reactivity of the thioether is dominated by its σ-donor ability. For gold(III) (reaction 5) the

$$[AuCl_3(amine)] + RSR' \xrightarrow[R,\ R' = \text{alkyl or aryl}]{\text{acetone, 25 °C}} [AuCl_3(RSR')] + amine \quad (5)$$

nucleophilicity of RSR′ was not as simply related to σ-donor ability as found for palladium(II) and platinum(II), indicating that steric effects were more important for gold(III).[158,160]

When reaction 4 is carried out in the forward direction, the influence of the leaving group is small whereas that of the entering group is large, suggesting a reaction profile such as that shown in Figure 1a. In the reverse direction, the rate of reaction 4 is sensitive to the nature of both the entering and leaving groups, implying a reaction profile such as that in Figure 1b. This anomalous behavior of thioethers probably results from interference between the nonbonded lone pairs of electrons on the sulfur and the distribution of charge on the complex. When thioethers are the entering ligands this stereoelectronic hindrance makes bond-making difficult, hence profile 1a, whereas when thioethers are the leaving groups this stereoelectronic hindrance promotes metal–thioether bond rupture (Figure 1b).

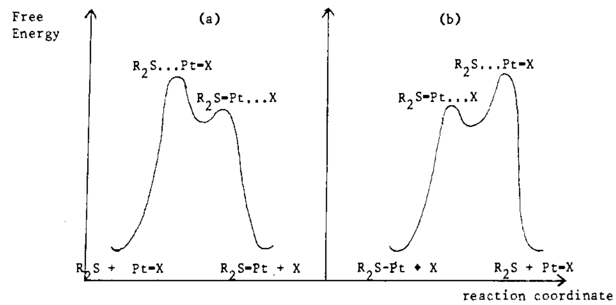


Figure 1. Profiles for reaction 4 in (a) the forward an (b) the reverse direction.

The kinetics of ring opening of bidentate thioether and selenoether complexes of palladium(II) and platinum(II) by amines have been studied in detail.[164-168] In the case of palladium(II), the activation enthalpy is larger (less positive) for the selenoether than for the thioether complexes, which could indicate more π bonding in the palladium–selenium than in the palladium–sulfur bond.[168] This would lead to palladium carrying a greater positive charge in the selenoether complexes and so to stronger bonding in the transition state and hence also to the observed greater capacity of the selenoether complex to discriminate between entering nucleophiles.

3. Dipole Moments and Molar Conductances

An analysis of the Pt–EEt_2 group dipole moments show that these decrease in the order E = S (4.7 D) > Se (4.4 D) > Te (2.2 D).[105] The reverse trend would be expected on the basis of the decrease of electronegativity from sulfur to tellurium as well as the increase in size from sulfur to tellurium. However a significant increase in π back-donation on going from sulfur to tellurium would account for the observed trends. The relatively small decrease in bond moment on going from sulfur to selenium suggests relatively little π back -donation from platinum to selenium. That the platinum(II)–selenium bond is anomalous in having relatively little π bonding is further suggested by the following: (i) Platinum(II)–selenoether complexes undergo much less ion association than platinum(II)–thioether complexes, whereas with palladium(II) the reverse is true.[105] (ii) The order of stability of $[Pt(R_2E)_2Cl_2]$ and $[Pt(R_2E)Cl_2]_2$ complexes with respect to decomposition is E = S > Te > Se,[169] whereas for the palladium(II) analogues it is E = S > Se > Te.[170] (iii) Replacing S by Se gives a larger drop in ν_{Pt-E} stretching vibrations for Pt^{II} than for Pd^{II} (see ii). Thus whereas the relative π-bonding contribution in palladium(II)–chalcogen bonds increases in the order Pd–S < Pd–Se < Pd–Te, the order for platinum(II) appears to be anomalous (Pt–Se < Pt–S < Pt–Te). The anomalously small π component in the Pt–Se bond is ascribed to a poor match between the relevant orbitals.

C. Bonding

The outer electron configurations of sulfur, selenium, and tellurium in the ground state are ns^2, np^4, nd^0. In their dialkyl compounds two of these valence electrons are involved in bonding to the alkyl groups, leaving four electrons retained in nonbonding orbitals on the chalcogen. The orbitals on the chalcogen vary from an sp^3-hybrid set on oxygen to virtually an s and three p orbitals at tellurium, with intermediate situations at sulfur and selenium. For simplicity thioethers are often considered to involve sp^3-hybridized sulfur with two lone pairs. One or both of these lone pairs may form a covalent link to an electron acceptor. If only one lone pair is involved in bonding, then the other lone pair may either (i) remain nonbonding, in which case it will result in stereoelectronic repulsion, or (ii) take part in π donation by rehybridization to sp^2 followed by π donation of the lone pair from a p orbital on the chalcogen to the electron acceptor.

Although π donation might be anticipated with early transition metals having empty suitable symmetry d orbitals to act as acceptors, there is very little evidence, apart from the thermochemical evidence in section IIIB1, for such bonding. The importance of the repulsive interaction between the lone pair on the chalcogen and electrons on the acceptor can readily be seen from the added strength of the metal–sulfur bond in $[Br_2Pt(SEt_2)_2PtBr_2]$ when both the lone pairs are involved in bonding to electron acceptors (see sections IIIA1 and IIIA2).

As has been emphasized previously,[15] the ability of electron donors, such as the present ligands, to take part in strong σ bonding depends on the effective electronegativity of the donor as well as its size (for matching of orbital energies and orbital overlap with the electron acceptor), dipole moment, and polarizability. Of these factors electronegativity and size are generally the most important and result in metal–ligand σ-bond strengths decreasing in the order M–S > M–Se > M–Te.

In addition to the filled valence orbitals, all the chalcogens have empty nd orbitals, some of which have the correct symmetry to take part in π back-donation from metal to ligand. Whenever there are orbitals of correct symmetry available for bonding there is always a possibility of such bonding occurring depending on the degree of overlap and relative energies of the orbitals concerned. As a consequence of this a great deal of effort has been expended looking for evidence to support the existence of π back-donation in chalcogenoether complexes of the transition metals to the right-hand side of the transition series. As we stated some years ago[171] in connection with tertiary phosphine complexes, it is exceedingly difficult, if not impossible, to find unequivocal definitive evidence in support of the existence of π back-donation. Nevertheless there are many facets of the structure and reactivity of these complexes, described in sections A and B above, that are most simply explained in terms of small amount of π back-donation from metal to chalcogen. This back-donation is certainly less than exists in phosphine, arsine, and stibine complexes. In general it increases in importance as group 6 is descended, although platinum(II) appears to be anomalous in this respect (see section IIIB3), emphasizing the importance of orbital overlap. The absence of strong π back-donation, the modest σ-donor abilities of the chalcogenoether ligands, and the stereoelectronic repulsion resulting from the presence of the nonbonding pair of electrons on the chalcogen all combine to make chalcogenoethers relatively poor ligands. A comparison of the corresponding ligands containing group 5B, 6B, and 7B donors (e.g., R_3P, R_2S, RCl, or R_3As, R_2Se, RBr, or R_3Sb, R_2Te, RI) show a steady decrease in σ-donating ability with increasing group number, reflecting both the increasing electronegativity and the increasing number of nonbonding lone pairs of electrons on the donor atom. Thus the group 5B ligands are good σ donors that form a wide range of complexes with all the transition metals. The group 6B ligands are much poorer σ donors that, as is apparent from this review, form a wide range of complexes with metals lying to the right-hand side of the transition series but form only a limited range of complexes with those on the left-hand side of the series. Alkyl and aryl halides do not normally form complexes with transition metals. Indeed the only report of any bonding interactions that we are aware of concerns the interaction between silver(I) and the aryl iodides iodobenzene and diiodobenzene.[172]

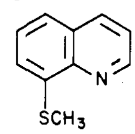
IV. S-Dealkylation and S-Alkylation at Coordinated Sulfur

A. S-Dealkylation

S-Dealkylation was first reported in 1883[173] when the S-demethylation of dimethyl thioether by $PtCl_2$ as in eq 6 was observed. However, the subject was neglected

$$PtCl_2 + 2(CH_3)_2S \rightarrow Pt(SCH_3)_2 + 2CH_3Cl \quad (6)$$

until the 60s when it was found[174,175] that 8-(methylthio)quinoline (1 (N-SMe)) complexed as a neutral



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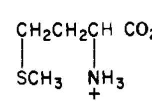

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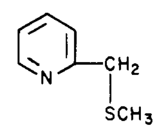

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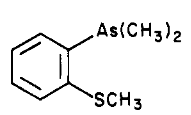
ligand toward palladium(II) and platinum(II) as in [M(N-SMe)X_2] but on reaction with Na_3AuCl_6 in acetone the nonelectrolyte [Au(N-S)Cl_2] formed. This complex is identical with that prepared from 8-mercaptoquinoline, showing that the ligand 1 had spontaneously S-dealkylated in the presence of $AuCl_6^{3-}$. If the complexes [M(N-SMe)Br_2] (M = Pd, Pt) are heated in *N,N*-dimethylformamide (dmf) for 10 h, the complexes [M_2(N-S)$_2Br_2$] can be isolated; again S-demethylation has occurred. This is the first instance of a comparison being suggested to biological systems, for example, the transmethylation of S-adenosylmethionine.[176] The palladium(II) and platinum(II) complexes of methionine (2) are coordinated via the sulfur and nitrogen sites,[177] but attempted S-dealkylation leads to decomposition.[178] In vivo S-dealkylation of methionine occurs via a sulfonium salt[176] so that any comparison of coordination S-dealkylation to biological systems is somewhat tenuous. It is interesting to note that attempted S-dealkylation with complexes of 2-(methylthio)methylpyridine (3) also leads to decomposition;[178] this is really not surprising, since S-dealkylation is almost entirely dependent on an aromatic group also being attached to the sulfur atom. The S-demethylation of [M(N-SMe)X_2] (M = Pd, Pt; X = Cl, Br) in dmf was again reported,[179] and the products were thought to be thiolo bridged, but whether they were dimers or higher oligomers was not proven due to their insolubility. Complexes of dimethyl[*o*-(methylthio)phenyl]arsine (As–SMe) (4) with palladium(II) and platinum(II) undergo S-demethylation in refluxing dmf over 8 h for the chloro and bromo salts in reactions 7,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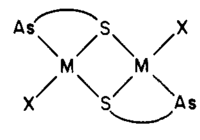
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8, and 9. Again insolubility prevented molecular weight

$$[M(As\text{-}SMe)_2]X_2 \rightarrow [M(As\text{-}S)_2] + 2CH_3X \quad (7)$$

$$[M(As\text{-}SMe)X_2] \rightarrow [M(As\text{-}S)X]_n + CH_3X \quad (8)$$

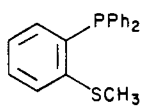
$$[Pt(As\text{-}SMe)_2][PtX_4] \rightarrow 2[Pt(As\text{-}S)X]_n + 2CH_3X \quad (9)$$

determination, but a dimeric structure (**5**) was assumed for the products of reactions 8 and 9 since similar μ-thiolo complexes have been reported.[180,181] The interconversions among the complexes of palladium(II) with As-SMe (**4**) are shown in Scheme I, including S-alkylation reactions. The palladium(II) complex of diphenyl[*o*-(methylthio)phenyl]phosphine (P-SMe), **6** ($Pd(P\text{-}SMe)Cl_2$), S-dealkylates in refluxing dmf in over 4 h forming either $Pd(P\text{-}S)_2$ if the reaction is performed with addition of 1 equiv of free ligand, or the dimer $[Pd_2(P\text{-}S)_2Cl_2]\cdot{}^2/_3$dmf without the addition of free ligand.[182] This ligand also readily S-dealkylates in refluxing ethanol with a little dmf present when coordinated to nickel(II), as in reaction 10, the first example

$$[Ni(P\text{-}SMe)_2](ClO_4)_2 \rightarrow [Ni(P\text{-}S)_2] \quad (10)$$

of S-dealkylation with nickel(II). The fate of the methyl and perchlorate groups were not discussed.

The palladium(II) dichloride complex of *o*-methylthioaniline (**7**) has also been S-dealkylated in a reaction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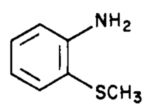
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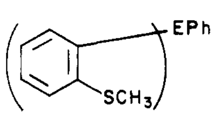
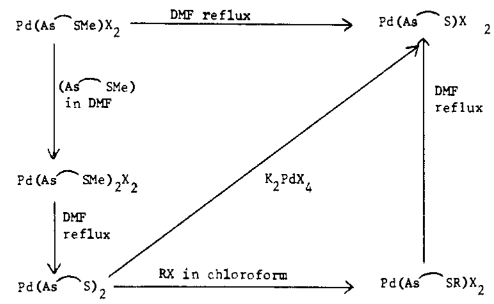
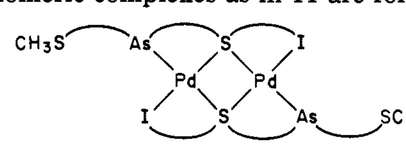

8, E = P
9, E = As

analogous to reaction 8,[183] and the platinum(II) complex as in reaction 9. However, S-demethylated products of the nickel(II) diiodide comples of **7**, NiL_2I_2, could not be obtained. The first case of Se-dealkylation with the selenium analogue of **6** (P-SeMe) was observed when $Ni(P\text{-}SeMe)_2Cl_2$ was refluxed in butanol, dmf, or a mixture of these solvents for 5–15 min, yielding $Ni(P\text{-}Se)_2$.[184] Gas bubbles were evolved, but the gas was not analyzed. The same product is obtained by Se-dealkylation of $Ni(P\text{-}SeMe)_2(NCS)_2$ or $[Ni(P\text{-}SeMe)_2Br]ClO_4$. The diamagnetic complex $Ni(P\text{-}Se)_2$ is monomeric in chloroform, NMR shows the absence of CH_3 protons, and the absorption spectrum indicates a planar structure. An X-ray structure determination shows a trans configuration of the ligands.[185] Similarly, the palladium(II) dithiocyanate complex $[Pd(P\text{-}SeMe)(SCN)_2]$ readily dealkylates to dmf/butanol in over 15 min, forming $[Pd(P\text{-}Se)(SCN)]_2$ probably as the selenium-bridged dimer. The selenium ligand Se-dealkylates more readily than the sulfur analogue, and this may be due to the relative weakness of the C–Se bond compared to the C–S bond.[186] A study has been made[187] of the S-dealkylation reactions of the palladium(II) complexes of P–SMe, **6**, the arsine analogue of **6**, and the two tridentates bis[*o*-(methylthio)phenyl]phenylphosphine (MeS-P-SMe) (**8**) and the arsine analogue

Scheme I



MeS-As-SMe (**9**). The bidentates S-dealkylate, as in previous work, giving either the monomeric or μ-thiolo products. With the tridentate MeS-P-SMe, S-dealkylation of the monochelated palladium(II) diiodide complex gives products of varying composition, and this may be due to the metal having a coordination sphere of PSI_2 but with the thioether donor atoms behaving in a fluxional manner. However, with the arsine analogue, the complex $[Pd(MeS\text{-}As\text{-}S)I]_n$ is obtained and probably has structure **10**. If excess ligand is present the monomeric complexes as in **11** are formed.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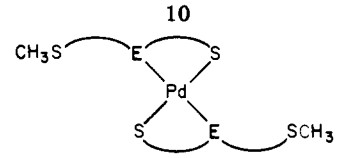
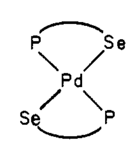

11, E = P or As

If the *o*-C_6H_4 backbone in ligands **6** and **8** are replaced by *o*-C_6F_4, then S-dealkylation becomes extremely facile.[188] In the presence of nickel(II) and iodide ions these fluorinated ligands spontaneously S-dealkylate even at −78 °C in a variety of solvents yielding products of the type shown in **12** for the bidentate and **11** for the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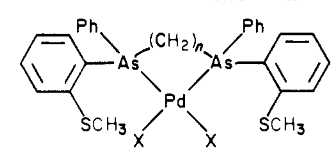
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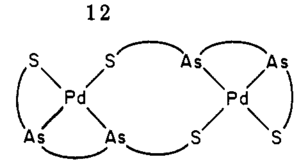
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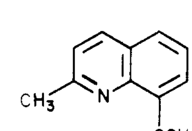
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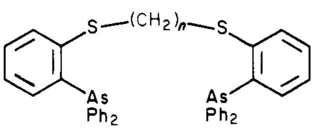
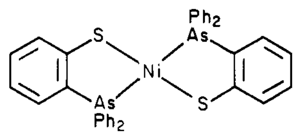
tridentate. Similarly the palladium(II) complexes S-dealkylate much more readily than with the unfluorinated ligand analogues. In some cases the interaction between metal ion and sulfur atom need not be strong to effect S-dealkylation; for example,[189] the complex $Pd(MeS\text{-}As\text{-}As\text{-}SMe)X_2$ (**13**) in which the thiomethyl groups appear uncoordinated in solution forms the dimer **14** in refluxing dmf. However, the observation[190] that the complexes of 1-methyl-8-thiomethylquinoline (MMTQ) (**15**), $Au(MMTQ)Cl_3$, and $Pd(MMTQ)Cl_2$ will not S-dealkylate has been attributed to steric hindrance of the 1-methyl group weakening the M–S bond in the complexes since in the absence of the 1-methyl group S-dealkylation readily occurs.[174,175] Steric strain on coordination of bis[(o-(diphenylarsino)phenyl)thio]alkanes **16** has been sug-



16, n = 2, 3, or 4



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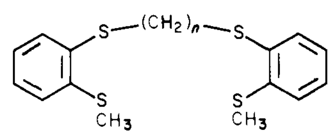
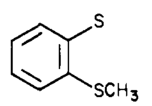
gested[190] as the main factor in their facile bis-S-dealkylation when coordinated to nickel(II) ions. On heating the ligands with nickel(II) salts in acetone at 30 °C a deep purple color forms, indicative of a five-coordinate species; then a green precipitate of the S-dealkylated complex **17** rapidly forms. The organic residues of the reactions using nickel dichloride were identified by GLC for the cases where n was 2 and 3 and were shown to be 1,2-dichloroethane and 1,3-dichloropropane, respectively. The complex **17** is also formed if nickel(II) perchlorate is used, and it may be interesting to speculate on the fate of the methyl and perchlorate groups in that reaction due to the instability of alkyl perchlorates. The S-dealkylation of palladium(II) and platinum(II) complexes of the open-chain tetrathioethers **18** (M_2LCl_4) is extremely complex since



18 (n = 2, 3, or 4)



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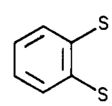

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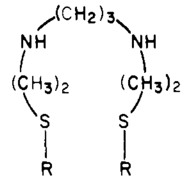
there are four sites capable of fission.[191] Complexes of both **19** and **20** can be separated by TLC. Attempts to S-dealkylate nickel(II) dihalide complexes of **18** leads to simple M–S fission. Bromo complexes of the ligands **21** S-dealkylate when the metal ion is Hg^{2+} but not



21, R = benzyl or trityl

when it is Co^{2+}.[192] For the Ni^{2+} complexes only the ligand R = trityl S-dealkylates. In all cases the products are $(M_3L_2)Br_2$.

Thus, in summary, S-dealkylation is promoted by coordination of the thioether to a metal ion with class b character and then heating or refluxing the complex in the presence of dmf. Ease of S-dealkylation is in the order $Ni^{2+} > Pd^{2+} > Pt^{2+}$ and for counterion $I^- > Br^- > Cl^-$. It appears preferable for the other hydrocarbon group on the sulfur to be aromatic, and if this group is fluorinated the reaction is more facile.

Although there has been no kinetic study of S-dealkylation to ascertain a reaction mechanism, the most favored postulate has been a comparison with the Zeisel cleavage reaction for ethers[193] as in reaction 11. Protonation of the oxygen atom forms a good potential leaving group ROH for an S_N2 attack of the iodide ion on the methyl carbon atom. However, when a transition metal takes the place of the proton in making the sulfur atom δ^+, the comparison may not be strictly correct.

$$ROCH_3 + H^+ + I^- \rightarrow RO(H)^+CH_3 + I^- \rightarrow ROH + CH_3I \quad (11)$$

The mercaptide sulfur atom in the S-dealkylated complex is much more strongly bound to the metal ion than that in the original thioether complex, and this may make the reaction thermodynamically viable. A weakening of the S–C bond is quite probable on coordination, and it has been shown that if a $-C_6F_4-$ group is also attached to the sulfur atom, further increasing the positive charge on the sulfur, the ease of S-dealkylation is greatly increased. The reaction is again envisaged as a halide ion attack on the carbon atom of the group removed. This is consistent with the ease of S-dealkylation being in the order $I^- > Br^- > Cl^-$, that is the most nucleophilic anion best. In the case of the metal ions the order of reactivity, $Ni^{2+} > Pd^{2+} > Pt^{2+}$, may simply be the relative labilities of these ions allowing the halide ions to react at the S-dealkylation site. As to the role of the solvent, it can be seen that in nearly all cases dmf is used, and the most likely explanation is that the dmf acts as a solvolyzing agent, thus promoting nucleophilic attack by halide ions on the complex. This postulate of S_N2 attack is supported by the fact that dearylation does not occur.[194] It is difficult at this time to explain the mechanism of reaction when the counterion is perchlorate as it would be difficult to see how perchlorate would undergo the mechanism proposed for halide complexes.

Thus, S-dealkylation occurs almost exclusively at d^8 metal ion centers, Ni(II), Pd(II), Pt(II), and Au(III), particularly with the nickel triad. This may be due to thioethers forming relatively strong bonds to these metal ions; however, it appears that there has been no attempt to effect S-dealkylation with rhodium or iridium in oxidation states I or III. O-Dealkylation has been reported[195–197] and also S-dealkylation at W(VI) and W(V)[198] and at Co(II).[199] Se-Dealkylation is rare, and there are no reports of Te-dealkylation of coordinated telluroethers.

B. S-Alkylation

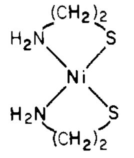
S-Alkylation is the reaction of a coordinated mercaptide group with an alkyl halide to form a thioether either coordinated or uncoordinated after the reaction. This reaction was first postulated in 1883[200] for platinum(II) complexes and was soon proved correct in the reactions of $Pt(SEt)_2$ with iodoethane and iodomethane.[201,202] Other early work used mercury(II) mercaptide complexes;[203,204–206] for example, mercury(II) sulfide reacts with iodoethane in ethanol in a sealed tube at 100 °C, producing $Hg(SEt_2)I_2$. S-Alkylation was also used as a route to prepare thioethers using mercury(II)[207] and copper(I)[206,209] in reactions 12 and 13. A

$$PhHgSPh + Ph_2CH_2Cl \rightarrow PhHgCl + PhSCH_2Ph \quad (12)$$

$$PhSCu + RX \rightarrow PhSR + CuX \quad (13)$$

gold(III) mercaptide complex, (diethyl-2-mercaptoethylamine)gold(III), undergoes S-alkylation with bromoethane to give the thioether complex which may be isolated as the picrate salt.[210] This reaction is explosive when neat bromoethane is used. The nucleophilicity of the mercaptide sulfur atom in the complex is demonstrated by its reaction with chloramine-T to form the sulfilimine.

The S-alkylation of mercaptoamine complexes of nickel(II) and palladium(II) has been studied.[211,212] With the complex bis[(2-aminoethyl)mercapto]nickel(II) (22), S-alkylation in dmf first gives a trimeric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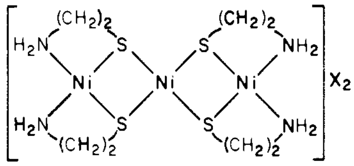
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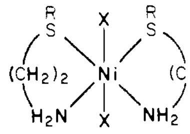
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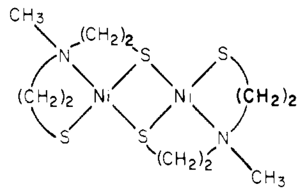
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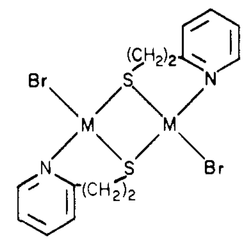
species 23 which then S-alkylates to the final product 24.

S-Alkylation has increased the coordination number and yielded a high-spin complex, indicating that the thioether donor has a smaller ligand-field contribution than the thiolo donor. This weakness accounts for the appearance of the trinuclear species as shown in reaction 14. The alkyl halides used were iodomethane and

$$Ni(NH_2CH_2CH_2SR)_2X_2 + 2Ni(NH_2CH_2CH_2S)_2 \rightarrow [Ni(Ni(NH_2CH_2CH_2S)_2)_2]X_2 + 2NH_2CH_2CH_2SR \quad (14)$$

the benzyl halides. As expected, the rate of S-alkylation depends on which benzyl halide is used, and the following order of reactivity is found: $C_6H_5CH_2Cl < C_6H_5CH_2Br < C_6H_5CH_2I$. The reaction of iodomethane on $Pd(NH_2CH_2CH_2S)_2$ gives the S-alkylated $Pd(NH_2CH_2CH_2SCH_3)I_2$ and presumably free $NH_2CH_2CH_2SCH_3$, the iodide displacing the weaker thioether donor to form a neutral complex. The ligand *N*-methyl-2,2′-dimercaptodiethylamine reacts with the nickel(II) ion, forming the dimeric μ-thiolo complex 25. This complex readily S-alkylates with iodomethane or benzyl bromide, but only at the terminal thiolo positions. Forcing conditions do cause further S-alkylation, but with accompanying destruction of the complex. S-Alkylation of bis[2-(2-mercaptoethyl)pyridine]nickel(II) and the palladium(II) analogue with benzyl bromide gives the binuclear μ-thiolo complexes 26, M = Ni(II) and Pd(II). This again shows that the terminally coordinated thiolo donor can act as a better ligand than a thioether group. The μ-thiolo groups in this complex also cannot be S-alkylated.

S-Alkylation has been used[193,211–213] in a deliberate attempt to close chelate rings in what is termed the "kinetic template reaction". Complexes of several α-diketobis(mercaptoethyl)imines with nickel(II) (27, R = CH_3, C_2H_5, and C_5H_{11}) react smoothly with monofunctional alkylating agents, and it was reasoned that a bifunctional reagent ought to close the ring. It was found that α,α′-dibromo-*o*-xylene did indeed undergo this reaction, forming monomeric octahedral complexes (28) of the macrocyclic ligands. The distance between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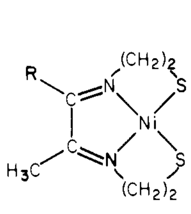
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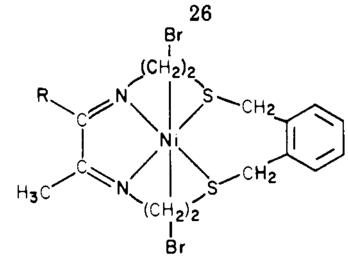
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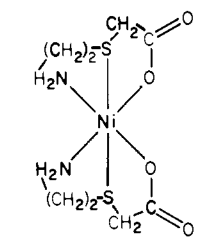
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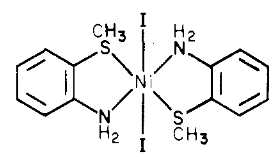
the sulfur atoms in 27 is relatively large,[214] requiring a ring-closing agent which can match this span. Thus, 1,2-dibromomethane fails to ring-close whereas the 1,3- or 1,4-dibromoalkanes do yield macrocycles. A similar reaction forms a coordinated tridentate ligand, the complex *cis*-bis[(2-aminoethyl)mercapto]nickel(II) reacting with the chloroacetate anion to yield 29.[215] The complex bis(*o*-aminobenzenethiolato)nickel(II) reacts with iodomethane, forming the octahedral complex 30,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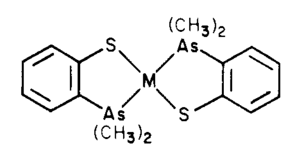

31

but is unreactive toward 2-(chloromethyl)pyridine or benzyl chloride.[216] The complexes $M(As\text{-}S)_2$ (31, M = Pd(II) or Pt(II)) have been S-alkylated in chloroform, giving the complexes $M(As\text{-}SR)X_2$ and free ligand.[179] The μ-thiolo species 5, however, does not S-alkylate, showing again the reluctance of bridging thiolo atoms to undergo S-alkylation. In agreement with this, complexes with μ-thiolo moieties as in 10 do not S-alkylate whereas terminal thiolo atoms as in 11 readily S-alkylate.[187]

There have been three kinetic studies on S-alkylation. The first[211] studied the reaction of 22 with iodomethane, benzyl halides, *p*-chlorobenzyl chloride, and *p*-nitrobenzyl chloride. Simple second-order kinetics were found, and it was postulated that M–S bond fission before reaction was most unlikely but an S_N2 attack of the thiolo atom on the alkyl halide was feasible. In this system the reaction of the second terminal thiolo atom is faster than the first due to a lowering of the overall ligand field on conversion of a mercaptide to a thioether, thus making the second thiolo atom more nucleophilic. The activation energies for these reactions are in the region 6–12 kcal mol^{-1} whereas the activation energies for S_N2 reactions at a saturated carbon atom are usually in the range 15–30 kcal mol^{-1}. This suggests that a preequilibrium exists and that the most likely interaction is between the metal ion and the halogen atom of the alkyl halide. The sterically differing complexes $Ni(RR'NCH_2CH_2S)_2$ were then studied[217] in order to selectively alter the accessibility of the likely reaction sites to partially inhibit the S-alkylation reaction. The alkylating agent used was benzyl bromide, and here again heterocyclic cleavage of the M–S bond was discounted. Low activation energies and large negative entropies suggested an associative process. The data showed that the rate constants were dependent on steric requirements and provided strong support for a preequilibrium in which the metal ion polarizes the C–Br bond, thus accelerating the reaction. The kinetics of the reaction between **27** (R = Et) and benzyl bromide shows the presence of a significant amount of an intermediate,[218] i.e., the reaction of only one of the thiolo atoms. However, the reaction with α,α'-dibromo-*o*-xylene shows only a single rate-determining step and no intermediate formation. Thus the reaction of the second sulfur atom with the remaining alkyl halide site is so fast it cannot be measured. Again in this study low activation energies and large negative entropies are found.

S-Alkylation is not restricted to coordinated RS^- moieties.[219] The bridging sulfide ligand S^{2-} in $Pt_2S_2(PMe_2Ph)_4$ reacts with benzyl bromide in chloroform, yielding $[Pt_2S(SBz)(PMe_2Ph)_4]Br$. Further, coordinated thioether can be S-alkylated in certain manganese carbonyl complexes,[220] for example, reaction 15. The

$$[(\eta\text{-}C_5H_5)Mn(CO)_2SRR'] + CH_3SO_3F \rightarrow [(\eta\text{-}C_5H_5)Mn(CO)_2S(CH_3)RR']SO_3F \quad (15)$$

R_3S^+ ligand probably bonds via d_π–d_π back-bonding similar to that for coordinated PCl_3.

Recently it has been shown that alkylation of the μ-thiolo moiety is not unusual. The complex $Pt(\mu\text{-}SCH_3)_2R_2(PMe_2Ph)$ reacts[221] with iodomethane, giving $PtIPh(SMe_2)(PMe_2Ph)$ (R = Ph) or $PtI_2Me_2(SMe_2)(PMe_2Ph)$ (R = Me). Silver(I), copper(I), and mercury(II) complexes of 1,4-dimercaptobenzene also S-alkylate with iodomethane, forming *p*-(methylthio)thioanisole.[222] The polymeric complexes of palladium(II) with 1,2-ethanethiol and 1,3-propanethiol react readily with alkyl halides to form monomeric and dimeric complexes containing thioether donors.[223]

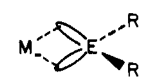
In conclusion, it appears likely that S-alkylation is promoted by the nucleophilicity of the coordinated mercaptide group. Thus nucleophilicity is demonstrated by the ability of coordinated mercaptides to displace a thioether ligand as in reaction 14. If this nucleophilicity is reduced, either by the presence of electron-withdrawing groups attached to the sulfur atom[188] or by the mercaptide bridging two metal ions,[179,187,211,212] then usually S-alkylation does not occur. In the cases where μ-thiolo groups have been S-alkylated[222,223] the polymeric complexes have only the mercaptide group as ligand. This probably allows more electron density to remain on the sulfur atom, thus retaining much of its nucleophilicity. Enthalpies of activation, where measured, point to the existence of a preequilibrium due to an interaction between the metal ion and the halogen atom of the alkyl halide. Whether the complete S-alkylation reaction occurs between one complex molecule and one alkyl halide molecule has not been resolved. At this time, no Se- or Te-alkylation has been reported.

V. Inversion

The use of NMR in the study of inversion at pyramidal sites is well established,[224] yielding information on barrier energies and mechanism. Observable barrier energies are limited to 5–20 kcal mol^{-1} due to the interaction time of the technique being of the order 10^{-3} s.

Inversion at a coordinated thioether site was first demonstrated by the low-temperature magnetic nonequivalence, two sets of triplets (the triplets arising from ^{195}Pt coupling), of the methyl protons in $PtCl_2$(2,5-dithiahexane) which coalesce to a single triplet above 95 °C.[225] This phenomenon is also demonstrated by the nonequivalence of the methylene protons in *cis*-$PtCl_2[(PhCH_2)_2S]_2$ at 35 °C, giving an ABX pattern (34%) due to ^{195}Pt, $I = {}^1/_2$ superimposed on an AB pattern (66%) for Pt, $I = 0$. On warming, these signals coalesce until at 55 °C only an A_2-type system exists.[226,227]

Much of the work in this field[118,225–234] determines coalescence temperatures of either MX_2L_2 or MX_2L' complexes, M = Pd(II) or Pt(II), X = halide, L = monodentate thioether, selenoether, or telluroether, and L′ = bidentate thioether or selenoether. Above the coalescence temperature where rapid inversion is occurring, the $^3J_{Pt-H}$ coupling is still present for all complexes containing Pt–S and Pt–Se bonds, indicating that the inversion is not a dissociative–associative mechanism. A simplistic view of the mechanism generally proposed[228] is the displacement at the central metal ion of the lone pair of the chalcogen used in the Me–E bond by the lone pair not involved in the bonding via a planar intermediate in which the chalcogen atom remains pyramidal, as in **32**. Since there can be no



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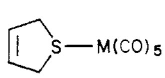
coupling in complexes of palladium(II) and coupling is not observed for any of the platinum(II)–telluroether complexes, a study of the variable-temperature NMR spectra of these complexes in the presence of excess free ligand was employed to rule out a dissociative–associative mechanism in these cases. This study[231,233] shows that for thioether and selenoether complexes the low-temperature spectra are unaffected up to and beyond the coalescence temperature, but at higher temperatures a second coalescence involving free and coordinated ligands is observed. Platinum(II) complexes also studied show that above the second coalescence temperature no $^3J_{Pt-H}$ coupling is seen. This shows that the first coalescence for palladium(II) complexes is comparable to that of the platinum(II) complexes and is therefore due to inversion. For the telluroether complexes only one coalescence is seen, and since these complexes decompose above this temperature and no $^3J_{Pt-H}$ is observed, no definite decision can be made on the mechanism. Ease of exchange between free and coordinated ligands is in the order $TeEt_2 \gg SeEt_2 > SEt_2$, as are the relative barrier energies.[230,232]

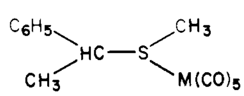
When bidentate thioether and selenoether ligands are used, the effect of the trans ligand may be observed.[118,229,230,232] The coalescence temperatures are ~50 °C higher than for the trans unidentate complexes, reflecting the lower trans influence of the halide ions vs. the chalcogens. For the bidentate complexes the inversion barriers are in the order $Cl^- > Br^- > I^-$. For $[Pt(Ph)_2$(3,6-dithiaoctane)$]$ the coalescence temperature drops to −70 °C, showing the large trans influence of

Ph⁻. This gives a trans-influence order, $Cl^- < Br^- < I^- < R_2S < Ph^-$, in agreement with other trans-influence studies, indicating that the σ-bond-weakening trans influence aids inversion at the trans position. This is supported by the relative barrier heights being in the order Pd(II) < Pt(II) for all cases, inferring a stronger Pt–E than Pd–E bond, as expected.

For bidentate complexes[118,229,235-238] a skew conformation is expected for a dimethylene bridge which would give rise to three different AA′BB′ patterns (meso, +, and − forms). The platinum(II) complexes will have superimposed AA′BB′X patterns. Inversion at the chalcogen leads to the interconversion of all the isomers, and this must occur one site at a time not solely together, as this would not interconvert meso and ± forms. There has been some controversy with bidentate complexes as to whether inversion of the methylene protons is due to inversion at the donor atom or conformational changes in the five-membered ring formed by the bidentate ligand.[239,240] By analysis of the variable-temperature NMR spectra of $[PdX_2L]$, $[M(CO)_4L]$, and $[M(CO)_4L']$, L = *i*-PrSe$(CH_2)_2$SePr-*i*, L′ = BzS$(CH_2)_2$SBz, M = Cr, Mo, or W, using computer simulation of the spectra obtained from complex spin systems under exchange conditions,[239] it has been demonstrated that it is the process of inversion at the donor atoms that occurs. The variable-temperature NMR study on the compound $[PtMe_3X(dth)]$ also favors inversion at the sulfur atoms.[241] A similar study on the complexes *trans*-$[MX_2L_2]$, M = Pd(II) or Pt(II), X = Cl, Br, or I, L = 1,4-oxathiane or 1,4-oxaselanane,[240] where exchange could be due to conformational changes in the ring or site inversion at the donor atom, shows that again it is the inversion process which occurs. Band shape fitting gave ΔG and ΔH values too high to be caused by conformational changes, indicating site not ring inversion. A further report of inversion at Cr(0) and W(0) in the complexes **33a,b** and **34a,b** gives the



33a, M = Cr
33b, M = W



34a, M = Cr
34b, M = W

coalescence temperatures **33a** −59 °C, **33b** −49 °C, **34a** −76 °C, **34b** −76.5 °C. Below coalescence temperatures the methylene proton signals in complexes **33a** and **33b** are an AB quartet and the S–CH_3 protons in **34a** and **34b** are two singlets of unequal intensity. A more detailed thermodynamic analysis was performed on compound **34a**.[242]

In order to study the effect of backbone in bidentate thioether complexes the variable-temperature ¹H NMR of the complexes $[M(CH_3S(R)SCH_3)X_2]$, R = $-(CH_2)_2-$, $-(CH_2)_3-$, *o*-C_6H_4–, *cis*-CH=CH–; X = Cl, Br, I; M = Pd, Pt, has been studied.[243] Solubility problems with these complexes required the use of $(CD_3)_2SO$ as solvent, and above the melting point of the solvent (18.5 °C) all but one of the palladium and seven of the platinum complexes were above coalescence temperature. However, the following conclusions were drawn: (i) inversion is easier for palladium than platinum, (ii) coalescence temperatures fall in the order Cl > Br > I, consistent with the trans influence, and (iii) coalescence temperatures decrease with the ligand backbone in the order $-(CH_2)_2-$ > *o*-C_6H_4– > *cis*-CH=CH– > $-(CH_2)_3-$. Observations i and ii are in keeping with other studies (vide supra). Since inversion is thought to be a function of M–S bond strength,[232] the results obtained by altering the backbone may be said to demonstrate the greater stability of five- over six-membered rings. For the three C_2 backboned ligands inversion is easier with the unsaturated systems, and this may be due to delocalization of the sulfur lone pair(s) in the inversion transition state.

A novel addition to inversion with bidentate ligands occurs in the dimeric complexes $PtMe_6X_2$(MeECH(R)EMe), X = Cl, Br, I; E = S, Se; R = Me, H.[242,244] At low temperatures, ca. −95 °C, two signals can be seen in the ¹H NMR from the E–Me protons, indicating the presence of the two isomers. On warming, coalescence occurs due to inversion at E. At higher temperatures a fluxional behavior is encountered where the E atoms swap between metal centers.

Complexes of the ligand $E[CH_2Si(CH_3)_3]_2$, E = S or Se, have been studied[245,246] to obtain spectra more amenable to total analysis. The chalcogen atom in the complex represents a prochiral center as do the (trimethylsilyl)methyl groups, making the pairs of hydrogen atoms diastereotopic and thus anisochronous when no interconversion occurs, giving an AB quartet pattern. The methylene proton environments can be interchanged by inversion at the chalcogen atom but not by rotation about any of the bonds. With *mer*-$MCl_3(S[CH_2Si(CH_3)_3]_2)_3$, M = Rh(III) or Ir(III), two AB quartet patterns are seen in a 2:1 ratio and two different coalescence temperatures occur for the two sets of signals.[245]

Here inversion occurs more readily at S trans to Cl⁻ than trans to another S, contrary to the idea that inversion occurs more readily the greater the trans influence of the trans ligand (vide supra). Inversion is also significantly faster at the heavier Ir(III); cf. palladium(II) vs. platinum(II) where it has been suggested that inversion is faster at palladium(II) since the Pd–S bond is weaker than the Pt–S bond.

A variable-temperature NMR study using band-shape fitting methods on *trans*-$MCl_2(E[CH_2Si(CH_3)_3]_2)_2$, M = Pd(II) or Pt(II), E = S or Se, yields precise data for the energy barriers to inversion.[246] Since the rates of inversion are $\sim 10^{20}$ times faster than those for sulfoxides,[247] the mechanism must differ from one involving a trigonal-planar transition state. Again the planar intermediate **28** is suggested and also the metal having a distorted five-coordinate configuration. The increased rate of inversion is explained as a stabilization of the transition structure by p_π–d_π overlap between E and M. It is not possible in this system to distinguish between inversion at single sites and simultaneous inversion at both sites. The four pairs of methylene protons are enantiomerically related, giving spectra which are simpler to analyze.

Single-site inversion is shown to dominate by studying *trans*-$MX_2[ER[CH_2Si(CH_3)_3]]_2$, M = Pd(II) or Pt(II), E = S or Se, R = CH_3 or Ph, X = Cl or Br, as before.[248] Now the methylene proton spin system is of the type AB + CD since E is a chiral center (see Figure 2). Both single-site inversion at E_1 or E_2 and simultaneous inversion at E_1 and E_2 are depicted in Figure 2. Simultaneous inversion at both sites will only give

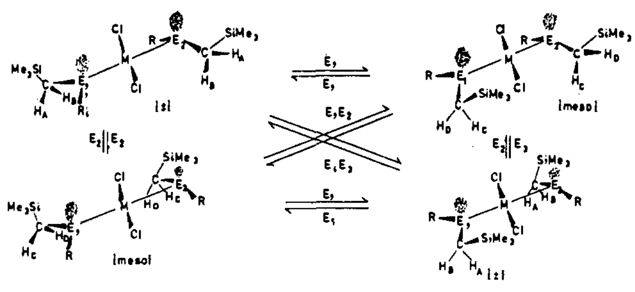


Figure 2. Effects of chalcogen inversion, E_1 represents inversion at site 1, on the magnetic environments of the diastereotopic CH_2 protons of the $ECH_2Si(CH_3)_3$ groups. Rotation about the E–M and E–C bonds is assumed and only the preferred conformers are shown. Reproduced with permission. Copyright The Royal Society of Chemistry

rise to exchange between ± forms and meso forms, not between ± and meso.

There is one report of inversion at sulfur in cobalt(III) thioether complexes with $[Co(tren)L]^{3+}$, tren = triethylenetetramine, L = $CH_3SCH_2CH(R)NH_2$, R = COOH or H.[249]

Inversion at coordinated chalcogen has been studied in complexes of chromium(0), molybdenum(0), tungsten(0), rhodium(III), iridium(III), palladium(II), and platinum(II). There has also been a brief report of inversion at gold(I) and gold(III) in the complexes $AuCl(Bz_2S)$ and $AuCl_3(Bz_2S)$.[250]

VI. Literature Survey

A. Scandium, Yttrium, and Lanthanum

These metals invariably form only the M^{3+} ions having a noble gas configuration.[251] The compounds thus formed by these ions are essentially ionic in nature, and as expected no thioether complexes are known.

B. Titanium, Zirconium, and Hafnium

Titanium(III) complexes have been isolated with the ligands 1,4-thioxane, $OCH_2CH_2SCH_2CH_2$,[252-256] tetrahydrothiophene (tht), $CH_2CH_2CH_2CH_2S$,[257,258] 1,4-dithiane, $SCH_2CH_2SCH_2CH_2$,[256] and dimethyl thioether.[257,258] The antiferromagnetic $TiCl_3$·thioxane has a Néel temperature of ~100 K with the ligand coordinated through both donor atoms in what must be a polymeric structure. The complexes TiX_3·2thioxane, X = Cl, Br, contain only S-bonded ligands and in the solid state are six-coordinate with halide bridges. Dithiane forms the insoluble polymeric $TiCl_3$·dithiane. The two monodentate ligands form the complexes TiX_3·2L, X = Cl, Br, I,[257,258] which, for X = Br and I, are six-coordinate with halide bridges. The two chloro complexes, however, are strongly antiferromagnetic, with Néel temperatures ~320 K, unlike the bromo and iodo complexes which exhibit more normal magnetic behavior and obey the Curie–Weiss law. The antiferromagnetic behavior shown by these complexes may be due to Ti···Ti interaction in packing between two square-pyramidal molecules. All the complexes are unstable to moisture and to heat; $TiCl_3$·$2SMe_2$ heated under vacuum forms $TiCl_4$·$2SMe_2$.[259]

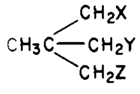
With the ambidentate ligand 1,4-thioxane and the selenium analogue 1,4-selenoxane, TiX_4, X = Cl, Br, react in nondonating solvents to form the isolable complexes TiX_4·2L[255,256,260] in which the ligand is shown by infrared and NMR evidence to be bonded via the sulfur or selenium donor atom. The complexes TiX_4·thioxane, X = Cl, Br, and $TiCl_4$·selenoxane have also been isolated[255,256] and on similar evidence are thought to be polymeric with both donor atoms coordinated. This demonstrates that both oxygen and chalcogen will bond to the Ti(IV) center to form the preferred six-coordinate complex. However, in the complex having a stoichiometry of two ligand molecules per metal site, the bonding is exclusively via the chalcogen. This cannot be a steric phenomenon in this case, and thus it appears that TiX_4, X = Cl, Br, act as class b acceptor sites with the large polarizability of the chalcogen atoms being of particular relevance. The dithiane complexes TiX_4·dithiane, X = Cl, Br, have been reported and are almost certainly polymeric in structure with bridging ligands.[259,260]

Titanium(IV) complexes with monodentate thioethers of the type TiX_4·2L, X = Cl, Br; L = SMe_2, SEt_2, SPr_2, SBu_2, SBz_2, $CH_2CH_2CH_2S$, $CH_2CH_2CH_2CH_2S$, $CH_2CH_2CH_2CH_2CH_2S$, can be sublimed in vacuo and have been shown to be monomeric species in solution.[259,261-264] An infrared study of the cyclic ligand complexes[263] has shown that these complexes are cis octahedral, having six vibrational modes associated with the metal–halogen bonds (C_{2v} symmetry). The monoligand adducts have also been studied: TiX_4·L, X = Cl, L = SEt_2, SBu_2, SBz_2; X = Br, L = SPr_2; X = Cl, Br, L = $CH_2CH_2CH_2S$, $CH_2CH_2CH_2CH_2S$, $CH_2CH_2CH_2$-CH_2CH_2S.[259,261-264] It has been suggested that in the solid state this type of complex is a halide-bridged dimer as evidenced by a weak absorption at 293 cm^{-1} in the infrared spectrum of $TiCl_4(CH_2CH_2CH_2CH_2S)$ which is not present in the analogous $TiCl_4$·2L complex.[263] In benzene solution a disproportionation probably occurs (eq 16). The complex $TiCl_4(SeEt_2)$ can

$$2TiX_4{\cdot}L \rightarrow TiX_4 + TiX_4{\cdot}2L \qquad (16)$$

also be prepared; however, reacting $TiCl_4$ with $TeEt_2$ appeared to chlorinate the telluroether.[264]

The following monomeric complexes with bidentate thioether ligands have been isolated: TiX_4·L, X = Cl, Br, L = $MeSCH_2CH_2SMe$,[259,265] $EtSCH_2CH_2SEt$,[262,266] $BuSCH_2CH_2SBu$,[262] $PhSCH_2CH_2SPh$.[259,264,266] The NMR spectrum of $TiBr_4(EtSCH_2CH_2SEt)$ indicates that both sulfur donors are coordinated, and molecular weight measurements on this complex and the chloro analogue show them to be monomeric. Three complexes with bidentate selenoethers have also been reported: $TiCl_4$·L, L = $MeSeCH_2CH_2SeMe$,[265] $MeSeCH_2CH_2CH_2SeMe$,[265] $PhSeCH_2CH_2SePh$;[264] the former two were shown to be monomeric in benzene solution. All of these titanium(IV) complexes are highly colored from orange through red-black. Since these are d^0 complexes, these colors must be due to low-energy charge-transfer absorptions in their visible spectra. Competition between O, N, and S donors for ligand sites on titanium(IV) was studied by reaction of $TiCl_4$ with a series of terdentate ligands **35**, X = Y = Z = OMe; X = Y = OMe, Z = SMe; X = Y = OMe, Z = NMe_2; X = OMe, Y = SMe, Z = NMe_2. In all cases



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cleavage of an O-methyl group occurred.[267]

Thioether complexes with methyltitanium trichloride have been prepared and are moisture and air sensitive. Complexes reported are $MeTiCl_3 \cdot 2L$, L = SMe_2, tetrahydrothiophene and $MeTiCl_3 \cdot L$, L = $MeSCH_2CH_2SMe$, $MeSCH_2CH_2OMe$, $MeSCH_2CH_2NMe_2$.[268-270] Reaction with oxygen converts these complexes to the methoxy analogues $TiCl_3(OMe) \cdot 2L$ or $TiCl_3(OMe) \cdot L$.

The zirconium(IV) complex $ZrCl_4$(thioxane) is thought to be polymeric, analogous to the titanium(IV) complex.[256] Thermochemical studies of the reaction between ZrX_4, X = Cl, Br, and tetrahydrothiophene, have shown that, for the chloro complexes, hafnium(IV) is a better acceptor for thioether sulfur than is zirconium(IV). It was suggested that hafnium will have a somewhat greater effective nuclear charge than zirconium due to the 4f subshell, thus giving hafnium a greater polarizing ability. The complex $HfBr_4$(tht) was not formed, and this was rationalized on steric grounds as seen from models. There is a suggestion that d_π–p_π bonding is important in the Zr–S bond.[138,139]

C. Vanadium, Niobium, and Tantalum

The moisture-sensitive vanadium(III) complexes of the monodentate thioether ligands, SMe_2 and tetrahydrothiophene (tht), VX_3L_2, X = Cl, Br, have been shown to be five-coordinate in benzene solution.[271-274] They exhibit one band in their far-infrared spectra and two bands in the near-infrared region. From crystal-field parameters derived from the spectra, comparison of observed to calculated spectra indicate D_{3h} symmetry, i.e., a trans trigonal-bipyramidal structure.[274] In the solid state the evidence suggests the structure changes to a six-coordinate dimer with a halide bridging.[272-278] For example, on going from solid to solution $[VCl_3(tht)_2]$ shows a change in the near-infrared spectrum by the disappearance of the two bands associated with a five-coordinate structure and a change in the far-infrared spectrum from a singlet at 420 cm^{-1} to two absorptions between 380 and 360 cm^{-1}.[258] There is some controversy over the structures of the complexes $[VX_3(SEt_2)_2]$, X = Cl, Br. It is agreed that in solution they are identical with those mentioned above, trans trigonal-bipyramidal.[271,273,275] However, in the solid state one report indicates no change to six-coordinate dimers as the spectra, both near-, and far-infrared, do not change from those in solution.[275] A previous report suggested that the dimers did form in the solid state.[273] Dipole moments of around 2.5 D have been rationalized as being due to the asymmetry of the ligands.[271,273] Magnetic moments measured for these complexes lie in the region 2.5–2.7 μ_B.[271,273]

The reaction of VCl_4 with monodentate thioethers does not give vanadium(IV) complexes but some reduction to vanadium(III) with possible chlorination of the thioether.[271,276] However, when bidentate thioether ligands are employed, the moisture-sensitive complexes VCl_4L, L = $RSCH_2CH_2SR$, R = Me, Et, Ph, can be isolated.[266] The magnetic moments of these complexes are ~1.7 μ_B, expected for such a d^1 system, and a broad asymmetric band in the visible spectrum between 20 000 and 17 000 cm^{-1} suggests a lowering of the metal symmetry to C_{2v}. Two complexes with bidentate selenoether ligands, VCl_4L, L = $MeSeCH_2CH_2SeMe$, $MeSeCH_2CH_2CH_2SeMe$, are also stable, decomposing at 114 and 60 °C, respectively.[265]

The vanadyl complexes $VOCl_2L_2$, L = SMe_2, SEt_2, tetrahydrothiophene, may be prepared either directly by reaction with $VOCl_2$[277] or via a reduction of $VOCl_3$.[277,278] The oxidation states of the products were established by magnetic moments, ~1.7 μ_B.[278] The visible spectra are dominated by the V=O bond absorbance.

The complexes of niobium(IV) with monodentate thioethers are of two types.[279,280] Diadducts NbX_4L_2 can be isolated where X = Cl, Br, I, and L = SMe_2 or tetrahydrothiophene (tht). These are cis octahedral complexes as shown by their vibrational spectra and are paramagnetic with magnetic moments in the range 0.8–1.4 μ_B. Monoadducts NBX_4L have been found for X = Cl, Br; L = SMe_2 or SEt_2. It appears that an equilibrium exists of the type shown in eq 17.[280] The

$$NbX_4L_2 \rightleftharpoons NbX_4L + L \qquad (17)$$

stability of the diadduct with respect to this equilibrium decreases in the order X = I > Br > Cl. It seems that steric factors play an important role in this system, as shown by the above order of stability and the inability to form a diadduct of SEt_2, the most hindered of the three ligands used, or a monoadduct of tetrahydrothiophene, the least hindered.

The eight-coordinate complexes $NbX_4(dth)_2$, X = Cl, Br, I, are formed by reaction of NbX_4 with an excess of dithiohexane.[281,282] As with all complexes between the vanadium subgroup metals and thioether ligands, these complexes are extremely air sensitive. Eight-coordination is verified by stoichiometry and spectral studies.[14] An EPR study suggests that the complexes $[NbX_4(dth)_2]$, X = Cl, Br, have the idealized triangular dodecahedral structure,[282] $g_\parallel < g_\perp$. A ten-line spectrum is seen, Nb(IV) (d^1, $I = {}^9/_2$, 100% abundance); $\langle g \rangle$ in solution is the same as $\langle g \rangle$ in the solid state, indicating that the same species is present.

It has been suggested[137] that bonding in the complexes NbX_5L is dependent on (i) steric effects, (ii) dipole moment of L, and (iii) polarizability of the ligand. The ether ligands of $NbCl_5(OEt_2)$ and $NbCl_5(OPr_2)$ are easily replaced by their thioether analogues whereas $NbCl_5(OMe_2)$ is unaffected by SMe_2.[137] The thioether complexes NbX_5L,[255,283-287] X = F, L = SMe_2, SEt_2; X = Cl, L = SMe_2, SEt_2, S-n-Pr_2, SC_4H_8, SC_4H_{10}, SC_4H_8O, SeC_4H_8O; X = Br, L = SMe_2, SC_4H_8, SC_5H_{10}, SC_4H_2O, can all be either distilled or sublimed unchanged whereas $NbBr_5(SEt_2)$ decomposes on heating. An infrared and NMR spectral study of the complexes with the ambidentate ligands shows bonding exclusively via the chalcogen.[285] A Raman spectral study has confirmed this type of complex to be mononuclear, six-coordinate.[287] With the ligands SMe_2 and SC_4H_8 there is evidence for 2:1 L:NbX_5 adducts.[283,284] These may be seven-coordinate or six-coordinate and ionic $(NbX_4L_2)X$. A definite assignment is impossible due to insolubility. A similar problem arises with the bidentate ligand complex of stoichiometry $NbCl_5$(dth) in which the ligand is shown by infrared to be in the gauche (chelating) form.[288] With bidentates having bulky end groups, t-BuSCH$_2$CH$_2$S-t-Bu and PhSCH$_2$CH$_2$SPh, the ligands are in the trans form and complexes (NbCl$_5$)$_2$L are formed with the ligand bridging the metal ions. This is also found with 1,4-dithiane.[288] The structure determinations of the complexes M$_2$Br$_6$(SC$_4$H$_8$)$_3$ show the metals to be bridged by two halides and one thioether ligand.[17]

A kinetic study of the ligand exchange with MX$_5$-L, M = Nb, Ta; X = Cl, Br; L = OMe$_2$, SMe$_2$, SeMe$_2$, and TeMe$_2$ (eq 18), has shown that, although the process

$$[MX_5L] + L^* \rightleftharpoons [MX_5L^*] + L \qquad (18)$$

is dissociative for the ether ligand, the mechanism considered more normal, with the chalcogen ligands the process is associative.[289,290]

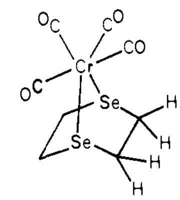
Adducts have been reported between thioether ligands and the compounds Me$_x$NbCl$_{(5-x)}$, x = 1, 2, and 3.[291-293] With monodentate ligands, six-coordinate complexes are formed (x = 1 and 2).[291-292] With bidentate ligands RSCH$_2$CH$_2$SR, R = Me, Et, seven-coordinate complexes appear to form as evidenced by infrared of the coordinated ligand (x = 3)[293] together with conductance and molecular weight measurements.[292] With ligands 1,4-dithiane and PhSCH$_2$CH$_2$SPh only dimeric ligand bridged species were found.[291,292] The reaction of NbCl$_5$ with cyclic polythioether ligands forms dimeric complexes in which two NbCl$_5$ units are bridged by the ligands.[18,19,294] The coordination chemistry of Ta(IV) and Ta(V) is analogous to that described above for Nb(IV) and Nb(V).[137,279,283-285,287-291,293]

D. Chromium, Molybdenum, and Tungsten

The majority of the complexes formed with chromium contain the metal in its zero oxidation state stabilized by π-acceptor ligands. There are very few reports of monodentate ligands complexing to chromium(0). The tetrahydrothiophene complex Cr(CO)$_5$(tht) can be isolated as a stable solid from the reaction of Cr(CO)$_6$ with the ligand, promoted by irradiation.[295] This type of complex may also be prepared by reaction of the tetrahydrofuran adduct Cr(CO)$_5$(thf) with thioethers as in the formation of the crystalline complex (SBu$_2$)-Cr(CO)$_5$.[296] In a UV PES study of Cr(CO)$_5$L complexes which include L = SMe$_2$, SEt$_2$, S(CH=CH$_2$)$_2$ and S-(CH$_2$Cl)Me, it was concluded that SR$_2$, like PR$_3$, places a significantly greater electronic charge at the metal center than CO.[297] It was noted that care must be taken in evaluating π-acceptor ability of ligands by analysis of the ν(CO) frequencies of the complex in the infrared spectrum since the ν(CO) values may also depend on the strength of the M–L σ bond. An inversion study (see part V) of the complexes Cr(CO)$_5$L, L = MeSCH-(Me)Ph or SCH$_2$CH=CHCH$_2$, suggests that in this case the mechanism of inversion is dissociative due to the Cr–S bond being very weak.[242]

Inversion studies at coordinated chalcogen have utilized group 6A metal carbonyl complexes with bidentate ligands as these are very soluble. Studies include the complexes Cr(CO)$_4$L, L = MeSeCH$_2$C-(Me)$_2$CH$_2$SeMe,[236] i-PrSeCH$_2$CH$_2$SePr-i,[237] and PhCH$_2$SCH$_2$CH$_2$SCH$_2$Ph.[238] A series of papers[298-300] on Cr(CO)$_4$(bidentate), bidentate = MeSCH$_2$CH$_2$SMe(dth) and t-BuSCH$_2$CH$_2$SBu-t, have demonstrated by a kinetic study that replacement of the bidentate ligand by phosphite occurs via an initial reversible dissociation of one end of the ligand.

There have been several other studies on Cr(CO)$_4$-(bidentate) complexes since the first report of the yellow complex Cr(CO)$_4$(dth).[301] An infrared study has used a range of bidentate ligands with N, P, As, and S donors to provide a comparison of donor properties; the thioether ligands include dithiahexane (dth) and t-BuSCH$_2$CH$_2$SBu-t.[302] The structure determination of Cr(CO)$_4$(EtSCH$_2$CH$_2$SEt) suggests that the Cr–S bond has some π character.[20] The NMR of the nonconducting monomeric Cr(CO)$_4$(1,4-diselenane), an AA′BB′ multiplet, is indicative of a structure comparable to norbornane (**36**). The preparation of Cr(CO)$_4$-



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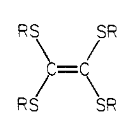
(MeSeCH$_2$CH$_2$SeMe) has shown that Cr(CO)$_4$(norbornadiene) is a useful starting material for the preparation of the chalcogen complexes.[304] The ligands MeS(CH$_2$)$_6$SMe and EtS(CH$_2$)$_n$SEt (n = 2, 4) form the dimers [Cr(CO)$_5$]$_2$L.[305] On standing, the complex containing the ligand with a dimethylene backbone disproportionates to the monomeric complex Cr(CO)$_4$L together with Cr(CO)$_6$. The versatility of bidentate ligands in this system is demonstrated by the different species formed between chromium(0) carbonyls and the ligands RSCH$_2$CH$_2$SR, R = Bu-t, p-XC$_6$H$_4$ (X = NO$_2$, Cl, H, Me).[306] The reaction of Et$_4$NCr(CO)$_5$Br with the ligands in the presence of Et$_3$OBF$_4$ yielded Cr(CO)$_5$L which were all characterized by spectroscopy in solution. Pure solids could not be obtained except with X = Cl. Further addition of the bromocarbonylchromium complex and Lewis acid gave [Cr(CO)$_5$]$_5$L as solids, stable in an inert atmosphere. The [Cr(CO)$_4$L] species were even more stable and could be exposed to dry air without reaction. The hybrid bidentate Ph$_2$PCH$_2$CH$_2$SMe readily forms octahedral Cr(CO)$_4$-L.[307]

The potentially tetradentate ligands **37** form three types of complex, Cr(CO)$_4$L, in which the ligand is chelating, Cr(CO)$_5$L, with L monodentate, and Cr-(CO)$_3$LL′, where L is chelating and L′ = CH$_3$CN and PPh$_3$. Cr(CO)$_5$L converts to Cr(CO)$_4$L on heating. With the ligand **38** no chelation was observed, only Cr(CO)$_5$L formed. In these compounds there is no spectroscopic evidence for interaction between the metal and double bond. This is further supported by a structure determination of Cr(CO)$_4$L, L = **37** (R =



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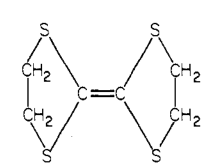

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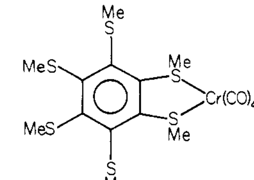

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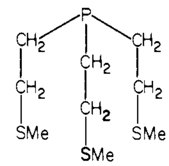
Me).[21] In contrast to this, the alkynyl thioether complex Cr(CO)$_3$(MeSC≡CSMe) formed by displacement of acetonitrile from $Cr(CO)_3(MeCN)_3$ contains only M–alkyne bonding to the thioether ligand. $Cr(CO)_2(MeSC{\equiv}CSMe)_2$ in the solid state or more quickly in solution forms the new complex **39** by trimerization of the alkyne.[308]

Two species can be prepared with the cyclic ligands $(RSCH_2)_n$.[309,310] The ligand may be tridentate $Cr(CO)_3(MeSCH_2)_3$ or monodentate $Cr(CO)_5(RSCH_2)_n$, R = H, Me, $n = 3$, and R = H, $n = 4$. For the case R = Me, $n = 3$, the $M(CO)_5$ moiety undergoes rapid intramolecular exchange between the three donor sites.

Chromium(III) complexes of monodentate thioethers have been prepared. The violet octahedral CrL_3Cl_3, L = SMe_2 and SEt_2, are soluble in the ligand and in benzene. However, recrystallization from benzene yields $[CrL_2Cl_3]_2$, a six-coordinate chloro-bridged dimer. The initial reaction is between anhydrous $CrCl_3$ and excess ligand with zinc dust as catalyst. The green bromide dimers can be prepared similarly.[275] The *fac* and *mer* isomers of $Cr(tht)_3Cl_3$ have been reported.[311] Reaction of $Cr(NMe_3)_3Cl_3$ with excess tetrahydrothiophene produces the blue-purple *fac* isomer. The lilac *mer* isomer is isolated from a benzene solution of the *fac* isomer. They are both nonelectrolytes in dichloromethane but differ in their visible spectra and infrared spectra in the ν(M–Cl) region.

The coordination chemistry of molybdenum in this system is dominated by the zerovalent oxidation state. Complexes with monodentate ligands are either fairly unstable, $Mo(CO)_3L_3$, L = SMe_2, tetrahydrothiophene, SEt_2,[312,313] or very unstable, $Mo(CO)_5L$, L = SBu-t_2, tetrahydrothiophene.[295,296] One monodentate selenoether complex has been reported with Mo(0), $Mo(CO)_3(o\text{-phen})(SePh_2)$, as part of an analysis of CO force constants in a series of analogous complexes.[314] Much of the literature on bidentate complexes compares with that of chromium(0) (vide infra). Complexes $Mo(CO)_4L$ have been used in inversion studies[236–238] and are comparable to the chromium analogues.[301–306] In contrast to chromium(0) coordination chemistry the species $\{Mo(CO)_5\}L$ do not form;[305,306] however the ligand-bridged $Mo(CO)_n$(1,4-dithiane) (n = 3, 4) have been reported.[315] The reason why the ligand in these latter complexes did not chelate was thought to be that the distance between the sulfur atoms in the boat form of 1,4-dithiane (2.9 Å) is less than that required to span two coordination sites on molybdenum(0) (3.3 Å). It is noteworthy that 1,4-diselenane does chelate to molybdenum(0).[303] Studies on the phosphite replacement of 2,5-dithiahexane in $Mo(CO)_4$(dth) indicated a difference compared to the chromium complex.[298,299] With molybdenum the reaction was thought to involve a seven-coordinate intermediate; however, reversible dissociation was the important step for the bidentate complex of t-$BuSCH_2CH_2SBu$-t.[300] With $(RCHS)_n$ type ligands molybdenum forms $Mo(CO)_3L$, L with R = Me, $n = 3$, as for chromium, but also $Mo(CO)_4L$, L with R = H, $n = 4$, in which the ligand acts as a bidentate. The mixed ligand complexes $[Mo(CO)_3(bpy)]_2(RCHS)_3$, R = H or Me, and $[Mo(CO)_3(bpy)]_n(CH_2S)_4$, n = 1 or 2, on reaction with tetrahydrofuran exchange the thioether ligand for tetrahydrofuran.[308] As with chromium these ligands also form $M(CO)_5L$ with M = Mo and the ligand monodentate.[309] Complexes of molybdenum(0) with ligands **37** are the same as with chromium(0).[21] With the hybrid $Ph_2PCH_2CH_2SMe$, however, not only $Mo(CO)_4L$ can be formed, but also $[Mo(CO)_2L_2]$ under forcing conditions.[306] Attempts to prepare the 2,5-dithiahexane analogue failed,[306] and attempts to prepare $Mo(CO)_2(TSP)$ yielded $Mo(CO)_3(TSP)$ having the same donor set as $Mo(CO)_3(DSP)$, TSP = **40**, DSP = **41**.[316]



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$MeSCH_2CH_2P(Ph)CH_2CH_2SMe$

41

The reaction of $ClCH_2SMe$ with $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$ at room temperature yields $(\pi\text{-}C_5H_5)Mo(CO)_3(\sigma\text{-}CH_2SMe)$ in which there is no M–S interaction. The action of heat or ultraviolet light on this complex converts it to the unusual $[(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}CH_2SMe)]$.[317] A structure determination of this complex suggests that the bonding of the thioether ligand is best described as a π-bonded three-electron neutral donor.[318]

Molybdenum(II) forms a variety of complex types with ligands containing thioether donor atoms. The cluster complex Mo_6Cl_{12}(dithiahexane)$_2$ contains the bidentate ligand in the trans conformation.[317] Two formulations are possible, $[(Mo_6Cl_8)Cl_2(dth)_2]^{2+}(Cl^-)_2$ in which the ligand is bridging or $(Mo_6Cl_8)Cl_4(dth)_2$ with the ligand monodentate. The true formulation was not determined. Also prepared were $Mo_6Cl_{12}(C_5H_{10}S)$ and $Mo_6Cl_{12}(C_4H_8OS)$. The complexes $[(\pi\text{-}C_5H_5)Mo(SRMe)X]PF_6^-$, R = Me, X = Cl, Br; R = ally, X = Cl, have been reported and the thioether ligand is easily replaced by phosphines, phosphites, and pyridine. The PF_6^- counterion confers stability since $[(\pi\text{-}C_5H_5)Mo(SMe_2)I]^+I^-$ on warming in acetone yields $(\pi\text{-}C_5H_5)MoI_2$ and free ligand.[318] The tetrahalodimolybdenum(II) complexes $Mo_2Cl_4(SEt_2)_4$ and $Mo_2Cl_4(dth)_2$ are considered to contain a Mo–Mo multiple bond analogous to $[Re_2Cl_8]^{-}$.[319] The dimeric tetrathioether-bridged complex of molybdenum(II) (see Table II) contains the unusual terminal SH groups.[22] Seven-coordinate complexes $[Mo(CO)_3I_2(Ph_2PCH_2CH_2SMe)][Mo(CO)_2LX_2]$, L = DSP (**40**) or DSA (arsine analogue of **40**), X = Br or I, L = TSP (**41**), X = I, have been prepared using mixed 5B–6B ligands.[316] The TSP ligand has only three of its four donor sites coordinated.

There is one report of a molybdenum(III) thioether ligand complex, $MoX_3(tht)_3$, X = Cl, Br.[320] A disproportionation reaction occurs when an attempt is made to prepare a complex in which the metal is in oxidation state two. A low magnetic moment (3.4 μ_B) is found compared to that expected for strictly octahedral Mo(III).

The tetrathioether-bridged dimeric complex of molybdenum(II) mentioned above converts to the monomeric $[MoO(SH)L]^+$ in ethanol solution.[23] Another molybdenum(IV) byproduct in this system is $[Mo_2O_2L(OC_2H_5)]^+$.[22] The faculative open-chain tetrathioethers $MeS(CH_2)_nS(CH_2)_mS(CH_2)_nSMe$ gave both seven-coordinate $MoCl_4L$ in which the ligand acts as a tridentate and $(MoOCl_3)_2L$ which contains six-coordinate metal with bridging ligand.[320] Molybdenum(IV) has been shown to be a poorer acceptor toward tetrahydrothiophene than zirconium(IV). It was considered that π bonding into the t_{2g} orbitals would be less favorable for a d^2 species than for d^0.[322]

There have been four reports of molybdenum(V) thioether complexes.[321,323-325] The reaction of $MoOCl_3(thf)_2$ with a variety of bidentate thioethers forms extremely air-sensitive green crystalline solids, $MoOCl_3L$, L = $RS(CH_2)_nSR$, n = 2, R = Me, Et, n-Pr, *cis*-RSCH=CHSR (R = Me, Et). If R = Ph no reaction occurs. The complexes are paramagnetic (~1.70 μ_B), typical of molybdenum(V). Octahedral symmetry with tetragonal distortion is the probable structure of $MoOCl_3L_2$, L = tetrahydrothiophene or $\overline{CH_2(CH_2)_4S}$.[324] Also reported $MoOCl_3L$, L = C_4H_8OS, SMe_2, SEt_2, and SPr-n_2 are considered to be six-coordinate dimers in the solid state (cf. TiX_3L). The hybrid tetradentates o-$H_2NC_6H_4S(CH_2)_nS$-o-$C_6H_4NH_2$, n = 2, 3, and 4, coordinate to molybdenum(V) as an SSN^- tridentate with RNH^- bridges and a free RN^+H_3 end.[325] These may be in equilibrium in solution with a monomeric species.

The coordination chemistry of tungsten(0) with thioethers and selenoethers is similar to that of chromium(0) and molybdenum(0). The monodentate ligand complexes $W(CO)_5L$, L = SBu-t_2, MeSBz, or tetrahydrothiophene, can be prepared from the hexacarbonyl as for the chromium and molybdenum analogues and are stable crystalline solids.[295,296,305] Tungsten(0) complexes have also been used in inversion studies both with monodentate ligands[242] and bidentate thioethers and selenoethers.[236-238] Further studies on the mechanism of ligand displacement from $M(CO)_4L$, M = Cr, Mo, W; L = bidentate thioether, have shown that when M = W, two reaction pathways are possible: (i) unimolecular ring opening and (ii) a concerted displacement of one end of the chelate by the entering replacement ligand.[300,326-330] The tungsten(0) complexes with the ligands **37**, **38**,[21] $Ph_2PCH_2CH_2SMe$,[307] and $(RCHS)_n$[309,310] parallel those of molybdenum(0). (π-C_5H_5)$W(CO)_2$(π-$MeSCH_2$) has been reported[317] (cf. molybdenum complex). Other complexes with bidentate ligands indicate the similarity between molybdenum and tungsten with 2,5-dithiahexane,[301,302,305] t-$BuSCH_2CH_2SBu$-t,[302,305] 1,4-diselenane,[303] 1,4-dithiane,[315] and $RS(CH_2)_nSR$,[305] R = Me, n = 6; R = Et, n = 2 or 4.

Tungsten(II) complexes with thioether ligands are also stabilized by π-acceptor ligands. Those reported are $W(CO)_3(SP)I_2$, SP = $Ph_2PCH_2CH_2SMe$, $W(CO)_2(DSP)Br_2$, $W(CO)_2(DSP)BrI$,[316] $[(\pi$-$C_5H_5)_2W(SMe_2)Br]PF_6$,[318] and $W(CO)_3(dth)(SnCH_3Cl_2)Cl$.[331] The latter of these is seven-coordinate, with capped octahedral symmetry.

The tungsten(IV) complexes *cis*-$WCl_4(SEt_2)_2$ and *trans*-WCl_4(tetrahydrothiophene)$_2$ can be isolated from the reaction of WCl_4 with excess ligand.[331] The geometry was ascertained by analysis of their far-infrared spectra. Attempts to prepare the bromo complexes gave impure oily solids. A detailed study of magnetic susceptibilities from 20–300 K indicated the presence of tungsten(V) impurities. $WCl_4(MeCN)_2$ reacts with 2,5-dithiahexane (dth) to give the seven-coordinate $WCl_4(dth)(MeCN)$. The thioether ligand is in the gauche configuration, the ν(CN) is shifted to higher frequency consistent with coordination, and the halides are all terminal. With the open-chain tetrathioethers $MeS(CH_2)_nS(CH_2)_mS(CH_2)_2SMe$ the seven-coordinate WCl_4L form by analogy to the dth complex. Insolubility prevents unambiguous characterization.

Reaction of WCl_5 with thioethers leads to nonstoichiometric complexes except for $WCl_5(tht)_2$ and $WCl_5(dth)$, which are 1:1 electrolytes in nitromethane and nitrobenzene.[333] The tht complex has a μ_{eff} of 0.83 μ_B, which is acceptable for tungsten(V). The oxotrichloro complexes $WOCl_3(dth)(thf)$ and $WOCl_3L$, L = tetrathioether, are thought to be seven-coordinate.[326] The tungsten(V) complexes with the N_2S_2 tetradentates are analogous to those of molybdenum(V).[325] The reaction of excess thioether ligand with either WCl_5 or WCl_6 leads to a series of reactions which include S-dealkylation, reductive elimination, and S-alkylation to finally yield $[R_3S][WCl_6]$.[198,334] However, the following tungsten(VI) complexes have been isolated: $[WCl_5(tht)_2]Cl$ and $[WCl_5(dth)]Cl$, $[WCl_5(SMe_2)]Cl$, all 1:1 electrolytes with abnormally high magnetic moments.[333] Two fluoro complexes have also been reported of stoichiometry WF_6L_2 where L is SEt_2 or $SeEt_2$. Both are involatile liquids and dissociate slightly in vacuo at 20 °C, the ^{19}F NMR show a single peak due probably to intramolecular exchange, and no ^{19}F–^{183}W coupling is seen.[335] With the bidentate 2,5-dithiahexane a ligand-bridged complex can be isolated: $(WSCl_4)_2(dth)$.[336]

E. Manganese, Technetium, and Rhenium

The coordination chemistry of manganese with thioether ligands is dominated by oxidation number one and the presence of π-acceptor ligands. With complexes (π-$MeSCH_2$)$M(CO)_4$, M = Mo, W, or Mn, it must be noted that the preferred mode of bonding of the bidentate π-$MeSCH_2$ group is a neutral allylic type.[318] There have been several studies on the π-cyclopentadienyldicarbonylmanganese(I) complexes with monodentate thioethers SR_2, R = Me, Et, Pr-n, Bu-n, Ph, $PhCH_2$, and also SC_4H_8(tht).[295,337-339] Substitution of the thioether by phosphine or phosphite proceeds via an S_N1 mechanism, i.e., M–S bond fission, as shown by a kinetic study.[339] The observation of four bands attributable to ν(CO) in the infrared spectrum was considered to be due to conformational isomerism about the M–S bond since only two were expected.[338] The complexes $Mn(CO)_3(TePh_2)_2X$, X = Cl, Br, or I, can be isolated from the reaction of $Mn(CO)_5X$ with $TePh_2$.[340] The butyl telluroether complex $Mn(CO)_4(TeBu_2)Cl$ dissociates to free ligand and the dimer $[Mn(CO)_4L]_2$. The reaction of $Mn(CO)_3(TePh_2)Cl$ with nitric oxide yields $Mn(NO)_3(TePh_2)$ and chlorinated ligand Ph_2TeCl_2. A cationic complex, $[Mn(CO)_4(TePh_2)_2]^+$, can be formed by the reaction of $Mn(CO)_3(TePh_2)Cl$ with $AlCl_3$ under carbon monoxide.[341] The reaction of $Mn(CO)_5(R)$, R = Me or Bz, with MeSBz in refluxing heptane yields a red oil, orthometallation occurring.[24,342] The subsequent reaction of this oil, $Mn(CO)_4$(o-$C_6H_4CH_2SMe$), with PPh_3 gives the crystalline $Mn(CO)_3(PPh_3)$(o-$C_6H_4CH_2SMe$), the structure of which has been reported.[24,25] With 2,5-diselenahexane and $Ph_2PCH_2CH_2SMe$ monomeric $Mn(CO)_3LX$ can be obtained.[304,307] However, as with molybdenum and tungsten, 1,4–dithiane prefers to bridge rather than chelate, forming $[Mn(CO)_3LBr]_2$.[315]

Interaction between sulfur and manganese(II) is very weak,[343] and this has been demonstrated by perturbing the absorption at 359 nm in the spectrum of a copper(II) tetrahydrothiophene complex by addition of manganese(II) ions. For Mn^{2+}–tht 1:1, $\log K^{Mn}{}_{Mn\text{-}tht} = -0.31 \pm 0.11$.[344]

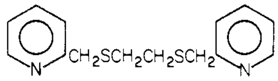
No complexes between technitium and thioethers, selenoethers, or telluroethers have been described.

Only one rhenium(I) complex has been reported, $Re(CO)_3X(MeSeCH_2CH_2SeMe)$, X = Cl or Br.[304] The rest of rhenium chalcogenoether complexes are dominated by the ligand 2,5-dithiahexane (dth). The reaction of $[Re_2Cl_8]^{2-}$ with dth yields several products of rhenium(II) and rhenium(III), one of which being $[Re_2Cl_5(dth)_2]$.[345] The structure determination[26,27] shows that both rhenium(II) and rhenium(III) are present in a dimer held together by a metal–metal bond. The magnetic moment ($\mu_{eff} = 1.73\ \mu_B$ per two rhenium atoms) is consistent with one unpaired electron occupying an orbital without spatial degeneracy.[27] Rhenium(III) coordination chemistry in this system is based on the Re_3Cl_9 unit.[345,346] The reaction of $ReCl_3$ with dth gives either $Re_3Cl_9(dth)_{1.5}$ which is polymeric with dth bridges or under longer reaction times products which approximate to $Re_3Cl_9(dth)_2$ and $Re_3Cl_9(dth)_3$. These latter complexes are probably due to breakdown of the polymer.[346] Twelve donors around the three rhenium atoms appear to be a general feature, as exemplified by $Re_3Cl_9(SEt_2)_2(H_2O)$.[347] An original formulation of the dth complex as $ReCl_3(dth)$[348] is now considered incorrect.[345] Under anhydrous conditions $ReCl_5$ together with thioxane gives the sulfur-bonded species $ReCl_4L_2$. An analogous complex, $ReBr_4L_2$, is formed by the reaction of thioxane in toluene with $K_2[ReBr_6]$ in concentrated hydrobromic acid.[349] The infrared spectra suggest that these complexes have the trans configuration. Several rhenium(V) oxo complexes have been reported of the type $ReOX_3L_2$, X = halide and L = monodentate or $^1/_2$ bidentate thioether.[345,349,350] $ReOCl_3(dth)$ was prepared from potassium rhenate in KI solution and has $\nu(ReO)$ at 980 cm^{-1}.[345] Replacement of $AsPh_3$ in $ReOX_3(AsPh_3)_2$, X = Cl, Br, by 1,4-dithoxane or 1,4-dithiane gave *trans*-$[ReOX_3L_2]$ in which the ligands are presumably monodentate and sulfur bonded.[349] Finally, the recrystallization of $ReOCl_3(EtSCH_2CH_2SEt)$ in acetone gives $ReO(OH)Cl_2L$ which reverst on acidification.[350]

F. Iron, Ruthenium, and Osmium

The complexes $Fe(CO)_4L$, L = tetrahydrothiophene (tht) or $TePh_2$, are prepared from $Fe_3(CO)_{12}$ and the ligand under the action of ultraviolet light.[295,340] $Fe(CO)_2(NO)_2$ reacts with $TePh_2$ to give $Fe(CO)(NO)_2TePh_2$.[340] It is surprising that no other iron(0) complexes could be found in view of the paucity of iron–thioether complexes in general.

The iron(II) complexes of ligand **42**, $FeLX_2$, X = Cl,



42

$MeS(CH_2)_nS(CH_2)_mS(CH_2)_nSMe$

$n = m = 2$ (2,2,2); $n = m = 3$ (3,3,3)
$n = 2, m = 3$ (2,3,2); $n = 3, m = 2$ (3,2,3)

43

Br, I, and NCS, have magnetic moments in the range 5.3–5.4 μ_B, consistent with a high-spin configuration and octahedral symmetry. In nitromethane solution dissociation occurs as shown in eq 19, and the tendency for

$$FeLX_2 + CH_3NO_2 \rightleftharpoons [FeL(CH_3NO_2)X]X \quad (19)$$

the equilibrium to lie to the right is in the order Cl ≈ NCS < Br < I.[351]

Iron(II) and iron(III) complexes with the ligand $HS(CH_2)_2S(CH_2)_5S(CH_2)_2SH$ have been prepared. They are polymeric and nonstoichiometric and have also had their thermal decompositions studied.[352,353] Another iron(III) complex to be reported is $FeCl_3(C_4H_8OS)$ in which the ligand is thought to act as an O,S-bidentate. However, the structural determination by spectroscopic means is inconclusive.[354] The open-chain tetrathioether ligands form the isolable complexes $[FeLX_2][FeX_4]$, L = (2,2,2), (2,3,2), X = Cl, Br; L = (3,3,3), X = Cl.[355] These complexes are extremely moisture sensitive, and in view of the "hardness" of the ferric ion it is surprising that they form at all. Both iron atoms have an $S = {}^5/_2$ ground state; the magnetic moment of $[Fe(2,2,2)Cl_2][FeCl_4]$ at 293 K was found to be 5.91 μ_B.

Several ruthenium(II) complexes have been reported, including neutral[356] and cationic species.[357-359] Neutral species include $RuCl_2(SMe_2)_4$ and $RuX_2(RSCH_2CH_2SR)_2$, X = Cl, Br, R = Et or Ph. The latter complexes have been shown to undergo two types of reaction. The complexes R = Et are oxidized by perchloric acid to the cationic ruthenium(III) species $[RuX_2(EtSCH_2CH_2SEt)_2](ClO_4)$. The complexes R = Ph react with carbon monoxide in refluxing 2-methoxyethanol to form the *cis*-dicarbonyl $RuX_2(CO)_2(PhSCH_2CH_2SPh)$.[356] The complex $RuCl_2(CO)[MeC(CH_2SEt)_3$ has been formed by carbon monoxide abstraction from refluxing dimethylformamide by the ruthenium(III) species $RuCl_3L$. This is a unique case of a thioether complex undergoing a reaction common among phosphine complexes. Forcing conditions of carbon monoxide in refluxing 2-methoxyethanol converts the $RuCl_3L$ complex into $RuCl_2(CO)_2L$ having cis carbonyls and no free SEt groups. This complex is therefore seven-coordinate.[356] Three cationic ruthenium(II) complexes reported are $[Ru(bpy)L](ClO_4)_2$, L = **42**,[357] $[Ru(SEt_2)_3(CO)_2(SnCl_3)]X$, X = Cl, BPh_4 [$\nu(CO)$ = 1955 and 1990 cm^{-1}],[358] and $[Ru(NH_3)_5(EMe_2)]^{2+}$, E = S, Se, or Te.[359] Study of the latter complexes has suggested that σ^* orbitals on EMe_2 may contribute to back-bonding and metal–ligand charge transfer.

There have been several reports of monodentate thioether complexes with ruthenium(III)[356,359-367] which include two basic species, a monomer, RuL_3X_3, and a dimer, $[ML_2X_3]_2$. A further type, $RuL_2L'Cl_3$, L = PhSPr-*i*, L′ = MeOH or MeCN, has also been reported.[356] Of the monomeric RuL_3X_3, the following have been isolated: X = Cl, L = SMe_2, SEt_2; X = Cl, Br, L = PhSMe, PhSEt, PhSPr-*n*, PhSBu-*n*. The main structural study has surrounded the complex $Ru(SEt_2)_3Cl_3$ which has the same X-ray powder diffraction pattern as its rhodium and iridium analogues.[361] The first assignment of a structure was to the iridium complex and was thought to be *facial*. However, later work has shown by NMR on the iridium complex,[363] EPR on the ruthenium complex,[356] and far-infrared spectroscopy of the complex $Ru(SMe_2)_3Cl_3$[365] that the configuration of these complexes is *meridonial*. Magnetic moments of 1.9–2.1 μ_B have been reported for the ruthenium complexes consistent with low-spin d^5 in an octahedral symmetry.[356,361] Interestingly the dimer $[Ru(SEt_2)_2Cl_3]_2$ has a magnetic moment of 0.95 μ_B per ruthenium which must be due to considerable spin coupling between metal atoms.[361] The electronic spectra of the ruthenium(III) thioether complexes exhibit charge-transfer absorptions as low as 24 000 cm^{-1} ($t_2 \leftarrow \pi - S$).[356] Little or no catalytic activity was shown by $[Ru(PhSPr\text{-}i)_2(MeOH)Cl_3]$ or $[Ru(PhSPr\text{-}n)_3Cl_3]$ toward the hydrogenation of alkenes or alkynes.[356] In the nitrosyl complexes $Ru(NO)L_2Cl_3$, L = SR_2, PhSR, (R = Me, Et, Pr-*n*), tetrahydrothiophene, EtSBu-*n*, $SeEt_2$, and PhSeEt,[360,362,364] there is little change in the ν(NO) in the infrared spectra, as compared to free NO, suggesting that there is little change in the electron distribution on coordination. The structure is thought to have *trans*-L–M–L.[364]

With the potentially bidentate ligand 1,4-thioxane the ligand bonds only through the sulfur, giving RuL_3Cl_3 complex.[367] With the dithioethers 1,4-dithiane and $RSCH_2CH_2SR$, R = Me, Et, Pr-*n*, or Ph, the predominant species formed is $[RuL_{1.5}Cl_3]_n$ in which the ligands appear to both chelate and bridge.[356,367] Other stoichiometries have been reported,[367,368] perhaps the most interesting being $Ru_2(Pr\text{-}iSeCH_2CH_2SePr\text{-}i)_3$ in which the ligands are in a cis conformation but not chelating and the three ligands all bridge between the two metal centers.[368] The tripod tridentate forms $Ru\{MeC(CH_2SEt)_3\}Cl_3$ whereas the linear tridentate ligands gave only insoluble powders.[356]

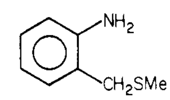
The only osmium thioether complex in the literature is $Os(SEt_2)_3Cl_3$, having a magnetic moment of 1.87 μ_B.[102] However, recently we have prepared a series of osmium(IV) complexes $[Os(bidentate)Cl_4]$ from $[OsCl_6]^{2-}$ plus ligand in 2-methoxyethanol;[369] the bidentate ligands used were 2,5-dithiahexane, 2,6-dithiaheptane, *cis*-MeSCH=CHSMe, 1,2-bis(phenylthio)ethane, and *o*-bis(methylthio)benzene. The grey/green products have magnetic moments of ~1.3 μ_B, consistent with a low-spin d^5 configuration.

G. Cobalt, Rhodium, and Iridium

For cobalt, the easiest grouping is by ligand type. Apart from one reference to thioxane complexes[354] in which it is suggested that the ligand is sulfur bonded in $[CoL_2Br_2]$, there are no reports of monodentate group 6B R_2E ligand complexes with cobalt in any oxidation number.

The weak interaction between cobalt and thioether donors is exemplified by the existence of only three references on bidentate thioether ligand complexes of cobalt(II). Complexes reported are of the type CoL_2X_2, where L = 2,5-dithiahexane (dth), 3,6-dithiaoctane (dto), and $i\text{-}PrSCH_2CH_2SPr\text{-}i$ and X = Cl, Br, I, and NCS, and also the perchlorato complex $Co(dth)_2(ClO_4)_2$. Spectra and magnetic moments indicate an octahedral geometry for these complexes,[370,371] and coordinated perchlorate is indicated by splitting of the ν_3 and ν_4-(ClO_4^-) bonds in the infrared spectrum[372] and by a crystallographic analysis.[28] The isopropyl ligand has a weaker ligand field than 2,5-dithiahexane due probably to steric effects.[371] Similarly, the 3,6-dithiaoctane complexes are less stable than those of 2,5-dithiahexane.[370]

For formation of more stable complexes hybrid thioether bidentates including nitrogen,[373,381] phosphorus,[382] arsenic,[383] oxygen,[373,375,384] and sulfide (RS^-),[375] have been used as the other donor site. A study of the cobalt(III) complexes of the type $[Co(RSCH_2CH_2NH_2)(en)_2]^{3+}$ and $[Co\{RS(CH_2)_nCO_2\}(en)_2]^{2+}$ where en = 1,2-diaminoethane and n = 1 or 2 has indicated that the thioether donor atoms are coordinated stereoselectively.[373] A study of the redox behavior[375,376] showed that sulfur allowed a high level of inner-sphere reactivity, and structure determinations of the former complex with R = Me and the latter with R = Bz and n = 1 showed that the sulfur atoms do not induce a significant structural trans effect.[374] The important biological implications of thioether sulfur as an electron-transfer bridge have been noted.[376] Sulfur nitrogen bidentate ligands which complex with cobalt(II) are 2-[(methylthio)methyl]aniline (44, mtma) and the 6-



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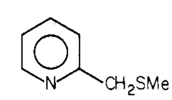

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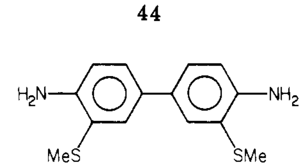

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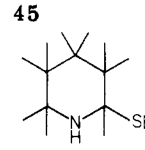

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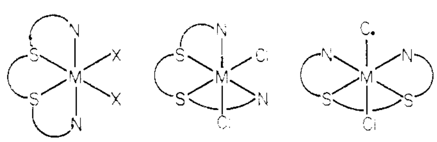
chloro, 6-methyl, and 4-chloro derivatives,[381] 2-methyl-9-(methylthio)quinoline (**15**, mmtq),[377] 2-[(methylthio)methyl]pyridine (**45**, mtp),[378] 2-(methylthio)aniline (**7**, mta), 3,3′-bis(methylthio)benzidine (**46**, mtb),[386] and *trans*-2-(ethylthio)cyclopentylamine (**47**, ept).[379] These papers demonstrate that for this system octahedral stereochemistry is the most favorable, although there is a fine balance between this and a tetrahedral geometry. The balance appears to be affected by both steric and electronic factors. Octahedral complexes of the type CoL_2X_2 have been isolated for all the ligands except (mtb). They are all very insoluble, but magnetic moments and electronic spectra indicate the octahedral stereochemistry. Values of μ_{eff} between ~4.4 and ~4.8 μ_B indicate tetrahedral cobalt(II) and above ~4.8 μ_B indicate octahedral cobalt(II). For mmtq only the thiocyanate was octahedral; the halide complexes with this bulky ligand were tetrahedral, as was $Co(mtb)Cl_2$. This latter complex shows uncoordinated NH in the infrared spectrum, and it is interesting that it is the thioether sulfur and not the amine nitrogen that coordinates to the cobalt(II) ion. The complex $Co(mtp)_2Cl_2$, a lilac solid, will dissolve slightly to give a green solution in which the cobalt may be in a tetrahedral environment. One tris-ligand perchlorate complex has been reported, $[Co(mtp)_3](ClO_4)_2$. Further effects of ligand field on stereochemistry are demonstrated by the cobalt(II) complexes of the hybrid bidentates **4** and **6**. The As–S ligand forms the square-planar $[CoL_2](ClO_4)_2$, μ_{eff} = 2.62 μ_B. However, this ligand also yields the octahedral $[CoL_2I_2]$, μ_{eff} = 5.31 μ_B.[383] With the P–S and P–Se bidentates the square-pyramidal $[CoL_2X](ClO_4)$, μ_{eff} = 3.1–3.5 μ_B, may be isolated. The electronic spectra show three distinct bands below 2200 cm^{-1}.[382] There is one report of hybrid bidentate complexes with sulfide as the second donor. Cobalt(III) forms the complexes $[Co(cis\text{-}SCH{=}CHSR)_3]$, R = Me, Et, and *n*-Bu.[385]

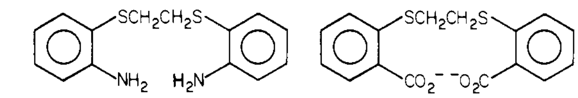
Thioether-containing tridentates of the type $H_2NCH_2CH_2S(CH_2)_nCO_2^-$, n = 1 or 2, have been complexed to cobalt(III), forming [Co(tridentate)[1,1,1-tri(aminoethyl)ethane]]$^{2+}$, [Co(tridentate)(L-methioninato)]$^+$, and [Co(tridentate)$_2$]$^+$.[373,386,387] These complexes can be resolved into stereoisomers by chromatography and have also been studied by NMR and circular dichroism spectroscopy. Two other tridentate ligands have been studied with cobalt(II), S-$(CH_2CH_2NR_2)_2$, R = H or Me.[388,389] For R = Me, spectra and magnetic moments indicate that the solid complexes of stoichiometry $CoLX_2$ are high-spin five-coordinate; however, in solution appreciable association occurs, probably forming octahedral dimers.[389] For R = H, the complex *u-fac*-[CoL$_2$]$^{3+}$ formed and had a stability constant β_2 = 38.3 compared to a value of 48.8 for [Co(dien)$_2$]$^{3+}$, dien = $N(CH_2CH_2NH_2)_2$. This indicates a low affinity of sulfur for cobalt(III) compared to nitrogen.[388] A study of the racemization suggested that Co–S bond cleavage occurred.

For octahedral complexes of an open-chain tetradentate with the donor sequence N–S–S–N there are three configurations, symmetric-cis (s-cis or α-cis) (**48**), unsymmetrical-cis (u-cis or β-cis) (**49**), and trans (**50**).



48 49 50

Ligands used to form these types of complex are $H_2N(CH_2)_nS(CH_2)_mS(CH_2)_nNH_2$, $n = m$ = 2, 1,8-diamino-3,6-dithiaoctane (EEE), n = 2, m = 3, 1,9-diamino-3,7-dithianonane (ETE), $n = m$ = 3, 1,10-diamino-4,7-dithiadecane (TET), and derivatives with methylated methylene linkages. The effect on configuration of altering the backbone lengths was studied by preparation of [Co(N(R)S(R)S(R)N)Cl$_2$]$^+$ for EEE, ETE, and TET.[390] With EEE, only the s-cis form was found, with ETE both trans and u-cis, and with TET both u-cis and s-cis. Changing the chloro ligands for several other anions still gave only the s-cis form. This was corroborated for [Co(EEE)X$_2$]$^+$ [391] and for X = Cl and NO_2 the complexes resolved into their optical isomers.[392] A series of complexes were also prepared with TET,[393] [Co(TET)X$_2$]$^+$, which were all u-cis except for X = Cl which gave a mixture of u-cis and trans as found above.[390] The structure of the complex [Co(ETE)-(NO_2)Cl]Cl has been determined.[29] The [CoLX$_2$]$^+$ series have been prepared for two methylated ligands, 1,8-dimethyl-EEE[394] and 4-methyl-EEE.[395,396] The 1,8-dimethyl ligand is L-(–), and the absolute configurations of the complexes have been studied by circular dichroism spectroscopy. The 4-methyl derivative of EEE formed s-cis complexes and for X = Cl was resolved into its optical isomers. The s-cis configuration can be identified by electronic spectra. In this geometry the $^1T_{1g}$ state is split, giving rise to a split band in the visible spectrum of the complex.[391,393] Reactions of this type of complex have been studied.[397,399–401] The iron(II) reduction of [Co(EEE)Cl$_2$]$^+$ was found to be 10^3 times faster than for the analogous complex with the N_4 ligand.[397] Comparable systems undergo this reaction by an inner-sphere mechanism,[398] and it was found that this mechanism operated for this case also.[397,399,400] The complexes [Co(EEE)(bidentate)]$^{n+}$, bidentate = 1,10-phenanthroline, α,α'-bipyridyl, and acetylacetonate, were not reduced by iron(II), which indicated that sulfur was not the bridging atom, which must therefore be chloride ion.[397] The increase in rate of reaction for the N_2S_2 ligand over the N_4 ligand must be due to the thioether donor trans to the bridging atom, a nonbridging ligand effect.[399,400] The acid- and base-catalyzed hydrolyses of *trans*-[Co(ETE)Cl$_2$]$^+$ [401] and the mercury-catalyzed hydrolysis of *s-cis*-[Co(EEE)Cl$_2$]$^+$ [402] have been studied. Other tetradentate ligands with the N_2S_2 donor set which have been complexed to cobalt are **51**,[403,404] **42**,[351] and **21**.[192] Ligand **51** gave *cis*-octa-



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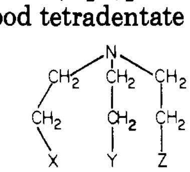
hedral [CoLCl$_2$]Cl[403] and *trans*-[CoLX$_2$], X = Cl, Br, I, NCS, with μ_{eff} = 4.6–5.0 μ_B. The trans geometry was indicated by a single ν(Co–X) stretch in their infrared spectra. Also isolated were the nitrato complex [CoL-(NO_3)$_2$](EtOH) and $Co_2L_3(ClO_4)_4$ which is probably ligand bridged.[404]

The pyridyl ligand **42** also gave the octahedral MLX_2, X = Cl, Br, I, NCS. In nitromethane solution an equilibrium was seen (eq 20). The steric effect of the

$$MLX_2 + \text{nitromethane} \rightleftharpoons [MLX(\text{nitromethane})]X \quad (20)$$

terminal alkyl groups with **21** was demonstrated by the isolation of the tetrahedral complex [CoL]Br$_2$, R = Ph_3C, and the octahedral $CoLBr_2$, R = Bz.[192] No dealkylation was found in this system. Attempts to prepare cobalt(II) complexes of the linear tetrathioethers **18**[191] and **43**[405] gave only the iodo complexes $CoLI_2$, L = **18**, n = 2, and L = **43** (2,2,2), μ_{eff} = 5.00 and 4.90 μ_B, respectively. This demonstrates the poor donor ability of thioether sulfur to cobalt(II). Replacement of the two terminal thioether groups in **43** (3,3,3) by Ph_2P[406] gave a ligand which readily complexed to cobalt(II). The P_2S_2 ligand formed the maroon square-pyramidal [CoLX]Y, X = Cl, Y = ClO_4 or BPh_4; X = Br or I, Y = BPh_4, with magnetic moments in the region 1.98–2.13 μ_B.

The dicarboxy dithioether tetradentate **52** has been reported to form $CoL(H_2O)_2$ with octahedral stereochemistry.[383] Tripod tetradentate ligands **53** have also



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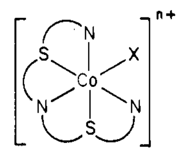
X = Y = Z = SR (N-S$_3$)
X = Y = NEt$_2$, Z = SMe (N-N$_2$S)
X = NEt$_2$, Y = Z = SMe (N-NS$_2$)
X = NEt$_2$, Y = SMe, Z = PPh$_2$ (N-NSP)

been studied with cobalt(II).[407,408,410–412] This type of ligand imposes five-coordinate geometry on its complexes; thus the species which formed were [Co(tripod)X]$^+$. A structure determination of [Co(N-S$_3$)Br]-PF_6, R = *t*-Bu, indicated a trigonal-bipyramidal geometry with a small tetrahedral distortion. The N and Br donor atoms were axial.[408] The electronic spectra of these complexes were typcial of this geometry for cobalt(II) in a high-spin state.[409] Magnetic moments confirmed the high-spin formulation, $\mu_{eff} = 4.3–4.6\ \mu_B$. If CoX_2 was used as starting material the complexes [Co(tripod)X][CoX_4] were isolated, indicating the stability of the five-coordinate species.[407,411] No spin-crossover ligand fields were found for cobalt(II) in this set of ligands. The complex $Co(SP_2)I_2$ is almost certainly also five-coordinate but was poorly characterized,[413] $SP_2 = S(CH_2CH_2PPh_2)_2$. Stereoselectivity in complexes of cobalt(III) has been studied with the pentadentate $H_2N(CH_2)_2S(CH_2)_2N(Me)(CH_2)_2S(CH_2)_2NH_2$.[414,415] With pentadentate ligands it is usual to obtain a mixture of isomers.[416] However, in this case only one isomer was found for $[Co(pentadentate)X]^{n+}$, X = Cl, Br, N_3, NCS, H_2O. This isomer is the α,α' form in which any three consecutive donor atoms in the multidentate are in *fac* positions (**54**). Extra stability



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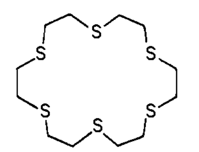
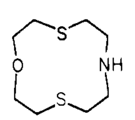


55, /‾\ = $(CH_2)_2$



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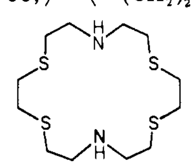

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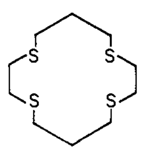
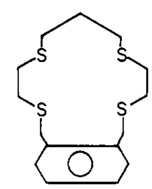


58 (TTP)



59 (TTX)

is conferred upon the cobalt–thioether bond if the sulfur atom is incorporated in a macrocycle. Thus, the following octahedral species have been prepared: $[CoL](picrate)_2$, L = **55**[417] and **57**;[418] $[CoLX_2]$, L = **56**, X = Cl, Br;[417] and $[CoLX_2]^+$, L = **58** and **59**, X = Cl, Br, I, NCS, NO_2.[419] The complex with the hexathioether ligand had a spectrum and a magnetic moment (3.01 μ_B) typical of octahedral stereochemistry.[417] However, with the analogous ligand in which two sulfur atoms were replaced by –NH– the magnetic moment was low for a high-spin d^7 system.[418] However, it was thought that this may be due to a high-spin, low-spin crossover. With the ligands **58** (TTP) and **59** (TTX) there was an interesting stereochemical difference between the complexes of the two ligands with cobalt(III). With the ligand TTX the complexes had the trans geometry for all X as shown above; however, only with X = I was this the geometry with TTP. All other cases had the tetradentate coordinated in a folded manner, and it was suggested that TTP was the borderline in size of macrocycle for encompassing a cobalt(III) ion. The iodide complex had a trans configuration probably because of the unfavorable steric interactions of cis iodides.[419] Stability constant studies have been performed on both macrocycle and straight-chain multidentate ligands as a series containing thioether donors.[420–424] Formation constant measurements on a variety of thioether-containing ligands with first row transition metals including cobalt(II) indicated that the interaction between thioether and cobalt(II) may be classed as being weak.[343,425–428] The bisthiol thioether tridentate $S(CH_2CH_2SH)_2$ showed interesting differences when coordinated to cobalt(II) and cobalt(III).[429] The higher oxidation state of the metal gave $[Co_2(S(CH_2CH_2S)_2)_3]\cdot H_2O$ containing two sulfide bridges whereas a μ-superoxo compound was formed with cobalt(II). Thermal decomposition has been studied with the polymeric complex of cobalt(II) with a bisthiol bis(thioether) ligand.[352,353] Octahedral complexes were isolated with three multidentate ligands containing both thioether and carbonyl donor sites. It was assumed that there was thioether coordination.[430]

Rhodium(I)–thioether complexes are not readily prepared from our experience, and this is borne out by there only being three papers on this type of complex.[431–433] The species $Rh(CO)L_2Cl$, L = SEt_2, $SeEt_2$, and $TeEt_2$, were prepared by reaction of excess ligand with $[Rh(CO)_2Cl]_2$ in pentane and subsequent recrystallization at −80 °C.[431] The products were yellow oils for the thioether and selenoether and a yellow-brown solid (mp 30 °C) for the telluroether. These complexes readily underwent oxidative addition with halogens and with HCl. With MeI oxidative-addition product $Rh(Me)(CO)L_2ClI$ reacted the carbon monoxide to give the acyl product $Rh(CH_3CO)(CO)L_2ClI$. The low π acidity and high polarizability of the EEt_2 ligands were thought to be the reason for the high reactivity toward oxidative addition that was found here. The ligands tetracyanoethylene and fumaronitrile (L) appeared to stabilize rhodium(I)–thioether bonding as the complexes $[Rh(PhSCH_2CH_2SPh)LL']Cl$, L′ = Ph_3P, pyridine, or *p*-toluidine could be formed.[432] With 2,5-dithiahexane (dth) the complex $[RhCl(CO)(dth)]_n$ exhibited $\nu(CO)$ at 1830 and 1800 cm^{-1}.[433] It was thought that the carbon monoxide took part in bridging between metal atoms. With 3,6-dithiaoctane (dto) the product exhibited five $\nu(CO)$ bands and was not characterized.

Octahedral rhodium(III) complexes are stereochemically inert, and therefore the species RhL_3X_3 may exist as either facial or meridonial isomers. Although one paper has suggested that the preferred isomer is facial,[361] all others find that the meridonial isomer is preferred.[245,363,433,434] When the ligand was PhSR it was found that both isomers could be isolated for R = Me or *n*-Pr.[433] Other ligands used to form this type of complex were SMe_2,[368,434–436] SEt_2,[361,363,366,434–438] C_4H_8S and $C_5H_{10}S$,[434] S-bonded thioxane,[440] and $S(CH_2SiMe_3)_2$.[245] This latter ligand when coordinated has the sulfur atom prochiral, as are the (trimethylsilyl)methyl groups, and the rhodium(III) complex has been used in inversion studies (section V). Selenoether analogues have been prepared with $SeMe_2$[366] and $SeEt_2$.[366] It was found by using the ligand SEt_2 in the complexes ML_3X_3, M = Ru, Rh, and Ir, X = Cl, Br, and I, that the rhodium complex was the most stable with respect to dissociation under vacuum and elevated temperature to MX_3 and free ligand.[361] For the rhodium series the stability was in the order Cl > Br > I. The reaction of $Na_3[RhCl_6]$ with monodentate thioether gave more than one product, and it has been demonstrated that the species $[RhL_2X_4]^-$ and $[RhL_4X_2]^+$ can be isolated.[366,435,436,438,439] A heavy atom analysis of $[Rh(SEt_2)_4Cl_2][Rh(SEt_2)_2Cl_4]$ indicated that both anion and cation had the trans structure.[439]

Little effort has been put into the study of thioether complexes as catalysts. This may be due to a prejudice against sulfur compounds in catalysts, a throwback to heterogeneous catalysts. The complexes RhL_3Cl_3, L = SEt_2 and SBz_2, have been shown to catalyze the hydrogenation of a variety of alkenes in dimethylacetamide solution.[441-443] It was suggested that a rhodium(I) intermediate was involved, stabilized by coordination of the alkene.

Two other types of rhodium(III)–monodentate thioether complexes are known, a dimer, $Rh_2(SMe_2)(Me)_4I_2$, which has had a structure analysis showing the metal ions bridged by two iodide and one thioether ligand,[34,444] and η^5-C_5Me_5-Rh species $[Rh(C_5Me_5)]_2(SMe_2)Cl_4$ and $[Rh(C_5Me_5)(SMe_2)_3]^{2+}$.[445]

With uncharged bidentate ligands several types of complex have been reported: the polymeric $[RhLX_3]_n$,[440] anionic $[RhLX_4]^-$,[369,446] cationic $[RhL_2X_2]^+$,[433,440,446,447] and $[Rh(C_5Me_5)L_2]^{2+}$.[445] The complex [Rh(dithiahexane)$_2Cl_2$] has been studied by NMR,[440,447] and conductivity measurements have shown it to be a 1:1 electrolyte in nitromethane solution.[440] The polymeric $[Rh(PhSCH_2CH_2SPh)Cl_3]_n$ has a halogen-bridged structure.[440] Attempts to prepare high oxidation state complexes of transition-metal–thioether complexes have shown that [Rh(dithiahexane)$Cl_4]^+$ cannot be oxidized.[369]

The cyclic tetrathioethers TTP (**58**) and TTX (**59**) gave rhodium(III) complexes of the type $[RLX_2]^+$ in which the ligands L were in the folded conformation.[419] Open-chain tetradentates of the type **42** or **51** always gave complexes of stoichiomtery $Rh_4L_3X_{12}$ irrespective of the ratio of reactants.[191,448] There has been a brief report on the complex $[Rh\{MeC(CH_2SEt)_3\}Cl_3]$.[433]

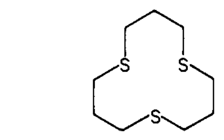
As with rhodium, very few examples of iridium(I)–thioether system have been reported. The known examples are stabilized by coordination of cyclooctadiene (COD) to the metal center, Ir(COD)[S$(CH_2CH_2SPh)_2$]Cl and Ir(COD)(dth)Cl.[433] There has been confusion in the literature over the isomers produced in the iridium(III)–thioether system. The yellow isomer, IrL_3Cl_3, has been prepared for a variety of monodentate thioethers and selenoethers.[102,245,361,363,366,433,434,449-453] It has a *mer* configuration.[245,363,434] It is probable that the red isomer is *trans*-$[Ir(SR_2)_4Cl_2]^+$-*trans*-$[Ir(SR_2)_2Cl_4]^-$.[453] The S_3X_3 chromophore was also found in $[Ir(MeC(CH_2SEt)_3)Cl_3]$ and $[Ir(S(CH_2CH_2SR)_2)X_3]$.[433] In our study on high oxidation state thioether complexes, the only method by which we could prepare iridium(IV) complexes was to prepare [Ir(bidentate)$Cl_4]^-$ and oxidize this to [Ir(bidentate)Cl_4].[369] These complexes have μ_{eff} = 1.6 μ_B, as expected for one unpaired electron in low spin d^5. The SMe_2 analogue $[Ir(SMe_2)_2Cl_4]^-$ exists as two isomers, and both oxidized to the iridium(IV) complex.[369]

H. Nickel, Palladium, and Platinum

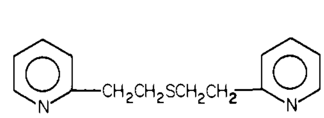
Although there are no reported monodentate thioether complexes with nickel(II), there are several papers on bidentate thioethers and selenoethers. Ligands used have been 2,5-dithiahexane,[371,454-459] 3,6-dithiaoctane,[455] and 2,5-dimethyl-3,6-dithiaoctane (*i*-$PrSCH_2CH_2S$-*i*-Pr)[371] and its selenium analogue.[456] All gave octahedral species of the type Ni(bidentate)$_2X_2$, X = halide or pseudohalide. An infrared isotope study gave ν(Ni–S) in the region 260–210 cm^{-1}.[457] A tris-ligand complex has also been reported, [Ni(2,5-dithiahexane)$_3$]$(ClO_4)_2$, isolated as a blue solid. The cyclic bidentate ligands 1,4-dithiacycloheptane (dtch) and 1,5-dithiacyclooctane (dtco) behave rather differently with nickel(II) salts.[127] Both ligands form the square-planar diamagnetic $[NiL_2]Y_2$, Y = ClO_4 or BF_4, but only dtco will form an octahedral chloro complex, $[Ni(dtco)_2Cl_2]_n$, shown to be polymeric with bridging ligands by an X-ray crystal structure.[35] The bromo and iodo complexes give several different species. Replacement of one thioether site in the bidentate by a sulfide (mercaptide) gives exclusively square-planar diamagnetic nickel(II) complexes, NiL_2, where L = *cis*-$^-SCH{=}CHSR$ (R = Me, Et, *n*-Bu),[385] $EtS(CH_2)_3S^-$,[384] or *o*-(methylthio)benzenethiolato.[384]

S-Alkylation studies have yielded complexes of the hybrid ligands $R_2NCH_2CH_2SR^1$, R = H or alkyl, R^1 = Me, Bz. These are octahedral $[Ni(N(R)S)_2X_2]$.[212,215,217] It was noted that in methanol solution $Ni(RSCH_2CH_2NH_2)_2I_2$ gave conductance values of a 2:1 electrolyte, indicating complete solvolysis.[212] Analysis of the electronic spectra of a series Ni(bidentate)$_2X_2$ where bidentates were S(R)S, S(R)N, and N(R)N, indicated that there was little change in the in-plane ligand field ($10Dq^{xy}$).[457] With the cyclic amine ligand *trans*-2-(ethylthio)cyclopentylamine (etp, **47**) octahedral complexes $Ni(etp)_2X_2$, X = Cl, Br, NCS, and $[Ni(etp)_3](ClO_4)_2$ were isolated: μ_{eff} = 3.18–3.23 μ_B. Magnetic and spectral data indicated that nickel(II) complexes of mtp (**45**), $Ni(mtp)_2X_2$, X = Cl, Br, I, NCS, were octahedral;[378] however with the sterically hindered mmtq (**15**) the structure was dependent upon the X ligand in $Ni(mmtq)_2X_2$.[377] For X = Cl or Br a pseudotetrahedral structure was indicated, whereas with thiocyanate a bridged octahedral structure was proposed. The structure with X = I was uncertain. With mtma (**44**)[381] and mta (**7**)[380] octahedral monomers were formed (NiL_2Cl_2), whereas with mtb (**46**) an octahedral polymer with bridging ligands and stoichiometry ($NiLCl_2$) was isolated.[380] With hybrid bidentates containing phosphorus the group 5B donor dominates the ligand field.[188] With weak ligands an octahedral stereochemistry is expected with nickel(II). With the *o*-phenylene P(R)S ligand **6**, the chloro complex is octahedral $[Ni(P(R)S)_2Cl_2]$; however, it is possible to convert this into five- and four-coordinate species.[188,458] The bromo and iodo complexes are square-planar. Fluorination of the *o*-phenylene backbone weakens the ligand strength, as shown by an octahedral bromo complex and only an octahedral chloro complex. The selenium analogue of **6** (Se(R)P) exhibits the same coordination chemistry as S(R)P.[184,458] These ligands all S-dealkylate readily (see section IV).[182,184,188] The five-coordinate complexes of the above ligands[188,458] and of the ligands $Et_2PCH_2CH_2SEt$[459] and $Ph_2PCH_2CH_2SR$ (R = Me, Et, Ph)[460] are square pyramidal from electronic spectra.[461] With the As(R)S bidentate **4** the isolated $[Ni(As(R)S)_2X_2]$, X = Cl, Br, I, tended to ionize in solution and decompose[462] in the presence of water.

The only all thioether tridentate, **60** (TTD), which has been coordinated to nickel(II), gave the complex $[Ni(TTD)_2](BF_4)_2$.[126] With $S(CH_2CH_2SH)_2$ a dimeric species (Ni_2L_2) has been isolated[463,464] in which the nickel atoms are bridged by two thiolo donors, the ge-



60 (TTD)



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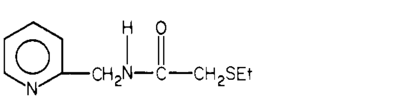
ometry around the nickel atoms is square planar, and the nickel atoms are ~2.7 Å apart.[37,38] An S-alkylation reaction has been used to prepare the hybrid ligand complex $Ni[H_2N(CH_2)_2SCH_2CO_2]_2$.[215] With SN_2 tridentate ligands both five-coordinate and octahedral geometries are found with nickel(II). With $(Me_2NCH_2CH_2)_2S$ the species $NiLX_2$, X = Cl, Br, NCS, have spectroscopic and magnetic properties indicating a high-spin five-coordinate system.[389] In solution association occurs to an appreciable extent, probably forming octahedral dimers.

With pyridyl ligand **61** the series $NiLX_2$, X = Cl, Br, I, NCS, has been reported as high-spin trigonal bipyramidal.[465] However, the chloro complex has also been reported as a chloro-bridged dimer.[466] It is quite probable that both chloro species may be isolated depending on the conditions used. Two stereochemical types have been reported with the SP_2 phosphorus–sulfur tridentate **41**. For $[NiLX]_2[NiX_4]$ the cation is square planar,[413] however, the diamagnetic five-coordinate complex [NiLX]X, X = Cl, Br, I, may also be isolated.[467] A structure determination for X = I shows the geometry to be intermediate between square pyramidal and trigonal bipyramidal.[468] With the S_2P tridentate **8** the complex $NiLI_2$ has a square-pyramidal structure.[39] The effect of pressure on the electronic spectra of five-coordinate nickel(II) has shown that increasing pressure gives a blue shift to the $^1A_1 \rightarrow a^1E$ (ν_1) transition.[469] This shift is much larger for trigonal-bipyramidal than for square-pyramidal cases. With $NiLI_2$, L = **8**, the shift is 12 cm^{-1} $kbar^{-1}$, a known square-pyramidal complex.[39] The nickel(II) complexes formed with the arsine analogue of **41** again show more than one geometry: the iodo complex is diamagnetic five-coordinate $NiLI_2$ whereas the bromo complex is octahedral in the solid state (NiL_2Br_2, μ_{eff} = 3.10 μ_B) but five-coordinate in solution.[470] The amide ligand **62** acts as an N_2S tridentate in the square-planar complex NiLX.[471] Tetradentate ligands can be divided into



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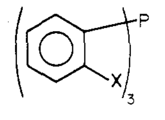
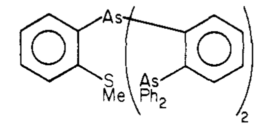
three types: tripod, open-chain (linear), and macrocyclic, and will be described thus. With the tripod ligands **53** a series of nickel(II) complexes have been reported.[407,408,410–412] With (N-SR_3) octahedral species are formed: Ni(N-SR_3)X_2, R = Me, Et, *i*-Pr; X = Cl, Br, I.[407,408] Magnetic moments are in the range 3.10–3.23 μ_B, and for R = Me it is reported that the same geometry is found in solution.[407] However, for R = *t*-Bu the steric demand does not allow formation of the octahedral complex and the trigonal-bipyramidal complex $[Ni(N\text{-}SR_3)X]^+$ is isolated. For R = Et, *i*-Pr, and *t*-Bu the five-coordinate complexes $[NiLX]^+$ can be prepared by design with uncoordinating anions.[408] These remain five-coordinate in $[Ni(N\text{-}NS_2)X]^+$. The complexes $[Ni(N\text{-}N_2S)X]^+$ and $[Ni(N\text{-}NS_2)X]^+$, X = Cl, Br, I, and NCS, are also trigonal bipyramidal and high spin (μ_{eff} = 3.16–3.45 μ_B).[410,411] The complexes $[Ni(N\text{-}N_2S)(NCS)_2]$ and $[Ni(N\text{-}NS_2)(NCS)_2]$ are formed at the expense of SMe and are still trigonal bipyramidal. $[Ni(N\text{-}NSP)X]^+$ is square planar due to the higher ligand field due to the phosphine site, and to give this the SMe is uncoordinated.[412] A trigonal-bipyrimidal structure is found for the nickel(II) complexes $[NiLX](ClO_4)$, X = Cl, Br, I, NCS, with ligands **63**-(P-S_3)[471] and -(P-Se_3).[472] A structure determination of



63, X = SMe(P-S_3)
X = SeMe(P-Se_3)



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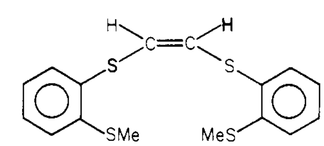
$[Ni(P\text{-}S_3)Cl](ClO_4)$ has shown that this is a nearly regular trigonal bipyramid.[40] A study of the effect of pressure on the electronic spectrum of this complex gave a blue shift of 33 cm^{-1} $kbar^{-1}$ indicative of trigonal-bipyramidal geometry.[469] A series of mixed-ligand complexes, $[Ni(P\text{-}S_3)L](ClO_4)_2$, L = PPh_3, $PMePh_2$, thiourea, and ethylenethiourea, which are five-coordinate, and $[Ni(P\text{-}S_3)(dppe)](ClO_4)_2$, which is distorted octahedral, has also been prepared. A distorted tetrahedral structure is proposed for $Ni(P\text{-}S_3)Br_2$ with two uncoordinated SMe sites.[472] All five-coordinate species are diamagnetic and low spin. With the ligand SAs_3 (**64**) the complexes $[Ni(SAs_3)X](ClO_4)$, X = Cl, Br, I, NCS, CN, are all intense blue, typical of low-spin trigonal-bipyramidal nickel(II).[474] A structure determination for X = Br has shown that the complex has an asymmetrical trigonal field and affects the electronic spectrum, splitting the e energy level. When open-chain tetrathioether ligands of the types **18**, **43**, and **65** are



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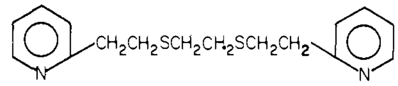

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reacted with the nickel halide salts, octahedral complexes $NiLX_2$, X = Cl, Br, and I, depending on L since all could not be isolated,[191,405,475] are obtained. The electronic spectra indicate that they have a tetragonal structure, and analysis of the spectra yields information on in-plane and out-of-plane ligand fields.[476–478] Octahedral complexes are also obtained with the N_2S_2 ligands **51** (eN_2S_2),[403,448] (pN_2S_2), (bN_2S_2), and (VN_2S_2) of the type $Ni(N_2S_2)X_2$. Analysis of the electronic spectra shows varying tetragonal distortions as found with the S_4 ligands above, due undoubtedly to varying strain caused by fitting the ligand around the metal in a square-planar fashion.[448] The $Ni(N_2S_2)X_2$ complexes exhibit some solvolysis, and this has also been found in similar complexes with the pyridyl ligands **42**[351] and **66**.[479] With the latter ligand the chloro and bromo complexes exhibit little dissociation; however, the iodo complex is a 2:1 electrolyte, suggesting a solvated complex, $[NiL(Solv)_2]^{2+}2I^-$. This ligand also furnishes an unusual complex containing coordinated perchlorate with apparently two isomers. Tetradentate N_2S_2 ligands have also been prepared by S-alkylation, giving, for instance, $\{Ni[H_2NCH_2CH_2SCH_2(o\text{-}C_6H_4)\text{-}CH_2SCH_2CH_2NH_2]Br_2$.[213,215] S-Dealkylation occurs with the nickel(II) complex of **21** (R = trityl).[192] If phosphine donor sites are incorporated into a linear tetradentate, as in $Ph_2P(CH_2)_3S(CH_2)_3S(CH_2)_3PPh_2$-($P_2S_2$), the nickel(II) complexes are either trigonal-bipyramidal $[Ni(P_2S_2)X](ClO_4)$, X = Cl, Br, I, or square-planar $[Ni(P_2S_2)](ClO_4)_2$ in the absence of halide ions.[406] The complexes are diamagnetic, and the phosphine dominates the ligand field. If the Ph_2P sites in the above ligand are replaced by $Me_2As(As_2S_2)$, then the ligand field is such that trigonal-bipyramidal, square-planar, and octahedral species may be isolated: $[Ni(As_2S_2)X](ClO_4)$, $NiLX_2$, X = Cl, Br, NCS, $[Ni(As_2S_2)I]I$, and $[Ni(As_2S_2)](ClO_4)_2$.[479] This balance is so fine that it is solvent dependent. In nonpolar solvents the complexes are octahedral, but when a polar solvent is used to stabilize ion formation, then the five-coordinate species form. For X = Cl this goes further to a square-planar complex. A nonstoichiometric complex of a bisthiol bis(thioether) ligand has been prepared with nickel(II) and the thermal decomposition studied.[352,353] One open-chain tetraselenoether has been reported, $MeSe(CH_2)_3Se(CH_2)_3Se(CH_2)_3SeMe$, and forms $Ni_2(Se_4)I_4$.[480] Nickel(II) complexes of the cyclic tetrathioethers **58** (TTP) and **59** (TTX) exhibit several stereochemistries.[125,126,481] $Ni(TTP)X_2$, X = Cl, Br, I, NCS, are tetragonal, paramagnetic nonelectrolytes except for X = I which is predominantly five-coordinate in solution.[124,125] The monomeric square-planar diamagnetic $[NiL]^{2+}$, L = TTP, TTX, can be isolated as perchlorate or tetrafluoroborate salts;[125,481] however, with TTC with a smaller ring the ligand folds to form $[Ni_2(TTC)_3](BF_4)_4$. This dimeric species can also be formed with the ligand TTP. A ^{13}C NMR study of the TTP complex indicates interconversion between two conformers,[482] and a study of stability constants in nitromethane solution compared with the open-chain analogue showed a ratio of 180 compared to $10^{6.4}$ for the nitrogen ligands.[483] With sexadentate ligands octahedral $[NiL](picrate)_2$ can be isolated,[417,418] and with the octadentate OTO the complex $[Ni_2(OTO)](BF_4)_4$ in which the metal ion is square planar. This complex plus thiocyanate ion gives $Ni_2(OTO)(NCS)_4$ in which the metal ion is tetragonal.[484] Stability constant studies of nickel(II) with macrocyclic ligands[420-422,424] and linear multidentates containing thioether donors plus nitrogen donors[423,425,428,485,486] or oxygen donors[343,426,427,487] all indicate that nickel(II) has an affinity for thioether sulfur.

When the coordination chemistry of thioethers, selenoethers, and telluroethers with palladium and platinum is considered, there is such a similarity for the two metals in their complexes that they will be dealt with together and any major differences noted.

There are no authenticated examples of palladium(0) or platinum(0) complexes with this type of ligand. This is probably due to their poor π-acceptor ability compared, for instance, with phosphine ligands which readily form complexes with these metals in the zero oxidation state.[1]

Much of the historical work on coordination chemistry used palladium(II) and platinum(II) as the metal ion.[488-502] These references are chosen to give a broad view of the early work and are by no means comprehensive. It should be noted that as early as 1893 Werner[488] had concluded that the complexes of palladium(II) and platinum(II) were square planar. With monodentate thioether ligands complexes of the type *trans*-$M(SR_2)_2X_2$, M = Pd, Pt; R = aryl or alkyl; X = anionic ligand, *cis*-$Pt(SR_2)_2X_2$, and $[Pt(SR_2)_4]^{2+}$ have been reported.[102,488-507] The cis and trans isomers can be readily distinguished by infrared spectroscopy when X is halide. The geometry of this type of complex has been studied with SEt_2 by dipole moments, and it appears that in solution the trans isomer predominates.[505] The tendency toward forming trans isomer from the cis isomer in solution is in the order Pd > Pt for the metal ion, Te > Se > S for the donor, and I > Br > Cl for the halide. The mechanism of isomerization has been studied.[508] Separation of *cis*- and *trans*-$Pt(SEt_2)_2Cl_2$ by chromatography as a method of preparation of this type of complex has been effected.[503,504] This work rationalizes cis and trans with the old terminology α and β forms: α is the trans form and β the cis. Many examples of this type of complex, $M(SR_2)_2X_2$, have been studied by variable-temperature NMR to study inversion at coordinated sulfur[227,228,230-234,240] (see section V). The vibrational spectra of these complexes have been studied, especially those of the trans isomers[97,99-102,509-511] (see also section III). Electronic spectra have also been reported,[102,512] and it was noted that for *trans*-$Pt(SPh_2)_2Cl_2$ a strong charge-transfer band at ~303 nm was seen when measured in a noncoordinating solvent. In coordinating solvents the charge-transfer band was destroyed. This band is possibly due to ligand orbital–Pt_6p_2 interaction which is destroyed by solvent interaction in coordinating solvents, raising the energy of the Pt_6p_2 orbital. The ^{195}Pt NMR have been recorded for $Pt(SMe_2)_2(CNS)_2$, *trans*-$Pt(SR_2)_2X_2$, and *cis*-$Pt(SR_2)X_2$, R = Me and SR_2 = SMePh.[120,513] Studies on thermal isomerization suggest that the difference in free energies and crystal lattice energies of the isomers decide which way the direction is favored, i.e., cis → trans or trans → cis.[157,514-516] Thus *trans*-$Pt(PPh_3)(SR_2)Cl_2$ (R = Et, *i*-Pr) on heating give the cis isomer, and *trans*-$[Pt(SR_2)X_)]$, SR_2 = $(C_5H_{10}S)$, X = Cl, Br, give the cis isomers. For the chloro complex the heat change is 21 kJ mol^{-1}. *trans*-$Pd(SR_2)X_2$, SR_2 = SMe_2, SEt_2, C_4H_8S, $C_5H_{10}S$; X = Cl, Br do not thermally isomerize; however *cis*-$Pt(SR_2)_2Br_2$, R = Me, Et, do give the trans isomers on heating. A further type of thermal isomerization has been reported[157] where $[Pt(SMe_2)_4][PtX_4]$, X = Cl, Br, yield *trans*-$Pt(SMe_2)_2X_2$ on heating.

Complexes of the type $[M(SR_2)X_3]^-$, M = Pd, Pt; X = Cl, Br, I; R = Me, Et, are known and have been studied by vibrational and ^1H NMR spectroscopy.[96,97] They can be used as precursors for mixed thioether–N donor ligand complexes by reaction with amines,[517] hydroxylamine, or oximes.[518] The trans-directing ability of thioethers would predict a trans product, and this was found for the reaction of a series of 15 amines with $[Pt(SMe_2)Cl_3]^-$ giving *trans*-$Pt(SMe_2)(am)Cl_2$.[517] However, with hydroxylamine and oximes both cis and trans products were reported.[518] These mixed-ligand complexes may also be prepared by cleaving halo-bridged dimeric complexes, either $Pt_2Cl_4(am)_2$ with SMe_2[519] or $M_2X_4(SR_2)_2$ with amine.[520,521] The product *trans*-[Pd-

$(SR_2)(am)Cl_2]$ once formed is unstable to disproportionate, giving a mixture of *trans*-$Pd(SR_2)_2Cl_2$ and *trans*-$Pd(am)_2Cl_2$.[521] For reaction 21, the equilibrium

$$Pt_2X_4(SR_2)_2 + 2am \rightleftarrows 2trans\text{-}Pt(SR_2)(am)X_2 \quad (21)$$

lies to the right side for X = Cl and Br but to the left for X = I.[520] Much of the early work on trans influence used mixed-ligand complexes of this type, $M(am)LX_2$ where L included thioether.[124,522–525] The change in ν(N–H) was studied with changing trans ligands. Other mixed thioether–amine complexes have been reported.[526,527] For a discussion of kinetic studies relating to mixed thioether–amine systems, see section III and references 528–530. The mixed thioether–σ carbon ligand complexes have been prepared by reaction of dihalo complexes with a series of aryllithium compounds, giving *trans*-$Pt(SEt_2)_2(R)X$, but not with palladium.[531] Both halides can be replaced giving *cis*- or *trans*-$M(SEt_2)_2(R)_2$, but reactions attempting to prepare complexes with R = Me gave decomposition.[531,532] A study of the kinetics of substitution with *trans*-$Pt(SEt_2)_2(Ph)X$ where X is the leaving group indicates that the SEt_2 complex discriminates less than the PEt_3 analogue.[533] Attempts to effect internal metalation using butyl naphthyl thioether gave only the ML_2Cl_2, M = Pd, Pt, complexes.[534] Several ylide–metal complexes containing a thioether ligand have been reported: $M(SR_2)(Sy)X_2$, M = Pd, Pt, X = Cl, Br, I, R = Me, Et, Sy = $CH_3(C_6H_5)SCHC(O)C_6H_4Cl$-*p*.[535] The ν(Pt–Cl) values found for *cis*-$[Pt(SR_2)(Sy)Cl_2]$ indicate trans influence is in the order Sy > SR_2. Also two methyl signals are seen in the ^1H NMR as expected for a thioether complex which is below coalescence temperature.

Dimeric complexes with thioether ligands have also been studied.[42,94,99,107,109,169,170] Initial studies with $M_2(ER_2)_2X_4$ were concerned with the relative stabilities of the complexes E = S, Se, and Te.[169,170] These complexes were assumed to be halide bridged; however, subsequent work has now proven that the palladium complexes are, in fact, halide bridged whereas the platinum complexes are sulfur bridged when R = alkyl.[42,94,109] If R = Ph then the platinum complexes are also halide bridged.[109] Other bridged species reported are $[Pt_2(SMe_2)X_6]^{2-}$, X = Cl, Br, with only the thioether ligand bridging the metal ions, $[Pt_2(SMe_2)_2X_5]^-$, X = Cl, Br, with both S and X bridging, and $Pt_2(SMe_2)_3Cl_4$ in which only one SMe_2 ligand is bridging.[109]

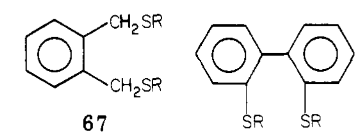
Much of the above work with monodentate thioether ligands has been repeated with selenoether and telluroether analogues (ref 52, 77, 99, 104, 120, 122, 124, 128, 169, 170, 230, 232–234, 240, 493, 494, 509, 511, 520–525, 531, 532, 538). Early work prepared a series of $M(SeR_2)_2X_2$, M = Pd, Pt, R = alkyl or phenyl.[493,494] The structure determination of *trans*-$[Pd(SeEt_2)_2Cl_2]$ indicated that the selenium atom adopts a pyamidal geometry.[77] Vibrational spectra have been studied with *cis*- and *trans*-$M(ER_2)_2X_2$, M = Pd, Pt; X = Cl, Br, I; E = Se, Te; R = Me, Et.[99,509,511] It was noted that *trans*-$Pt(TeMe_2)_2Cl_2$ is difficult to prepare, the cis isomer being strongly favored.[99] The ^{195}Pt chemical shifts have been reported for a series of complexes *trans*-$[Pt(ER_2)_2X_2]$, ER_2 = $SeMe_2$, $TeMe_2$; X = Cl, Br, I (only X = I for $TeMe_2$), and X_2 = mixed halides, $[Pt(SeMe_2)_3X]^+$, X = Cl, Br, I; $[Pt(EMe_2)X_3]^-$, E = Se, Te; X = Cl, Br, I; $[Pt(EMe_2)XYZ]^-$, E = Se, Te; X, Y, Z = Cl, Br, I; and *cis*- and *trans*-$Pt(SeR_2)_2Cl_2$,[120,122,536] R = Me, Et. The coupling constants ^{195}Pt–^{77}Se and ^{195}Pt–^{125}Te have been reported for several of these complexes.[122,536] The ^1H NMR spectra of *trans*-$[M(EEt_2)_2X_2]$, M = Pd, Pt; E = Se, Te; X = Cl, Br, I, and *cis*-$[Pt(TeEt_2)_2(o\text{-tolyl})_2]$ have been studied with respect to inversion about the chalcogen atom[230,232–234] (see also section V). The diaryl telluroether complexes *trans*-$[M(TeR_2)_2X_2]$, M = Pd, R = Ph, *p*-$EtOC_6H_4$, X = Cl, Br; M = Pt, R = *p*-$EtOC_6H_4$, X = Cl, Br, have been prepared by displacement of benzonitrile from *trans*-$Pt(PhCN)_2X_2$.[104] The mixed-ligand complexes *trans*-$[M(ER_2)(am)X_2]$, M = Pd, Pt; E = Se, Te; R = Me, Et, *n*-Pr have been prepared[124,128,520–525] and studied by vibrational and electronic spectroscopy. These complexes tend to disproportionate to the symmetrical species ML_2X_2. The reaction at amines (pyridine, 3,4-dimethylpyridine, and piperidine) with *trans*-$Pt(SeEt_2)_2I_2$ replaces an iodide ligand and not an $SeEt_2$.[537]

The bridged complexes $M_2(ER_2)_2X_4$, M = Pd, Pt; E = Se, Te; R = Et, *n*-Pr; X = Cl, Br, I, give different orders of stability depending on the metal ion.[169,170] For M = Pd, the order is $SR_2 > SeR_2 > TeR_2$, whereas for M = Pt, the order $SR_2 >> SeR_2 < TeR_2$ is found.

The σ-carbon donor complexes previously discussed for thioethers may also be prepared with $SeEt_2$ and $TeEt_2$, *trans*-$Pt(EEt_2)_2(R)X$ and *cis*- and *trans*-$Pt(EEt_2)_2(R)_2$, R = Ph, *o*-tolyl, and mesityl.[531,532] Selenoether ligands may be used in the determination of palladium(II) ion.[538]

The complexes $Pt(EPh_2)_2Cl_2$, E = S, Se have been used with $SnCl_2$ as hydrogenation catalysts but are inferior to the PPh_3 and $AsPh_3$ analogues.[539]

There were several early studies with bis(thioether)bidentate ligands.[540–544] These included the ligands $RS(CH_2)_nSR$, R = Me, Et, *n*-Pr, *n*-Bu; *n* = 2; R = Et, *n* = 3, and also EtSCH=CHSEt complexing with platinum(II) and $RS(CH_2)_2SR$, R = Me, Et, Bz, Ph, *p*-tolyl complexing with palladium(II). It soon became evident that two isomeric forms were possible, MLX_2 and $[ML_2][MX_4]$, the latter complex only forming when M = Pt.[544] More recent work has used not only these simple bidentates[510,545,546] but also more complicated ligands (**67**, **68**),[547] a cage molecule (**44**), and a series with



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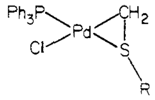
unsaturated backbones.[548] There has been a comprehensive study of bidentate thioether ligands $RS(CH_2)_nSR$, R = Me, Ph, *n* = 2, 3, *cis*-RSCH=CHSR, *o*-$C_6H_4(SR)_2$, and $PhS(CH)_nSPh$, *n* = 6, 8, 12.[243] With the small backbones the normal MLX_2 are readily obtained. However, for *n* = 6 and 8 polymeric materials are formed of formula $[PdLX_2]_n$. The bisbidentate complexes $[ML_2](ClO_4)_2$, *n* = 2, 3, may be obtained by using $[M(CH_3CN)_4](ClO_4)_2$ as precursor. Solid-state spectra have inferred intermolecular M···S interactions which may explain a proposed ionic association of a similar complex, $[Pd\{PhS(CH_2)_nSPh\}_2](ClO_4)_2$, *n* = 2, 3, showing nonlinear Onsager plots.[549] The ligand $PhS(CH_2)_{12}SPh$ on reaction with $[MCl_4]^{2-}$, M = Pd, Pt, gave monomeric complexes $MLCl_2$ in which the bidentate bonds in a trans chelating fashion.[243,550] This is the first sulfur donor trans chelation and is evidence that bulky terminal groups are not a prerequisite for this mode of bonding.[551] Complexes have been studied of fluorinated bis(thioether) ligands $CF_3S(CH_2)_nSCF_3$, n = 2, 3, $MeSCF_2CH_2SMe$, and $CF_3SCH(Me)CH_2SCF_3$.[552,553] Isomeric forms were indicated by ^{19}F NMR, and structural data suggested that metal–ligand bonding was not strongly influenced by electron-withdrawing CF_3 groups, unlike phosphine analogues.[95] Other studies with bidentate complexes have included inversion at sulfur[118,225,229] in the complexes $M(RSCH_2CH_2SR)X_2$, M = Pd, Pt; R = Me, Et, *n*-Pr, *n*-Bu; X = Cl, Br, I; Ph, ligand replacement kinetics,[140,164] and thermal transformations of $[PtL_2][PtX_4]$ into $PtLX_2$ species.[554-556]

There are three reports of complexes with bidentate thioether thiolate ligands.[385,557-559] With *cis*-RSCH=CHS⁻, R = Me, Et, Bu, cis and trans mixtures were obtained for ML_2, M = Pd, Pt,[385] whereas with $EtSCH_2CH_2S^-$ the thiolate-bridged species $Pt_2L_2X_2$ formed.[557] It was found that with $MeSCH_2CH_2SH$ the thiol can oxidatively add to M^0 species, thus with $Pt(PPh_3)_4$ the complex $Pt(MeSCH_2CH_2S)(H)(PPh_3)$ may be formed.[558] With *o*-$RSC_6H_4CO_2^-$ as ligand several species may be formed in which the ligand is bidentate in *trans*-PdL_2, monodentate *trans*-ML_2Cl_2, or a halide-bridged dimer, $Pd_2L_2X_2$.[560-562]

Various thioether–nitrogen bidentate ligands form complexes with palladium(II) and platinum(II); $EtSCH_2CH_2NH_2$,[563,564] *o*-(methylthio)aniline (**7**),[183] *trans*-2-(ethylthio)cyclopentylamine (etp, **47**),[379] 2-[(methylthio)methyl]pyridine (mtp, **3**),[179,378] 2-methyl-9-(methylthio)quinoline (mmtq, **15**), and 9-(methylthio)quinoline (mtq, **1**).[174] Much of the work has been on S-dealkylation of the coordinated ligands (see section IV). This is also the case for palladium(II) and platinum(II) complexes of the *o*-phenylene ligands (S(R)P) **6** and (S(R)As) **4**.[179,182,187,188] Complexes studied were of the type M(bidentate)X_2 and $[M(bidentate)_2]^{2+}$. Early work suggested that $Pd(S(R)As)_2X_2$, X = Cl, Br, I, were octahedral species since they were nonconducting in solution.[462] What is more probable is that the (S(R)As) ligand acted as a monodentate via the arsenic donor site. Five-coordinate species, however, were reported $[Pt(S(R)As)_2X](ClO_4)$, as were the square-planar $[Pt(S(R)As)_2](ClO_4)_2$[565] and $[Pd(S(R)P)_2](ClO_4)_2$.[566]

Although thioether ligands do not normally appear to promote internal metallation,[316,534,567] thioether–σ carbon bidentate systems can be prepared by reaction of allylic thioethers with $[PdCl_4]^{2-}$,[567] by oxidative addition of $MeSCH_2Cl$ to $Pd(PPh_3)_4$,[568,569] or by reaction of $PhSCH_2^-Li^+$ with $Pd(PhCN)_2Cl_2$.[571] The types of complex isolated were **69**, **70**, and an unstable tetramer,



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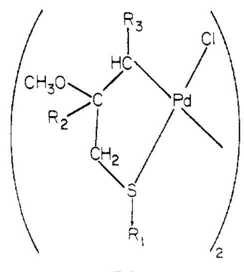

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$[Pd(CH_2SPh)_2]_4$. The platinum(II) analogues do not appear to form.[568] The tetramer was verified by a structural analysis at −160 °C.[571] Further examples of organometallic complexes with thioether donor sites are furnished with ligands 3-butenyl butyl thioether (bbt) and 4-pentenyl butyl thioether (pbt).[572,573] These ligands form the species MLX_2, M = Pt; L = bbt, pbt; X = Cl, Br, I, and M = Pd; L = (bbt); X = Cl, Br.[572] This initial study suggested that reaction of MLX_2 with PPh_3 totally removed the ligand L; however, a subsequent study yielded a complex, $Pd_2(bbt)(PPh_3)_2Cl_4$, on reaction of $Pd(bbt)Cl_2$ with PPh_3.[573] The dimer is bridged by bbt only.

Some of this work with bidentate thioether containing ligands has been repeated with selenoether analogues (ref 52, 78, 168, 184, 230, 232, 235, 237, 240, 265, 493, 494, 574, 575, 576); however, to date there are no reports of multidentate telluroether ligands. Early work prepared the complexes $M[EtSe(CH_2)_3SeEt]Cl_2$, M = Pd, Pt,[493,494] and later the analogues $M[MeSe(CH_2)_nSeMe]Cl_2$, M = Pd, Pt; n = 2, 3, were synthesized.[265] With *i*-PrSe$(CH_2)_2$Se-*i*- the series MLX_2, M = Pd, Pt; X = Cl, Br have been prepared and crystallized as such from acetone but apparently as dimers from chloroform,[574] and they are probably ligand bridged not halide bridged. The complex $PdLCl_2$ of this series has had its structure determined.[78] The ligands $RSe(CH_2)_2SeR$, R = Et, *i*-Pr, have been used in the study of inversion at coordinated chalcogen as MLX_2 species[230,232,235,237] (see section V). With the selenoether–alkene bidentates 3-butenyl butyl selenoether (bbs), 4-pentenyl butyl selenoether (pbs), 3-butenyl phenyl selenoether (bps), and 4-pentenyl phenyl selenoether (pps), the complexes MLX_2, M = Pt; L = bbs, pbs, bps, and pps; X = Cl, Br, I, and bps have been prepared.[575] Replacement of L by *p*-toluidine is more difficult for the selenoether than for the thioether ligands, and the stronger M–Se than M–S interaction is borne out by a kinetic study of ligand replacement by substituted pyridines on $Pd[PhSe(CH_2)_2SePh]Cl_2$.[168] The complexes of stoichemetry MLX_2, M = Pd, Pt; X = Cl, Br, I, and L = 1,4-diselenane are thought to be dimeric since 1,4-diselenane acting as a chelate would be too sterically strained.[576] The complex $Pd(P\text{-}Se)(SCN)_2$ (P–Se is the selenium analogue of **6**) has been used in the study of Se-dealkylation.[184]

There are several reports of tridentate ligand complexes with thioether donors. Reaction of $[EtS(CH_2)_2]_2S$ with $[PtCl_4]^{2-}$ first gave $[PtLCl][PtCl_4]$ which upon heating gave $[PtLCl]Cl$.[577] If, however, the ligand backbones are smaller as in $(RSCH_2)_2S$, then the ligand acts as a bidentate through the terminal sulfur atoms.[106] With the dimethylene backboned ligand the complex $[PtL(H_2O)]NO_3$ was prepared and also with the ligand in which the center sulfur atom was oxidized to a sulfoxide site. The acid dissociation constants were measured and compared to that for $[Pt(NH_3)_3(H_2O)]^{2+}$.[577] The thiolate ligand $[S(CH_2)_2]_2S$ forms polymeric materials with palladium(II) and platinum(II),[464] and it was shown for palladium(II) that a trimeric complex with bridging thiolate sites was formed.[41] If a phosphorus donor is included in the tridentate ligand as in **8**, then the ligand will normally act as a bidentate via S and P sites in the square-planar $PdLX_2$.[187,189,568] The sulfur donor sites are in fact fluxional.[187,189] There is, however, a tendency toward five-coordination, and this can be favored by having the right conditions to form $[PdLX](ClO_4)$. If the ligand is fluorinated, then this tendency is reduced and only square-planar complexes can be isolated.[188] If the tridentate contains two phosphorus sites, then five-coordination predominates, and $[PdLX](ClO_4)$ are readily formed when L = 41.[467] With *N*-(2-pyridylmethyl)-2-(ethylthio)acetamide (62) the ligand is tridentate via S,N,N$^-$, forming square-planar MLX, M = Pd; X = Cl, Br, NCS, M = Pt; X = Cl.[471]

There has been a comprehensive study on the open-chain tetrathioether ligands 18, 43, and 65.[191,405,475,578] If, in the preparation of palladium(II) and platinum(II) complexes, there is halide present, then only polymeric materials of formula $[M_2LX_4]_n$ can be prepared. Once the MS_2X_2 environment has formed, thioether will not replace the X ligands. If the halide is not present as in $[M(CH_3CN)_4](ClO_4)_2$, then the monomeric species $[M(S_4)](ClO_4)_2$, S_4 = tetrathioether, may be isolated. ^1H NMR studies suggest that 43 (2,3,2) has the best fit around the metal ion.[578] These multidentate ligands show no propensity to promote five-coordination. Also well studied are the thioether–arsine tetradentates, 13 n = 2, 3, and 4.[189,579,580] Several species can be prepared, $PdLX_2$, X = Cl, Br, I, SCN; n = 2, 3, $[Pd_2L_2X_2]^{2+}$, n = 2, 3, and 4, Pd_2LX_4, X = Cl, I; n = 2, 3, and 4, $[Pd_2L_2]^{4+}$, n = 2, 3. The monomeric species has the ligand bidentate via both arsenic sites; $[Pd_2L_2X_2]^{2+}$ has two arsines, one exchanging thioether and one halide donor per metal. The complex with no halide donors has both tetradentates bridging the two metal ions. Certain platinum analogues were also prepared.[579] The complexes $PdLX_2$ were reported for the thioether and thioether amine tetradentates 16 and 51.[403] The former ligand bonds via an As and S donor set whereas the latter bonds only through the two thioether sites. If the thioether–arsine ligand $Me_2As(CH_2)_3S(CH_2)_3AsMe_2$ is complexed with palladium(II) and platinum(II), then the products of stoichemetry MLX_2 show an interesting isomerization.[479] In the solid state or in polar solvents such as nitromethane they exist as $[MLX]X^-$ and the metal ion is five-coordinate; however, in nonpolar solvents they are monomeric nonelectrolytes and exist as MLX_2 in which the ligand is trans-bidentate via the arsine donor sites. With dithioether–diphosphine ligands of the type 41 square-planar $[ML]^{2+}$ complexes may be isolated[406,467] as well as five-coordinate species $[MLI]^+$.[406] The tripod ligands with P-S_3 (TSP) and As-S_3 (TSA) donor sets form the five-coordinate $[PdL_2](ClO_4)_2$ and square-planar $PdLCl_2$, the latter having the ligand acting in a bidentate fashion.[566] The ligands $[CH_2{=}CH(CH_2)_nSCH_2]_2$, n = 2, 3, act as bis(thioether) donors to palladium(II) and platinum(II) in MLX_2, X = Cl, Br, I.[572]

There is one report of a tetraselenoether which behaves the same as the thioether analogue, forming polymeric $[M_2LX_4]_n$ complexes. There is also a report of a Pd_4LCl_8 complex and platinum analogue with a cyclic octathioether ligand.[484]

Although there are no palladium(IV) complexes and attempts to prepare them have failed,[581] the platinum(IV) analogues are more stable, can be isolated with relative ease, and are almost as historic as platinum(II) thioether complexes.[499,582,583] They are prepared by oxidation of the platinum(II) complex with halogen and minimum isomerization occurs if a nonpolar solvent is used.[584] They may also be prepared from the corresponding platinum(II) sulfoxide complex and $SnCl_2$ in hydrochloric acid.[585,586] These complexes *cis*- and *trans*-$Pt(SMe_2)_2X_4$, X = halide, have been studied by infrared spectroscopy and by ^1H and ^{195}Pt NMR[110] as have $[Pt(SMe_2)X_5]^-$, X = Cl, Br. The solid-phase thermal isomerism cis to trans of $Pt(SR_2)_2X_4$ has been performed.[588] Other monodentate complexes reported have been with the ligand $S(CH_2CH_2Cl)_2$,[589] $Pt(SMe_2)(Me)_2I_2(PPhMe_2)$,[221] and $[Pt(SeMe_2)X_5]^-$.[122]

A series of bidentate thioether ligands have been used to prepare platinum(IV) complexes of the type Pt(bidentate)X_4 by halogen oxidation of the platinum(II) species.[581] A ^1H NMR study showed that although the shift of –S–Me protons on coordination was of the same magnitude as for the platinum(II) complexes, the $^3J_{Pt-H}$ coupling constants were significantly smaller for platinum(IV). There has been a brief report of bis(selenoether) ligands with platinum(IV) giving $PtLCl_4$.[265]

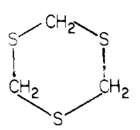
I. Copper, Silver, and Gold

There has been a great deal of interest in the thioether chemistry of these three elements, particularly copper, because of the importance of copper complexes of sulfur donors in biological chemistry. Thus vitamin H (*d*-biotin) involves tetrahydrothiophene,[590] and the "blue" copper redox proteins are thought to contain copper bound to methionine as well as cysteine and histidine.[111] In general, copper(I) has a much higher affinity for thioethers than has copper(II). The interaction of simple thioethers such as tetrahydrothiophene with copper(I) in aqueous ethanol is extremely weak—at 25 °C in 1 M $NaClO_4$ log K is 0.02 ± 0.04.[142] However, the use of multidentate ligands has enabled a wide range of complexes with copper(II)–thioether bonds to be prepared and isolated. With copper(I), simple thioethers form a range of complexes; thus Me_2S forms 1:1 complexes with copper(I) halides, whereas a similar reaction with Et_2S forms 3:4 complexes of which the iodide complex (see Table II) involves infinite chains of sulfide-bridged distorted cubic Cu_4I_4 cores. *n*-Bu_2S reacts with copper(I) halides to form 1:2 complexes.[57]

A range of bidentate thioethers including $RS(CH_2)_2SR$, *cis*-RSCH=CHSR, R = alkyl, and *o*-$C_6H_4(SMe)_2$ form complexes with copper(I) and copper(II), a number of which have been studied by X-ray diffraction (see Table II and ref 59, 61, 68, 129, 371, 548, 591–593). The copper(II) complexes of $RS(CH_2)_2SR$, $CuL_2(BF_4)_2$, and $CuLX_2$, X = halide, have tetragonally octahedral structures with weak BF_4–copper (II) bonding (Table II) in the former and bridging halides in the latter; the thioether ligands act as chelating groups.[59,129] The copper(I) complexes of $RS(CH_2)_2SR$, $[CuL_2](BF_4)$ and CuLX, X = halide, involve tetrahedral copper(I) with BF_4^- counterions in the former and halide bridges in the latter.[59,129] Examination of the copper–sulfur bond lengths in Table II shows that copper(I)–sulfur bonds are typically shorter than the sum of the covalent radii, indicating some π-bond character, whereas there is little evidence for π-bonding in copper(II)–thioether bonds. Treatment of copper(I) acetate in ether–benzene solution with $MeS(CH_2)_2SMe$ yields polymeric $[CuL(OAc)]_n$ in which the ligand is present in its trans form and links two "$Cu_2(OAc)_2$" dimeric units.[593]

The electronic spectra of the copper(II) complexes $[CuLX_2]_2$ and $[CuL_2](ClO_4)_2$ where L = $BuS(CH_2)_2SBu$ and related ligands have been studied in detail with particular emphasis on identifying the thioether (S) → copper(II) charge-transfer transition. Approximately planar CuS_2N_2, CuS_2Cl_2, and CuS_4 ligand sets exhibited strong absorptions in the 22 000–26 000-cm^{-1} energy region which were assigned to σ(S) → Cu^{II} ligand to metal charge-transfer bands. Ligand to metal charge-transfer transitions arising from thioether π orbitals were much less intense than those from the σ orbitals, red shifted by 500–700 cm^{-1} and not well separated in energy from interfering ligand-field absorptions.[130]

The tridentate cyclic thioether **71** reacts with cop-

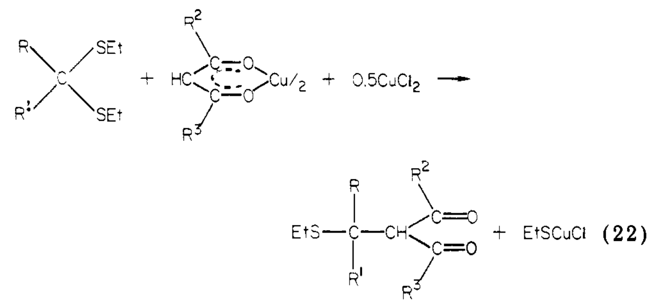


71

per(I) chloride to form CuL_2Cl_3 in which the chair form of the trithioether links three crystallographically independent copper atoms, each of which is bound to two chlorine and two sulfur atoms (see Table II).[594] Spurred on by the indication that the blue color in "blue" copper proteins may arise from a copper(II)–methionine bond, a number of studies of copper(II) with acyclic and macrocyclic tetrathioethers have been undertaken.[65,111,126,191,595–598,601] The emphasis has been on assignment of the electronic and resonance Raman spectra. As mentioned above, σ(S) → Cu^{II} ligand to metal charge transfer results in a strong band in the region 22 000–26 000 cm^{-1}. There are indications that a distorted coordinate site possible 5-coordinate may be involved in the "blue" protein, and in agreement with this a CuS_4O environment has been found to lead to spectra that closely resemble those of the "blue" proteins. The open-chain tetrathioethers give dimeric or polymeric complexes with copper(II) halides in which each copper prefers to bond to two sulfur and two halide ligands but is on occasion 5-coordinate with three sulfur and two halide donors.[191,597] In the absence of coordinating anions, macrocyclic tetrathioethers from either octahedral complexes in which copper(II) is held in a plane of four sulfurs[65,596] (if the macrocycle is large enough[126,598]); however, if coordinating anions such as halides are present, then the macrocycle may become bidentate toward two copper(II) ions, forming Cu_2Cl_4-L.[596] In agreement with the higher affinity of copper(I) than copper(II) for thioethers, copper(II) is the macrocyclic 13-ane-S_4 and 14-ane-S_4 complexes is readily reduced to copper(I).[595] The X-ray crystal structures of both the copper(II) and copper(I) complexes of 14-ane-S_4 **58** have been reported.[65,598] In the copper(II) complex $[CuL](ClO_4)_2$, copper(II) is coplanar with the four sulfur donors with two loosely interacting perchlorate ions along the perpendicular axis; comparison with other macrocyclic and open-chain tetrathioether ligands suggests that **58** is optimal for copper(II).[601] By contrast with copper(I), **58** forms $[CuL]ClO_4$ in which each copper(I) is coordinated by four sulfurs in an irregular tetrahedral geometry; only three of the sulfurs come from one **58** ligand, the fourth coming from a second ligand because the ligand cannot distort sufficiently to accommodate the tetrahedral geometry shown by copper(I).[598]

$HS(CH_2)_2S(CH_2)_5S(SH_2)_2SH$ reacts with copper(I) to form a polymeric 1:1 complex in which there are no bridging sulfur atoms but in which it is not clear whether copper(I) is 5- or 6-coordinate.[352] The thermal decomposition of this complex has been studied.[353]

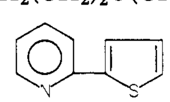
Two papers concerning the reactions of thioethers in the presence of copper are of interest. Thioethers of the type $R(R^1)C(SEt)_2$ react with 1,3-dicarbonyl complexes of copper(II) in the presence of copper(II) chloride to give substitution of the 2-carbon atom of the dicarbonyl ligand rather than form a thioether complex (reaction 22).[599] The copper(I) mercaptide complex of



1,4-dimercaptobenzene reacts with methyl iodide to yield 1,4-bis(methylthio)benzene and copper(I) iodide, which do not react together to form a thioether complex (reaction 23).[600]

$$[CuSC_6H_4SCu]_n + 2MeI \xrightarrow{\text{reflux}} 2CuI + MeSC_6H_4SMe \quad (23)$$

A wide variety of chelating ligands with both nitrogen and thioether donor groups have been studied. Equilibrium constant studies in solution have compared ligands such as $MeS(CH_2)_2NH_2$, $[CH_2S(CH_2)_2NH_2]_2$, $S[(CH_2)_2NH_2]_2$, $NH_2(CH_2)_2NH(CH_2)_2SMe$, $NH_2(CH_2)_2S(CH_2)_2OH$, $NH_2(CH_2)_2O(CH_2)_2S(CH_2)_2NH_2$, **72**,



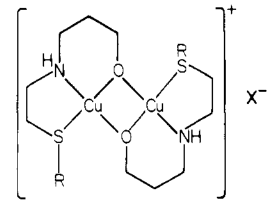
72

and a number of potentially octadentate ligands with corresponding nitrogen and ether ligands and shown that while thioethers form stronger bonds to copper(II) than ethers, they form weaker bonds than either primary amines or pyridine.[144,428,485–487,602,603] Many of these studies involve comparisons with other divalent metal ions, and the stability order $Hg^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+} > Mg^{2+} > Ca^{2+}$ is fairly typical.

1:1 and 1:2 copper(II) complexes of $NH_2(CH_2)_2SMe$ with halide ligands have been described; the 1:4 complex $[CuL_4]SO_4$ involves two bidentate N(R)S ligands and two bound only through nitrogen.[144,604]

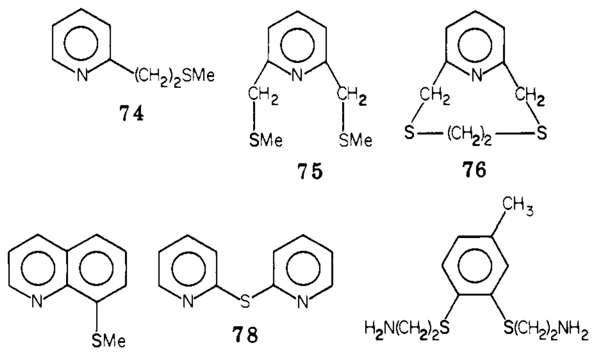
Binuclear copper(II) complexes of $RS(CH_2)_2NH(CH_2)_3OH$, R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, and *t*-Bu, have been prepared and compared to those formed by the analogues N(R)N(R)O ligands.[605] The thioether complexes have structure **73** where X = ClO_4^- or $CuBr_2^-$. The $CuBr_2^-$ anions are unusual and cannot be explained by any of the conventional theoretical formulas.

Tridentate $S(CH_2CH_2NH_2)_2$ forms 5-coordinate $CuLX_2$, X = Cl, Br, and $[CuL(OAc)]ClO_4$.[606] Tetra-



73

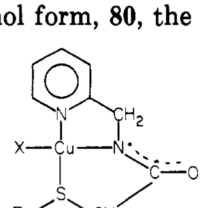
dentate $N(CH_2CH_2SMe)_3$ also forms 5-coordinate trigonal-bipyramidal copper(II) complexes such as [CuLBr]Br.[407] It has been suggested that the π delocalization arising from an aromatic ring significantly enhances the stability of copper complexes of S(R)N chelates.[64] Consistent with this a wide range of such ligands has been studied, including, **7**, **15**, **44–46**, **61**, and **74–79** (ref



74 75 76 77 78 79

175, 377, 378, 380, 381, 466, 607–610). Copper(II) complexes of all these ligands have been described, but only **77** appears to have been studied with copper(I) as well.[377,611] To fully characterize these complexes really requires an X-ray diffraction study of the crystal structure because spectroscopic methods are often unreliable. Thus infrared cannot readily show thioether coordination to divalent 3d metals due to (i) the possibility that the interactions between the thioether and the metal may be weak, (ii) the low intensities of modes involving sulfur, and (iii) the fact that the modes involving sulfur are often found in regions where a number of common vibrations occur, e.g., C–S in the region 600–700 cm^{-1}.[612] Although it is often possible to assign coordination numbers to copper(II) complexes on the basis of their electronic spectra,[613] this can be dangerous as there are several examples known where the overlap between classes such as five- and six-coordinate is considerable.[614] This emphasizes the even greater risks involved in attempting to assign the geometry of a five-coordinate complex on the basis of electronic spectral results.

A comparison of $(NCCH_2CH_2)_2S$ with its nitrogen analogue suggests that it forms five-coordinate copper(II) halide complexes, $CuLX_2$.[612] **62** reacts with copper(II) halides to form $CuLX{\cdot}2H_2O$ in which the ligand is coordinated in a tridentate fashion in the rarely found iminol form, **80**, the apical sites having



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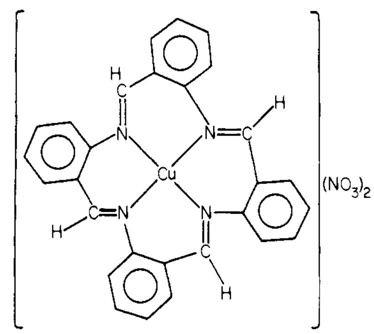
weakly bound water molecules. When **81** is treated with



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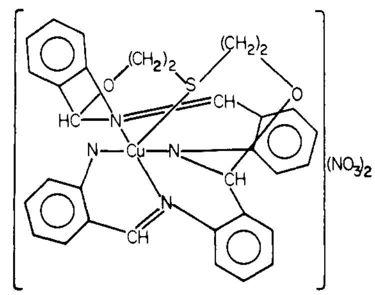
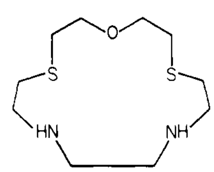


82

$S(CH_2CH_2O)_2$ the five-coordinate copper(II) complex **82** is formed by a template reaction.[615]

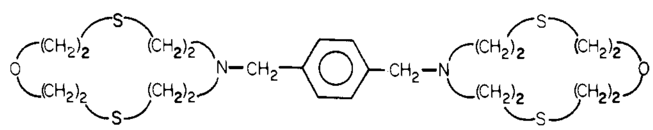
A systematic study of a number of acyclic and macrocyclic N,S,O ligands with a series of metal ions including copper(II) has shown that the macrocyclic effect which gives rise to enhanced stability is apparent in both the enthalpy and entropy terms.[420–424] The X-ray diffraction crystal structure of the copper(II) perchlorate complex of **83** shows copper(II) bound within



83

the cavity to two sulfur (Cu–S = 2.312 (4) Å), two nitrogen (Cu–N = 1.97 (2) Å), and one oxygen atom (Cu–O = 2.29 (1) Å) with copper virtually coplanar with one of the nitrogen atoms and both sulfur atoms.[424]

Copper complexes have been prepared from **84** in

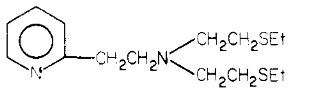


84

order to prepare complexes with two copper atoms that are bound by a tetradentate NS_2O ligand and held far enough apart to avoid their direct interaction but close enough together to allow a substrate to interact simultaneously with both.[616] Both copper(I) ($[Cu_2L](BF_4)_2$) and copper(II) complexes ($[Cu_2L](BF_4)_4$) were prepared; the copper(I) complex reversibly adds carbon monoxide and oxygen.

The crystal structure of (1,8-diamino-3,6-dithiaoctane)(1-methylimidazole)copper(II) perchlorate shows copper(II) to be in a distorted square-bipyramidal environment with a weakly bound perchlorate ligand

(Cu–O = 2.845 (5) Å) in the sixth position (Table II).[617] The axial Cu–S bond is 2.560 (2) Å long while that in the plane is 2.414 (2) Å, both of which are long compared to the sum of the covalent radii (2.34 Å; see Table II). The distorted square-bipyramidal geometry persists in solution. The similarity of the solution spectrum in the d–d transition region of this complex[618] and that of galactose oxidase,[619] and of the "nonblue" copper proteins, suggests that the coordination geometry in the present complex may be a model for that in the protein. When copper(II) nitrate solution is treated with **85**, an



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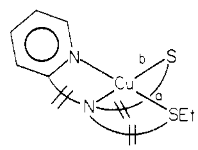
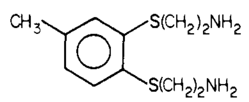


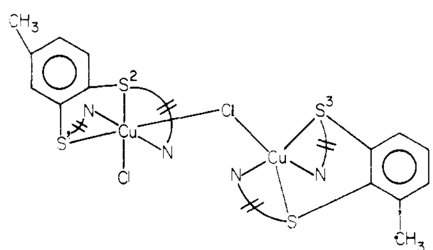
86

intense blue color develops from which copper(I) complex [CuL]BPh_4 can be isolated. The X-ray crystal structure shows copper(I) in a severely distorted tetrahedral environment **86** with Cu–S distances of 2.247 (a) and 2.342 (b).[62] When **85** is reacted with $Cu(BF_4)_2 \cdot 6H_2O$, the corresponding copper(II) complex $[CuL](BF_4)_2$ can be isolated without reduction to copper(I); the crystal structure of this latter complex has not been reported.[62] Ligand **87** when reacted with simple cop-



87

per(II) salts yielded binuclear $[CuLCl]_2(ClO_4)_2$ in which one copper center has a distorted octahedral stereochemistry and the other a distorted square-pyramidal stereochemistry, the two being linked by a bridging chloride, **88**.[64] The distorted octahedral copper atom

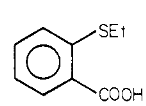


88

has two larger axial bonds (Cu–S^1 = 2.61 Å) and four shorter equatorial bonds (Cu–S^2 = 2.45 Å). The distorted square-pyramidal copper atom similarly has one longer (Cu–S^3 = 2.56 Å) and one shorter (Cu–S^4 = 2.43 Å) Cu^{II}–S bond. Attempts by the same authors to prepare a 1:1 copper(II) complex of the aliphatic analogue of **87**, $H_2N(CH_2)_2SCH(CH_3)CH_2S(CH_2)_2NH_2$, failed, suggesting that π delocalization in the aromatic rings effects a valuable enhancement of the bonding capacity of thioethers for copper(II).[64] However that aromaticity need not be adjacent to sulfur since **66** forms both copper(I) and copper(II) complexes.[357] The copper(I) complex [CuL]PF_6 has tetrahedral coordination of two pyridyl and two thioether donors with a mean Cu–S distance of 2.32 Å whereas the copper(II) complex $[CuL(OClO_3)]ClO_4$ involves square-pyramidal copper(II), with the nitrogen and sulfur donors occupying the basal plane (Cu–S = 2.311 (2) and 2.316 (2) Å) and a perchlorate oxygen bound to the apex (Cu–O = 2.264 (5) Å).[63] These two structures demonstrate a significant change of coordination by copper on oxidation that is of particular interest since the present ligand has two thioether and two heterocyclic nitrogen donors which resembles very closely the copper binding site in poplar plastocyamin[620] and in an azurin from *Pseudomonas aeruginosa*.[621]

To the best of our knowledge only one N(R)Se ligand has been studied, **61** (selenium analogue); this reacts with copper(II) to form $CuLX_2$, X = Cl, Br, NO_3, and ClO_4, in which the selenium is only weakly bound to copper(II).[622]

A number of 1:2 complexes of copper(I) with multidentate thioether carboxylic acid ligands $HOOC(CH_2)_nS(CH_2)_2S(CH_2)_nCOOH$, n = 1–3, have been prepared.[58,623,624] The copper(I) is tetrahedrally coordinated by four sulfur atoms[58,624] (see Table II), the stability decreasing with increasing value of n to the point where the complex with n = 4 cannot be prepared. A number of workers have studied the stability constants of copper(II) ions with multidentate thioether and selenoether carboxylic acid ligands such as $EtS(CH_2)_nCOOH$, $E(CH_2COOH)_2$, E = O, S, Se, $S(CH_2CH_2COOH)_2$, **89**, **90**, **91**, and **92**.[343,427,430,603,625–628] For the



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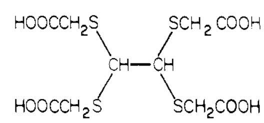

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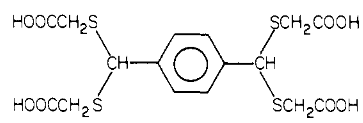

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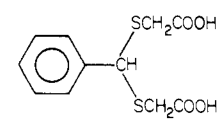


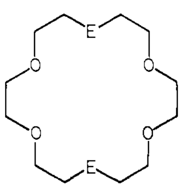
92

bidentate ligands $EtS(CH_2)_nCOOH$, the 5-membered rings were found to be more stable than the 6-membered rings. n values were anomalous in that they were dependent on the ligand concentration which was ascribed to CuL_2, in which both ligands were bidentate, reacting with further ligand to form CuL_3 in which one L was bidentate and two were monodentately bound through sulfur.[625] With the ligands $E(CH_2COOH)_2$, copper(II) showed a preference for sulfur rather than selenium or oxygen.[343] **90** and **91** formed complexes to copper(II) through only one-half of the donors; by comparison with **92** it appeared that each end could bind a copper(II) ion.[430]

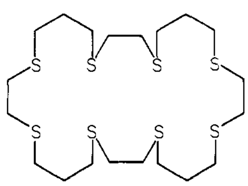
The S(R)As ligands **4** and $MeS(CH_2)_3AsMe_2$ form copper(I) complexes $[CuL_2]ClO_4$ and $[CuL_2][CuX_2]$, X = Cl, Br, I, the aromatic ligand forming the stronger complexes.[628a,629]

The coordination about the copper(I) in diaryl telluride complexes appears to be either tetrahedral as in $Cu(Ph_2Te)_3Cl$ and $[Cu(Ph_2Te)_2Br]_2$ or trigonal planar as in $[Cu(Ph_2Te)I]_2$, the dimers being halide bridged.[630]

Dialkyl and diaryl thioethers react with silver(I) salts to form 1:1 complexes.[631–634] The diphenyl thioether complex $Ph_2SAgClO_4$ reacts with alkyl iodides to yield the sulfonium salt $Ph_2RS^+ClO_4^-$.[634] The relatively high stability of the R_2S complexes of silver has been demonstrated by stability constant studies: tetrahydrothiophene reacts with silver perchlorate in 50% aqueous ethanol with a formation constant of $10^{3.51}$ at 25 °C in 1 M $NaClO_4$;[142] for 2,2′-thiodiethanol a value of $10^{3.60}$ at 20 °C in 1 M aqueous KNO_3 has been determined.[635] With bidentate thioethers such as $RS(CH_2)_nSR$, n = 2–5, *cis*-R′SCH=CHSR′, and o-$C_6H_4(SMe)_2$, silver(I) forms 1:2 chelate complexes involving tetrahedral silver(I).[548] The stabilities in aqueous solution of some of these in which R = CH_2CH_2OH have been reported.[635] A number of macrocyclic polyether thioether ligands that complex silver(I) have been reported.[636] The replacement of two ether donors by thioethers in **93** significantly enhances its coordinating ability for

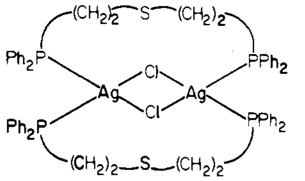


93, E = O, S



94

silver(I); replacement of both sulfurs by >NH further enhances this effect.[637] The same donor order (i.e., N > S > O) is found for acyclic ligands.[487] The macrocyclic thioethers **58** and **94** are both effective for the extraction of silver(I) from aqueous solution; **58** forms both $[AgL]ClO_4$ and $[Ag_2L](ClO_4)_2$ whereas **94** only forms $[AgL]ClO_4$.[638] $\{Ph_2P(CH_2)_2\}S$ forms 1:1 complexes with silver halides[639] which are dimeric with uncoordinated sulfur (**95**).[640] Rather than forming a complex



95

with $Me_2C{=}CHCH(Me)SR$, aqueous silver nitrate promotes its hydrolysis to the corresponding alcohol $Me_2C{=}CHCH(Me)OH$ together with $MeCH{=}CHCMe_2OH$ and the silver salt of the alkyl mercaptide, $AgSR{\cdot}AgNO_3$.[641]

Silver(I) complexes of thioethers containing carboxylic acid groups have been widely studied in solution and are discussed in section IIIB. Only for $[HOOC(CH_2)_nSCH_2]_2$ have complexes been isolated for n = 1–3. The silver(I) is tetrahedrally coordinated by two bidentate thioether ligands, the carboxylic acid moieties remaining noncoordinated. The stability decreases as n increases so that no complex can be isolated when n = 4.[642,643]

When $AuCl_3$ is treated in aqueous solution with a thioether, the first complex formed is R_2SAuCl_3;[644–647] if an excess of thioether is presented, then the thioether is oxidized to the sulfoxide[647] and R_2SAuCl is isolated. Similar complexes are formed with thioxane, *trans*-$RS(CH_2)_2SR$, R = Me, Ph,[69,648] with the bifunctional thioethers bridging two gold units (see Table II). However gauche $MeS(CH_2)_2SMe$ reacts with $AuCl_3$ to form $[Au(MeS(CH_2)_2SMe)Cl_2][AuCl_4]$ in which the thioether acts as a chelate ligand.[646] In the gold(I) LAuCl complexes the thioethers exchange rapidly with excess ligand. Both the gold(I) and gold(III) complexes of dibenzyl thioether undergo inversion at sulfur;[250] in $(PhCH_2)_2SAuCl$, inversion is extremely rapid even at −95 °C whereas in $(PhCH_2)_2SAuCl_3$ coalescence of the peaks starts at 30 °C. These results could be due to the gold–sulfur bond being weaker in the gold(I) than in the gold(III) complex. The gold–sulfur vibration in the far-infrared spectra of gold thioether complexes is often too weak to be observed, although a band at 344 cm^{-1} has been assigned to ν_{Au-S} in $Au(Me_2S)Cl$.[98,649]

Dimethylgold(III) chloride forms cis-square-planar 1:1 complexes $AuMe_2ClL$ with dimethyl thioether and dimethyl selenoether.[650] In solution ligand exchange occurs with the selenoether having a higher activation energy than the thioether. Bidentate ligands form binuclear $AuMe_2ClRS(CH_2)_nSRAuMe_2Cl$, n = 2, 3, except with dimethylgold(III) nitrate which forms ionic $[AuMe_2(MeSCH_2CH_2SMe)]NO_3$ in which the thioether bonds in a chelating manner.[650]

It is interesting to note that while $AuEt_2N(NH_2CH_2CH_2S)$ reacts explosively with neat ethyl bromide to form the thioether complex $[AuEt_2N(NH_2CH_2CH_2SEt)]Br$, attempts to prepare a gold(III) complex of **77** by reaction with $NaAuCl_4$ led to instant demethylation and the isolation of the green mercaptide complex.[175,210] A number of macrocyclic polyether thioether ligands that complex gold have been reported.[636]

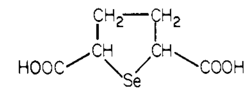
The kinetics of substitution of amines by thioethers at gold(III) have been discussed in section IIIB2.

J. Zinc, Cadmium, and Mercury

The metal ions in the subgroup zinc, cadmium, and mercury become increasingly "soft" as the group is descended. This is reflected in their coordination to group 6B ligands with zinc fairly readily forming complexes with ethers, reluctantly forming complexes with thioethers, and very reluctantly forming complexes with selenoethers; as far as we are aware no zinc complexes of telluroethers have yet been reported. As the subgroup is descended, the affinity of the metal ions for forming complexes with thioethers increases sharply, mercury forming a very wide range of such complexes.

In the case of zinc few thioether complexes have been isolated, although several have been studied in solution. $Zn(EtSCH_2CH_2SEt)_2Br_2$ has been prepared,[651] and the polymeric zinc(II) complex of $HS(CH_2)_2S(CH_2)_5S(CH_2)_2SH$ has been described and its thermal decomposition reported.[352,353] $Zn\{N(CH_2CH_2SCH_3)_3\}I_2$ has been isolated, but it is not known whether the zinc is octahedrally or tetrahedrally coordinated.[407] **46** forms a polymeric complex with zinc(II) of stoichiometry $ZnLCl_2$ in which the zinc is believed to be octahedrally coordinated by two chloride and two bidentate **46** ligands.[380] The reluctance of the relatively "hard" zinc to form complexes of thioethers is well demonstrated by the observation that whereas ethoxyacetate ions form a chelate complex with zinc(II), (ethylthio)acetate ions bond only through their carboxylate groups.[145] A number of groups have shown that multidentate ligands with both thioether and carboxylate functional groups form much stronger complexes with cadmium(II) than with zinc(II) and that in several cases there is no evidence of any direct S–Zn bonding.[427,652–655] Consistent with this is the report that the ligands $HOOCCH_2ECH_2COOH$ where E = O, S, and Se show a relative stability order of E = O > S > Se for both zinc(II) and cadmium(II);[343,656] the stability order Zn^{II}

> Cd^{II} is found when E = O and S, but when E = Se this order is reversed as it is for the cyclic selenoether **96**.[657] If, in accordance with the principle of sym-



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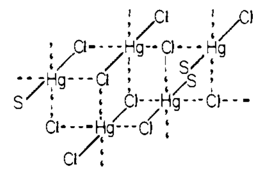
biosis,[658] zinc(II) is made softer by prior coordination to a "soft" ligand, then its affinity for thioethers increases. Thus a number of multidentate thioether carboxylate ligands which bond to zinc(II) only through the carboxylate group when the only other ligand present is water[659] bond also through the thioether group in the presence of bipyridyl;[660] however, even in the presence of bipyridyl, aryl thioether groups (SAr) are reluctant to bind to zinc whereas alkyl thioether groups (SR) bind readily. A number of studies have been made of both open-chain and macrocyclic ligands containing thioether, ether, and amine donors[420–424] which show that whereas cadmium(II) in common with Cu^{II}, Ni^{II}, Co^{II}, and Ag^{I} forms more stable complexes with the macrocyclic ligands, zinc(II) in common with Pb^{II} prefers the corresponding open-chain compound. Although cadmium(II) normally forms stronger complexes than zinc(II) with ligands containing thioether donors, a series of multidentate amine thioether ligands, $[(H_2NCH_2CH_2S)_2CH]_2$, $(H_2NCH_2CH_2S)_2CH(CH_2)_nCH(SCH_2CH_2NH_2)_2$ (n = 1–3), o-$C_6H_4[CH(SCH_2CH_2NH_2)_2]_2$, showed the reverse trend, indicating the importance of the amino donor groups in these complexes.[428]

Very few thioether and selenoether complexes of cadmium(II) have been isolated and characterized, although, $Cd(CH_3SCH_2CH_2SCH_3)_2Cl_2$, $Cd(EtSCH_2CH_2SEt)_2Cl_2$, Cd_2(1,4-dithiane)$_2X_4$, where X = Cl, Br, and I, and Cd_2(1,4-diselenane)Cl_4 have all been reported.[576,651,661–664]

Mercury forms a very wide range of complexes with thioethers; many of the compounds formed have been prepared in order to characterize the thioether through their melting points and analytical data. References to these have not been included here. Mercury halides readily form 1:1, 1:2, and 2:3 complexes with thioethers when the two are mixed in aqueous alcoholic solutions.[234,632,665–686] Thus complexes of symmetrical thioethers R_2S where R = Me,[632,665–670] Et,[234,665–667,669,671] n-Pr,[234,667–669,671] i-Pr,[669] n-Bu,[234,666,667,669,672] i-Bu,[234,666,667,669,672] sec-Bu,[234,666,669] t-Bu,[673] n-amyl,[666,671] i-amyl,[666,667,672] cyclopentyl,[672] unsymmetrical thioethers RSR′ where R and R′ are either both different alkyl groups or one is an alkyl group and one a phenyl group,[666,668,674–679] and cyclic thioethers $(CH_2)_nS$ where n = 3,[680–682] 4,[71,671,681–684] and 5[680,681,685] have been prepared. The 1:1 complexes involve essentially linear mercury(II) coordination, $[R_2SHgCl]Cl$.[70,71,686] The 1:2 complexes are thought to involve HgX_2 and $[R_2SHgX]X$ units held together by weak chloride bridges, **97**.[70,71,666,673,686] The 2:3 complexes appear to be a mixture of 1:1 and 1:2 since their infrared spectra contain bands characteristic of the mercury environments in both the 1:1 and 1:2 complexes.[666] Molecular weight measurements of all three types of complex show extensive dissociation in solution.[673] The nonconducting nature of the solutions suggests that dissociation is as



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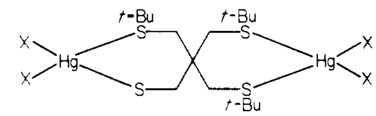
shown in reaction 24.[673] The thioether adducts react

$$R_2S{\cdot}nHgCl_2 \rightleftharpoons R_2S + nHgCl_2 \qquad (24)$$

with hydrogen peroxide to form sulfoxide adducts.[687] On being heated, t-$Bu_2S{\cdot}HgCl_2$ decomposes to yield $Hg_3S_2Cl_2$, Hg-t-BuSCl, HCl, and $(CH_3)_2C{=}CH_2$.[688]

Mercury(II) halides form 1:1 adducts with potentially bidentate $RS(CH_2)_nSR$, n = 2, R = Me, Et, $PhCH_2$, p-tolyl;[454,543,651,689,690] n = 3, R = Ph.[105] In general, the alkyl thioethers form more stable complexes than the aryl ligands,[543] a point that is further substantiated by the observation that whereas the spirocyclic *tert*-butyl tetrathioether $C(CH_2S$-t-$Bu)_4$ forms Hg_2X_4L, X = Cl, Br, and I (**98**), the phenyl analogue does not react with



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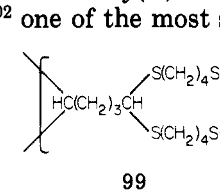
mercury(II).[691] 1,4-Thioxane forms tetrahedral HgL_2Cl_2[692,693] (see Table II for structural details). 1,4-Dithiane forms $HgLX_2$, X = Cl, Br, I, and CN, and $[HgL_2](ClO_4)_2$,[662,663,694,695] which probably contain tetrahedral mercury(II) linked by 1,4-dithiane bridges. 1,3,5-Trithiane forms $HgLX_2$, X = Cl, Br, and I (see Table II for structural details).[696,697] The crown thioethers 1,4,8,11-tetrathiacyclotetradecane and 1,4,8,11,15,19,22,25-octathiacyclooctaeicosane have been used to extract mercury(II) out of aqueous solutions.[698] A calorimetric study of the interaction of a series of crown ethers and crown thioethers with mercury(II) showed that the replacement of ether groups by thioether increase both the free energy and enthalpy of complex formation.[699] A number of polymeric thioether ligands have been prepared with a view to making one that is selective for mercury(II) in the presence of other metal ions;[700–702] one of the most successful is **99**.



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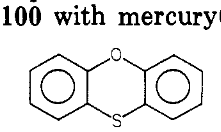
Many thioether ligands that contain further donor groups in addition to the thioether have been studied. $HS(CH_2)_2S(CH_2)_2SH$ formed an insoluble polymeric complex involving both mercaptide and thioether coordination.[36] Complexes of the S–O ligands $MeO(CH_2)_2SMe$ and **100** with mercury(II) chloride have



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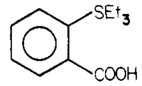
been described, and the crystal structure of the latter (see Table II) has been used to demonstrate the absence of any O–Hg bonding.[703]

There has been considerable interest for many years in ligands such as **101–104** which contain both thioether



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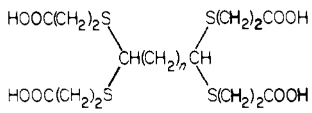
$EtS(CH_2)_2SCH_2COOH$

102



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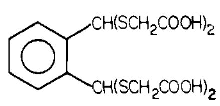

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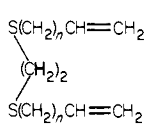
and carboxylate groups.[654,655,704–711] These ligands are water soluble and show a high selectivity for mercury(II) relative to other metal ions because mercury(II) is one of the few metal ions that can bind to thioethers in an aqueous environment. Of particular interest is the possibility of removal of mercury(II) accidentally ingested into the body. **104** in particular is quite selective for mercury(II)[710] and has been shown to have a pronounced protective action against CH_3HgCl poisoning in mice.[712] ^{13}C NMR has been shown to be a potentially useful technique for studying the coordination chemistry of these ligands.[713] A number of S(R)N chelates such as[74,103] and **104** have been studied.[428,607] While these form strong complexes with mercury(II), they do not show the same degree of selectivity for mercury(II) as compared to other metals that the thioether carboxylates do. The potentially tridentate phosphine thioether $[Ph_2P(CH_2)_2]_2S$ reacts with mercury(II) iodide to form $HgLI_2$ in which the ligand only binds in a bidentate fashion through the phosphorus atoms, demonstrating that while mercury(II) forms strong complexes with thioethers it forms even stronger complexes with tertiary phosphines.[714] Exactly the reverse situation applies with ligands containing both olefinic and thioether donors such as **105** and **106** in that mercury-



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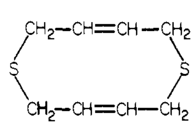

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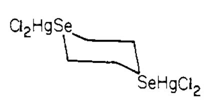
(II) spurns the olefinic site and bonds exclusively through the sulfur[74,572,715] (see Table II for the structure of the complex with **106**).

The coordination chemistry of mercury(II) with selenoethers is a much neglected area. Diethyl selenoether has been shown[234,651] to form $[Hg(Et_2S)X]_2$, X = Cl, Br, and I. 1,4-Diselenane reacts with mercury(II) chloride to form Hg_2LCl_4, which is believed to have structure **107**.[576] $PhSeCH_2CH_2SePh$ and $MeSe(CH_2)_nSeMe$ (n



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= 2, 3) both form 1:1 complexes with mercury(II) chloride.[105,265] The reaction of diorganyl diselenides with dialkylmercury(II) compounds (reaction 25) has been found to provide a convenient route to the preparation of unsymmetrical selenoethers.[716]

A reaction exactly analogous to reaction 25 also provides a convenient route to unsymmetrical telluroethers.[716] In contrast to the situation with selenoethers,

$$R_2Se_2 + R_2{}^1Hg \xrightarrow[\text{dioxane}]{\text{reflux in}} RSeR^1 + Hg$$
$$\xrightarrow[\text{room temp}]{\text{dioxane}} RSeR^1 + (RSe)_2Hg \qquad (25)$$

a wide range of telluroether adducts of mercury(II) halides have been prepared, many by Lederer during the first World War. These have been comprehensively reviewed recently, and the reader is referred to that source.[717,718] More recently the infrared spectra of $[Hg(Et_2Te)X]_2$, X = Cl and Br, have been reported,[234] as well as the ^{125}Te Mössbauer, infrared, and Raman spectra of $Hg(Ar_2Te)X_2$, X = Cl, Br, and I, Ar = C_6H_5 and p-$EtOC_6H_4$.[113]

VII. Addendum

Since preparation of the manuscript several recent publications have come to the notice of the authors. These will be included here in the same order as in section VI.

C. Niobium

The reaction between $NbCl_5$, Mg, and SMe_2 gives two products, $Nb_2Cl_6(SMe_2)_3$ and $Nb_3Cl_8(SMe_2)_2(Et_2O)$.[719] Metal–metal bonds are thought to be present since these species are diamagnetic on the grounds of sharp ^1H NMR spectra.

D. Chromium and Molybdenum

The ligand $S[CH_2CH_2N(CH_2CO_2H)_2]_2$ forms complexes with chromium(III); one having an O_3N_2 ligand donor set with H_2O in the sixth position but the other has an O_3N_2S donor set, presumably with chelation stabilizing the Cr–S bond.[720]

With another multidentate, $CH_3SCH_2CH_2N(CH_2CH_2SH)$ (LH_2), the complex MoO_2L has been studied by X-ray photoelectron spectroscopy (XPS) toward recognition of thioether and sulfide bound to metals in the same solvent.[721]

F. Ruthenium and Osmium

There has been a report of an improved synthesis of ruthenium thioether macrocycle complexes with ligands **58** (TTP) and **59** (TTX).[722] The complexes isolated were $RuLCl_2{\cdot}2H_2O$, L = TTP, TTX, and $[Ru(TTP)Cl_2](ClO_4){\cdot}H_2O$.

The osmium thioether complexes discussed in section VIF are now in the literature.[723]

G. Cobalt and Iridium

The weakness of a cobalt(II) thioether bond has been shown in the structure determination of dichlorobis(2,2′-thiodiethanol)cobalt(II).[724] In this complex the potentially tridentate ligand is bidentate (O,S), and the Co–S bond length is 2.508 Å compared to the sum of the covalent radii of 2.31 Å. The iron(II) reduction of two cobalt(III) complexes with pentadentate amine thioether ligands has been shown to occur via a coordinated azide ligand.[725]

Unpublished work[369] on iridium(IV) thioether complexes discussed in section VIG has now been published.[723] Further work on mer-$Ir(SEt_2)_3Cl_3$ has shown that this complex can be converted by ultraviolet energy to be a halide-bridged dimer and also to an unusual dimer in which bridging occurs via a halide and a thioether ligand.[726] This behavior of thioether ligand bridging is well-known for platinum(II)[42,94,109] but it is unusual for iridium(III).

H. Nickel, Palladium, and Platinum

The pseudotetrahedral complex $[Ni(NO)(Ph_2PCH_2CH_2SEt)_2](BPh_4)$ contains one bidentate and one monodentate P–S ligand, and ^{31}P NMR indicates fluxional behavior due probably to bidentate–monodentate interchange.[727]

In an attempt to prepare a cyclopalladated thioether complex, reactions with *t*-BuSBz were reported as unsuccessful; however, with 2,6-(Bu-*t*-$SCH_2)C_6H_4$, the complex $[PdCl\{C_6H_3(CH_2SBu\text{-}t)_2\text{-}2,6\}]$ can be prepared and the structure has been determined.[728] Another study with Bu-*t*-SBz indicates that with $PdCl_2$ under mild conditions S-dealkylation occurs with loss of the Bu-*t* group; however, with palladium acetate an acetate-bridged dimer containing a metalated ligand Bu-*t*-$SCH_2(o\text{-}C_6H_4)$[729] forms. With the complex *cis*-Pt$(OAc)_2(SEt_2)_2$ a range of complexes may be synthesized.[730] Reaction with *o*-hydroquinones and dihydroxybenzoquinones replaces the acetate ligands whereas reaction with phosphines replaces the thioether ligands first. Thiols first replace acetate and then thioether. With the bidentate Bu-*t*-$S(CH_2)_5$SBu-*t* of intermediate chain length and sterically demanding terminal groups the complexes with palladium(II) and platinum(II) are thioether ligand bridged dimers shown by structure determination to have the so-called "barge" conformation.[731] The reaction of $CH_2(CH_2SCH_2CH_2SH)_2$ with palladium acetate gives a mononuclear product in which the ligand acts as a tridentate.[732] This species will react with Ni^{2+} to form a trimetallic species in which the nickel ion coordinates to four-coordinated sulfide sites.

There have been several reports of inversion at coordinated thioether sites.[733-736] With $MeSCH_2C(Me)_2CH{=}CHR$, the complexes $PdLX_2$, L has R = Me, X = Cl, Br; R = H, X = Cl, Br, I, have been studied.[733] For R = H, X = Cl, Br they can be converted to π-allyl species, and NMR studies of the alkene complexes shows first inversion at sulfur and then labilization of the coordinated alkene. Two structure determinations are reported. Inversion has been noted with palladium(II) and platinum(II) halide complexes of fluorinated bidentate thioethers.[734] With *trans*-$MX_2[\overline{S(CH_2)_5}]_2$, M = Pd, X = Cl, Br, I; M = Pt, X = Cl, energy barriers are reported for ring reversal and pyramidal inversion.[735] Perhaps the most remarkable study has been with dimeric platinum(IV) complexes bridged by two halide ligands and a bidentate, MeECH(R)EMe, E = S, Se; R = H, Me $[(PtXMe_3)_2(MeECHREMe)]$.[736] At least four dynamic processes occur, and barrier energies have been measured. The preparation of these and mononuclear $PtXMe_3[MeE(CH_2)_nEMe]$ is reported separately.[737]

There have been further kinetic studies.[738-740] The attack on $Pd(o\text{-}MeEC_6H_4PPh_2)X_2$, E = S, Se; X = SCN, I, by I^- or SCN^- forming MeI or MeSCN supports the Zeisel cleavage model for S- and Se-dealkylation, as previously discussed.[738] The trans effects of SMe_2 and SEt_2 have been studied,[739] as has the kinetics of ring closure using an NSN tridentate ligand on platinum(II).[740]

I. Copper and Gold

A variety of copper complexes have been studied as possible analogues of "blue" copper proteins.[741-743,745,746] Ligands used have been either multidentate thioethers or multidentate thioether nitrogen ligands. The mixed valency complexes $Cu^I_2Cu^{II}(dth)_6X_4$, X = ClO_4, BF_4, have EPR spectra similar to those exhibited by copper proteins.[741] Redox studies have also been used on the models as the copper proteins undergo reversible redox reactions.[742,743] This indicates a stereochemical problem since a tetrahedral geometry is needed to stabilize copper(I). Since it has now been shown that the copper proteins have the copper ion coordinated to two histidine imidazoles, one methionine thioether and one cysteine thiolate,[744] then perhaps the closest model has a bis(benzimidazole) thioether donor set and coordinated perchlorate which reacts with RS^- at −77 °C to form a species having absorptions in the electronic spectra very like the "blue" copper proteins.[745] Other species have been prepared in which imidazole bridges are present.[746] A structure determination of $Cu_2[EtS(CH_2)_2NH(CH_2)_3O]_2Cl_2(H_2O)_2$ in which the metals are alkoxy bridged has shown that the Cu–S bond is relatively weak, 2.4101 Å compared to the sum of the covalent radii, 2.32 Å.[747]

The reduction of gold(III) to gold(I) by thioether appears to involve reaction of the thioether with a coordinated halide. Reactivity is in the order SMe_2 < SEt_2 < SPr-i_2, indicating that polar effects are more important than steric effects.[748]

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