Inorganica Chimica Acta, 17 (1976) 247–252
© Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Coordination Complexes Containing Multidentate Ligands. Part X. The Reaction of Divalent Cobalt, Nickel, and Palladium Salts with Open-chain Tetrathioethers, α,ω-Bis(methylthioalkylthio)alkanes. The Effect of Chelate Chain Length on Donor and Spectral Properties

W. LEVASON, C. A. McAULIFFE and S. G. MURRAY
Department of Chemistry, University of Manchester, Institute of Science and Technology, Manchester M60 1QD, U.K.

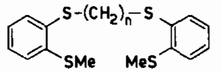
Received September 15, 1975

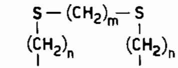
The aliphatic open-chain tetrathioethers, 1,2-bis(2-methylthioethylthio)ethane, 1,3-bis(2-methylthioethylthio)propane, 1,2-bis(3-methylthiopropylthio)ethane, and 1,3-bis(3-methylthiopropylthio)propane have been synthesised and reacted with divalent metal salts. They form complexes of the type $[Co(ligand)I_2]$, $[Ni(ligand)X_2]$ *(X = Cl, Br, I), and* $[Pd_2(ligand)X_4]$ *(X = Cl, Br, I), but not all ligands form each type of complex, and the donor properties of these tetrathioethers are discussed in terms of the chain lengths between the sulphur atoms. Calculation of in-plane ligand field in the trans-*$[Ni(ligand)X_2]$ *complexes indicates that the field strengths of the tetrathioethers changes from the solid state to solution and are also dependent on the nature of the coordinated halide.*

Introduction

Interest in multidentate chelates containing heavy donor atoms P, As, Sb, S, Se continues to grow (refs. 2–4 are recent reviews of this area) but, whereas initial efforts were concentrated on the tripod tetradentate type of ligand attention is increasingly being paid to the open-chain type of chelate. The tripod tetradentate has provided workers with a vast number of complexes, but because the trigonal symmetry of such ligands tends to enforce, or at least encourage, the formation of trigonal bipyramidal complexes,[5] open-chain tetradentate chelates are undergoing investigation[4] because they allow the resultant complex structure and stoichiometry to be dictated to a larger extent by the electronic properties of the metal ion. Thus planar,[6] square pyramidal,[7] trigonal bipyramidal,[6] and octahedral[8] stereochemistries have been assigned to complexes containing open-chain chelates.

We have recently become interested in multidentate sulphur and selenium ligands. The interaction of metal ions with several sulphur centres is important biologically, *e.g.* in nitrogenase enzyme[9] and in high potential iron proteins,[10] and also metal catalysed S-dealkylation reactions continue to intrigue inorganic chemists.[11,12] Apart from the macrocyclic tetrathioether, 1,4,8,11-tetrathiocyclotetradecane, of Rosen and Busch[13] the only other tetrathioether ligands which have been prepared are our series α,ω-bis(*o*-methylthiophenylthio)alkanes, (I, n = 2,3,4).[1]


(I)


(II)

These ligands complexed readily with heavy transition metal ions yielding complexes of type $Pd_2(ligand)X_4$, $Pt_2(ligand)X_4$, $Rh_4(ligand)_3X_{12}$, and somewhat less readily with first row transition metal salts to yield the hexacoordinate $[Co(ligand)I_2]$ and $[Ni(ligand)X_2]$. Although these complexes are fairly varied their structural and stoichiometrical variety in no way match those formed by the structurally similar dithioether-diarsine chelates of Dutta, Meek, and Busch.[14–16] We have thus synthesised a series of open-chain tetrathioether chelates containing only aliphatic linkages, (II), in order to discover whether the relative paucity of metal complex variety of derivatives of ligand type (I) is in any way connected with the rigid *o*-phenylene linkages. Four new chelates of type (II) have been synthesised: 1,2-bis(2-methylthioethylthio)ethane (II, n = 2, m = 2), (2,2,2), 1,3-bis(2-methylthioethylthio)propane (II, n = 2, m = 3), (2,3,2) 1,2-bis(3-methylthiopropylthio)ethane (II, n = 3, m = 2), (3,2,3) 1,3-bis(3-methylthiopropylthio)propane (II, n = 3, m = 3), (3,3,3). Reactions of these ligands with divalent cobalt, nickel, palladium, and platinum salts are reported here.

Experimental

Ligands

(i) 2-Hydroxyethylmethylsulphide

In a 3 litre three-necked round-bottomed flask fitted with a nitrogen inlet, condenser, and mechanical stirrer, was dissolved sodium (80.5 g, 3.5 g atom) in absolute ethanol (1.5 litres). When the sodium was completely dissolved, the flask was cooled in an ice/salt bath and methanethiol (168 g, 3.5 mol) added and the mixture stirred for 1 hr in the cooling bath. After this time the flask was heated to reflux, after which heating was discontinued and 2-chloroethanol (302 g, 3.75 mol) added dropwise over 2 hr. Heating at reflux was continued for a further hour and most of the ethanol was allowed to evaporate, after which the mixture was cooled and filtered to remove the sodium chloride. The salt cake was washed with ethanol (3 × 100 cm^3) and the combined filtrate distilled firstly to remove the ethanol using water pump vacuum, then distilling the product. B.Pt. 75–76°C/25 torr. Yield 250 g (78%).

(ii) 2-Chloroethylmethylsulphide

In a one litre three-necked round-bottomed flask were mixed 2-hydroxyethylmethylsulphide (150 g, 1.63 mol) and dry chloroform (200 cm^3). The flask was fitted with a dropping funnel, mechanical stirrer, and condenser. A solution of thionyl chloride (204 g, 122 cm^3, 1.7 mol) in dry chloroform (135 cm^3) was added dropwise over a period of about two hours. The reaction mixture was stirred vigorously during the reaction and heated when necessary to maintain reflux. Stirring was continued for four hours after the addition, but not the heating. Finally the solvent was removed by distillation and the residue distilled *in vacuo.* B.Pt. 55–56°C/30 torr. Yield 142 g (79%).

[CARE! *The product is a vesicant boiling at 140°C under atmospheric pressure, cf. "mustard gas", β,β'-dichlorodiethylsulphide.*]

(iii) 1,2-Bis(2-methylthioethylthio)ethane

In a 500 cm^3 three-necked round-bottomed flask fitted with a nitrogen inlet and condenser, sodium (9.2 g, 0.4 g atom) was dissolved in absolute ethanol (250 cm^3) with magnetic stirring. 1,2-Ethanedithiol (18.8 g, 0.2 mol) was added and the mixture stirred for 30 min after which time the 2-chloroethylmethylsulphide (44.4 g, 0.4 mol) was added over 5 min. The mixture was refluxed for one hour after which the ethanol was removed by distillation and the remaining oil cooled. After standing overnight the oil had crystallised, and this impure solid was recrystallised from hot ethanol, to give soft shiny white crystals. Yield 34.2 g (70%). *Analyses:* Found C, 39.4; H, 7.5; S, 53.3%. $C_8H_{18}S_4$ requires C, 39.7; H, 7.5; S, 53.0%.

(iv) 1,3-Bis(2-methylthioethylthio)propane

This ligand was prepared by the procedure described in (iii) except here the compound could not be induced to crystallise, nor did it distil. After isolation of the oil, it was heated to 180°C at 0.2 torr for 3 hr to remove impurities. Reagents used in the preparation were: sodium (9.2 g, 0.4 g atom), 1,3-propanedithiol (21.6 g, 0.2 mol), and 2-chloroethylmethylsulphide (44.4 g, 0.4 mol). Yield 44.2 g (87%). *Analyses:* Found C, 42.3; H, 7.8; S, 50.1%. $C_9H_{20}S_4$ requires C, 42.2; H, 7.8; S, 50.0%.

(v) 3-Hydroxypropylmethylsulphide

Here the intermediate was prepared as in (i), the reagents used being sodium (48.0 g, 2.09 g atom), methanethiol (100 g, 2.09 mol), and 3-chloropropanol (211 g, 187 cm^3, 2.25 mol). The addition of the 3-chloropropanol took 35 min. B.Pt. 95.0–95.5°C/30 torr. Yield 199.6 g (90%).

(vi) 3-Chloropropylmethylsulphide

The procedure followed in this preparation was identical to that described in (ii). Reagents used were: 3-hydroxypropylmethylsulphide (173 g, 1.63 mol) and thionyl chloride (204 g, 1.7 mol). B.Pt. 74–75°C/28 torr. Yield 153.2 g (76%).

(vii) 1,2-Bis(3-methylthiopropylthio)ethane

The preparative procedure for the formation of this ligand was analogous to that described in (iii). The oil obtained as product was heated to 180°C/0.5 torr for 3 hr to remove impurities. Reagents used: sodium (9.2 g, 0.4 mol), 1,2-ethanedithiol (19 g, 0.2 mol), and 3-chloropropylmethylsulphide (50 g, 0.4 mol). Yield 48.5 g (90%). *Analyses:* Found C, 44.5; H, 8.2; S, 47.4%. $C_{10}H_{22}S_4$ requires C, 44.5; H, 8.2; S, 47.4%.

(viii) 1,3-Bis(3-methylthiopropylthio)propane

Procedure as in (iv), the product being heated at 180°C/0.5 torr for 3 hr to remove impurities. Reagents used: sodium (9.2 g, 0.4 mol), 1,3-propanedithiol (21.7 g, 0.2 mol), and 3-chloropropylmethylsulphide (50 g, 0.4 mol). Yield 52.8 g (89%). *Analyses:* Found C, 46.2; H, 8.0; S, 45.3. $C_{11}H_{24}S_4$ requires C, 46.5; H, 8.4; S, 45.1%.

Metal Complexes

Pd_2LCl_4 [L = (2,2,2), (2,3,2)]

Sodium tetrachloropalladate(II) (0.59 g, 2.0 mmol) in ethanol (15 cm^3) and a solution of the ligand (1.0 mmol) in dichloromethane (15 cm^3) were mixed with rapid stirring. A precipitate formed immediately and stirring was continued for 1 hr. The solid was filtered, washed with ethanol (5 cm^3) and water (35 cm^3) to remove sodium chloride, and again with ethanol (15 cm^3) and diethylether (20 cm^3), and dried *in vacuo.* Yields 70–80%.

Pd_2LX_4 (X = Br, I)

These derivatives were obtained similarly except that the Na_2PdCl_4 was stirred with a 5 molar quantity of the appropriate NaX in ethanol for $^1/_2$ hr before addition of the ligand.

Pt_2LX_4 (L = (2,2,2), (2,3,2); X = Cl, Br, I)

Analogous routes to those above were used to prepare these complexes except that the metal salt was dissolved in water and ethanol was added until the water and dichloromethane layers became miscible. The precipitation of the complexes was not as rapid as for the palladium analogues.

$NiLX_2$ [L = (2,2,2), X = Cl, Br, I; L = (2,3,2), X = Br, I]

Hydrated nickel halide (~2.0 mmol) was dissolved in the minimum quantity of hot n-butanol, the solution was filtered and treated, when cold, with a dichloromethane solution (70 cm^3) of the ligand (2.0 mmol). After stirring for $^1/_2$–1 hr a precipitate was seen to form which was filtered off, washed with n-butanol (5 cm^3) and dichloromethane (20 cm^3) and dried *in vacuo*. Yields 50–70%.

$NiLI_2$ [L = (3,2,3), (3,3,3)]

The above procedure was followed to prepare these complexes except that precipitation was induced by pouring the mixture into a large excess (250 cm^3) of dry hexane. The products were filtered and dried *in vacuo*. Yields 20–50%.

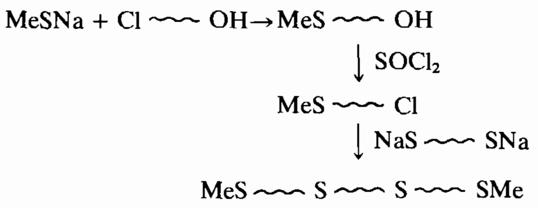
$Co(2,2,2)I_2$

This complex was prepared as for the $NiLX_2$ complexes above.

Results and Discussion

Ligand Synthesis

The four open-chain tetrathioethers were prepared by the following general route: sodium methylsulphide was reacted with the chloroalcohol in absolute ethanol (steps (i) and (v) in the Experimental), and the resulting hydroxyalkylmethylsulphide was chlorinated with thionyl chloride in dry chloroform to yield the potentially highly toxic chloroalkylmethylsulphide (steps (ii) and (vi) in the Experimental). For the final stage the precursor, the disodium salt of the alkanedithiol was prepared in absolute ethanol,



and to this was added the chloroalkylmethylsulphide (steps (iii), (iv), (vii), and (viii) in the Experimental). Only one of the four tetrathioethers (the 2,2,2 ligand) is a crystalline solid. None of the three oils could be distilled, but all attempts to induce them to crystallise failed. They were purified by heating to 180°C under high vacuum in order to ensure that any unreacted precursors were removed. Elemental analyses (C, H, S) indicated high purity for all the ligands and the ^1H NMR spectra, which are listed in Table I, confirmed the purity of these chelates.

Physical measurements were made as described previously.[1,17]

Metal Complexes

Attempts were made to react halide (chloride, bromide, iodide), and pseudohalide (thiocyanate) salts of divalent cobalt, nickel, palladium, and platinum with all four open-chain tetrathioether ligands. Many X-ray crystallographic studies and calculations[4,18,19] have shown that a two-carbon link between donor

TABLE I. Proton Nuclear Magnetic Resonance Spectra of the Ligands and Precursors.[a]

$CH_3SCH_2CH_2Cl$	CH_3S- (2.15 ppm, singlet), $-S\underline{CH_2}CH_2-$ (2.80 ppm, triplet), $-CH_2\underline{CH_2}Cl$ (3.67 ppm, triplet)
$CH_3SCH_2CH_2CH_2Cl$	CH_3S- (2.05 ppm, singlet), $-S\underline{CH_2}CH_2-$ (2.55 ppm, triplet), $-CH_2\underline{CH_2}Cl$ (3.62 ppm, triplet), $-CH_2\underline{CH_2}CH_2-$ (1.98 ppm, multiplet)
$CH_3SCH_2CH_2OH$	CH_3S- (2.12 ppm, singlet), $-S\underline{CH_2}CH_2-$ (2.62 ppm, triplet), $-CH_2\underline{CH_2}OH$ (3.70 ppm, triplet), $-OH$ (4.10 ppm, singlet)
$CH_3SCH_2CH_2CH_2OH$	CH_3S- (2.10 ppm, singlet), $-S\underline{CH_2}CH_2-$ (2.58 ppm, triplet), $-CH_2\underline{CH_2}OH$ (3.66 ppm, triplet), $-CH_2\underline{CH_2}CH_2-$ (1.78 ppm, multiplet), $-OH$ (4.08 ppm, singlet)
$(CH_3SCH_2CH_2SCH_2)_2$ (2,2,2)	CH_3S- (2.15 ppm, singlet), $-S\underline{CH_2}CH_2-$ (2.76 ppm, triplet)
$(CH_3SCH_2CH_2SCH_2)_2CH_2$ (2,3,2)	CH_3S- (2.15 ppm, singlet), $-S\underline{CH_2}CH_2-$ (2.74 ppm, triplet), $-CH_2\underline{CH_2}CH_2-$ (1.84 ppm, quintuplet)
$(CH_3SCH_2CH_2CH_2SCH_2)_2$ (3,2,3)	CH_3S- (2.16 ppm, singlet), $-CH_2\underline{CH_2}CH_2-$ (1.90 ppm, quintuplet), $S-\underline{CH_2}CH_2$ (2.70 ppm, multiplet)
$(CH_3SCH_2CH_2CH_2SCH_2)_2CH_2$ (3,3,3)	CH_3S- (2.10 ppm, singlet), $-CH_2\underline{CH_2}CH_2-$ (1.82 ppm, quintuplet), $S\underline{CH_2}CH_2-$ (2.60 ppm, triplet)

[a] With respect to TMS internal standard, 50% solution in $CDCl_3$.

TABLE II. Physical Properties and Analytical Data for the Complexes.

Compound	Colour	μ_{eff} (B.M.)	Λ[a] $\Omega^{-1}cm^2mol^{-1}$	%C[b]	%H[b]	%Hal[b]	Reflectance Spectra ($\times 10^{-3} cm^{-1}$)
$Co(2,2,2)I_2$	Red–black	4.90		17.2(17.3)	3.4(3.3)		27.4(sh), 20.2, 13.6(sh), 8.6
$Ni(2,2,2)Cl_2$	Green	2.90		25.6(25.8)	4.8(4.9)		24.7(sh), 15.4, 9.7, 8.9
$Ni(2,2,2)Br_2$	Green	2.93		20.8(20.8)	3.7(3.9)		24.7(sh), 15.3, 9.6, 8.8
$Ni(2,2,2)I_2$	Green–yellow	3.06		17.3(17.3)	3.3(3.3)		23.3, 15.5, 9.35, 8.5
$Ni(2,3,2)Br_2$	Green	2.89		22.9(23.0)	4.4(4.3)		24.7, 15.2, 10.1, 8.9
$Ni(2,3,2)I_2$	Yellow	3.18		18.7(18.6)	3.7(3.4)		22.7, 14.9, 11.0, 8.3
$Ni(3,2,3)I_2$[c]	Yellow	3.24	9	20.9(20.6)	4.1(3.8)		22.7, 14.8, 9.3, 8.4
$Ni(3,3,3)I_2$[d]	Light brown	2.92	9	21.7(22.1)	4.1(4.0)		23.8, 14.9, 11.0, 8.5
$Pd_2(2,2,2)Cl_4$[e]	Yellow			16.0(16.1)	3.0(3.0)	23.8(23.4)	25.8
$Pd_2(2,2,2)Br_4$	Orange			12.2(12.4)	2.7(2.3)	40.4(40.7)	23.4
$Pd_2(2,2,2)I_4$	Maroon			9.6(10.0)	1.8(1.8)		19.9
$Pd_2(2,3,2)Cl_4$[f]	Yellow			17.0(17.7)	3.1(3.3)	23.4(22.8)	25.4
$Pd_2(2,3,2)Br_4$	Yellow			14.0(13.7)	2.6(2.6)		24.4
$Pd_2(2,3,2)I_4$	Red			10.4(11.1)	1.9(2.1)		20.0
$Pt_2(2,2,2)Cl_4$	White			12.6(12.4)	2.3(2.3)		27.5
$Pt_2(2,2,2)Br_4$	Pale yellow			10.7(10.1)	2.0(2.0)		26.7
$Pt_2(2,2,2)I_4$	Brown			7.9(8.4)	1.4(1.6)	45.1(44.0)	23.4
$Pt_2(2,3,2)Cl_4$	Pink			13.9(13.7)	2.6(2.6)		27.5
$Pt_2(2,3,2)Br_4$	White			11.1(11.1)	2.3(2.1)	31.6(32.8)	26.8
$Pt_2(2,3,2)I_4$	Brown			9.5(9.3)	2.0(1.7)		21.4

[a] $10^{-3} M$ in nitromethane. [b] Found (calc.). [c] Solution spectra: 13.7, 8.83, 8.17 ($\times 10^{-3}$ cm^{-1}) dichloromethane; 14.1, 9.28, 8.28 ($\times 10^{-3}$ cm^{-1}) nitromethane. [d] Solution spectra: 13.5, 8.76, 8.31 ($\times 10^{-3}$ cm^{-1}) dichloromethane; 14.2, 9.55, 8.28 ($\times 10^{-3}$ cm^{-1}) nitromethane. [e] ν(Pd–Cl) 338, 323 cm^{-1}. [f] ν(Pd–Cl) 334, 315 cm^{-1}.

atoms (L) in a chelate results in a $\widehat{LML}$ of *ca.* 81–86°, whilst a three-carbon link results in a $\widehat{LML}$ of *ca.* 91–93°, and thus to relieve strain in a tetradentate open-chain ligand which coordinates in a planar or a non-planar arrangement the interdonor links should preferably be a 2–3–2 arrangement or, perhaps, a 3–2–3 arrangement. The only complexes which could be isolated from our preparative attempts (many different solvents and conditions were used), are listed in Table II. Without discussing the individual structures of the complexes it may be seen initially that exactly half of all the complexes isolated are with the 2,2,2 ligand, nearly as many with the 2,3,2 ligand, and only one each of the longer chain chelates 3,2,3 and 3,3,3. It may be tentatively concluded that with the ligands of type II used in this study terminal chain lengths of three carbon atoms (n = 3) are a barrier to facile complex formation. It would be interesting to speculate on the reasons for this phenomenon; we suspect that these are essentially steric in origin but until further studies on these systems have been performed the extent of the role of electronic factors cannot be estimated.

Cobalt(II) and Nickel(II) Complexes

The only cobalt(II) complex which could be isolated was the red–black $Co(2,2,2)I_2$. The magnetic moment of this compound, μ_{eff} = 4.90 B.M., suggests a hexacoordinate structure and since its infrared spectrum is very similar to the nickel(II) derivatives (see below) it is likely that this complex has a similar tetragonal structure.

With the *o*-phenylene linkage ligands of type I we had not been able to observe any complex formation with nickel(II) chloride,[1] but in the present study we have been able to isolate a nickel(II) chloride complex of the ligand 2,2,2 which may suggest that the expected better σ-donor power of type II ligands over type I has had an effect. However, as Table II shows, it is predominantly NiI_2 derivatives which have been isolated, and the importance of this heavy polarisable counteranion in stabilising the $NiLX_2$ complexes is no doubt an example of symbiosis.[20]

The magnetic moments of the seven $NiLX_2$ complexes, Table II, suggest that the complexes are pseudo-octahedral, μ_{eff} = 2.90–3.24 B.M. The moments of the iodo complexes are higher than the chloro or bromo derivatives and suggest that tetragonal distortion is greatest for the iodo species. We have been able only to identify one ν(Ni–X) (X = Cl, Br) in the far infrared spectrum of these compounds, indicatiye of a *trans* octahedral structure. The infrared spectra of all the NiX_2 (X = Cl, Br, I) complexes are very similar in profile, suggesting analogous structures for all. Table II lists the full reflectance spectral data for these generally insoluble complexes and the spectral profile

TABLE III. In-plane and Out-of-plane Ligand Field Strengths.

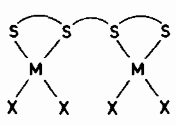
Compound	Physical State	Dq^{xy}	Dq^z
Ni(2,2,2)Cl_2	Solid Reflectance	9,700	810
Ni(2,2,2)Br_2	Solid Reflectance	9,600	800
Ni(2,2,2)I_2	Solid Reflectance	9,360	762
Ni(2,3,2)Br_2	Solid Reflectance	10,100	770
Ni(2,3,2)I_2	Solid Reflectance	11,000	566
Ni(3,2,3)I_2	Solid Reflectance	9,260	754
	Dichloromethane	8,830	751
	Nitromethane	9,280	728
Ni(3,3,3)I_2	Solid Reflectance	10,900	598
	Dichloromethane	8,760	786
	Nitromethane	9,550	700

is indicative of tetragonal geometry.[21] The splitting of the low-energy band, ν_1, which occurs here has been thought to be additional evidence of a *trans* structure.[22] Bosnich *et al.* found that with a similar open-chain tetraamine, 1,4,8,11-tetra-azaundecane, *trans* octahedral complexes were formed.[23] We have analysed the visible spectra according to the method of Rowley and Drago[24,25] and Brubaker and Busch[26] and have been able to assign in-plane and out-of-plane ligand fields, Table III. Several interesting phenomena can be discerned from this analysis. Firstly, the in-plane ligand field due to the tetrathioethers is affected by the counteranion, but there is no clear pattern to this dual interaction and it may well be due to a mixture of electronic and steric effects. It is clear, however, that the out-of-plane field strengths of the coordinated halides follow the expected pattern $Cl^- > Br^- > I^-$. Secondly, and perhaps most important of all, the in-plane field (and this trend seems to be independent of counteranion) is affected greatly as the carbon chain linkages between the sulphur atoms is changed. The general trend in ligand field strengths is 2,3,2 > 3,3,3 > 2,2,2 > 3,2,3. The spread of values within any Ni(ligand)I_2 complex is very large. Our intuitive feeling that the 2,3,2 linkage would best fit around a plane would seem to be reflected in the spectral results. These tetrathioethers all exert a fairly weak ligand field, about the same magnitude of the macrocyclic tetrathioether, 1,4,8,11-tetrathiocyclotetradecane, of Rosen and Busch which also forms *trans*-[Ni(S_4)X_2] complexes (Dq^{xy} = 1070 cm^{-1}).[13] Finally, it is interesting to note that for the two soluble complexes both Dq^{xy} and Dq^z are both influenced a good deal by the physical state of the complex, varying from solid to solution and from solvent to solvent. This is not surprising as the closeness of approach of the anions to the metal must depend to a great degree on the conformation the methylene groups adopt in the solid state. In solution flexibility will allow much closer approach of the iodides. This is especially seen in the complex of the most hindered ligand, Ni(3,3,3)I_2, where dissolution in either dichloromethane or nitromethane is accompanied by a big decrease in Dq^{xy} and a big increase in Dq^z. It should be noted that there is also very slight ionisation in nitromethane (Table II), and so in this solvent a small amount of [Ni(ligand)I]I or [Ni(ligand)($MeNO_2$)I]I is present.

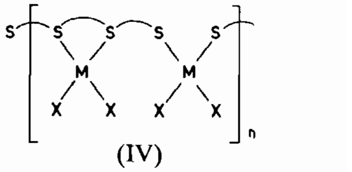
Palladium(II) and Platinum(II) Complexes

Dutta *et al.*[14–16] prepared a varied series of palladium(II) and platinum(II) complexes with their diarsine–dithioether chelates, but our efforts to prepare complexes of these metals with tetrathioether ligands of type I resulted only in the isolation of the dimeric [M_2(ligand)X_4] species. We wondered if the more flexible aliphatic ligands of type II would lead to stoichiometries other than this. Despite the reaction of Na_2MX_4 (M = Pd, Pt; X = Cl, Br, I) with the four ligands in metal:ligand ratios 1:1, 1:2, 1:3, 2:1, only [M_2(ligand)X_4] (M = Pd, Pt; ligand = 2,2,2, 2,3,2; X = Cl, Br, I) could be isolated. Similar complexes were isolable with the ligands 3,2,3 or 3,3,3. However, no reaction was obtained between $Na_2M(SCN)_4$ and these ligands; this parallels our experience with type I ligands[1] and that of Goodall[27] who also failed to obtain thiocyanato complexes of the spirocyclic $C(CH_2SR)_4$ ligands.

The visible absorption bands of these M_2(ligand)X_4 complexes, Table II, move to lower energy in the order Cl > Br > I, indicating halide coordination, and the energy of these absorptions is in the range accepted for four-coordinate and not five-coordinate complexes.[28] Neither the electronic or the infrared spectra show the presence of $[MX_4]^{2-}$ ions, and these complexes undoubtedly have similar structures to those of the analogous type I ligands. Possible structures are III or IV.



(III)



(IV)

Prolonged reflux of all M_2(ligand)X_4 complexes in DMF led to S-dealkylation reactions. The products of these reactions (at least four separate products result from each reaction) are exceedingly complex and difficult to separate; the complexity arises from the possible number of sites of C–S bond fission. We are presently not able to report any definitive results on this aspect of this work.

Conclusion

It is seen that the more flexible type II ligands tend to form analogous complexes as those of type I ligands.[1] These are hexacoordinate [Ni(ligand)X_2] and tetracoordinate dimeric [M_2(ligand)X_4] (M = Pd, Pt) species. The stoichiometry of the complex depends on the "normal" coordination number of the metal ions and the preference for halide over sulphur coordination. Thus, in palladium(II) and platinum(II) complexes no [M(ligand)]X_2 species are observed, halides displacing sulphur coordination and thus dimeric [M_2(ligand)X_4] species are formed. However, six-coordinate nickel(II) can accommodate four sulphur donors in addition to the halides, and thus the monomeric molecular [Ni(ligand)X_2] derivatives are formed. It is also seen that the number of carbon atoms between donors in these tetrathioether open-chain ligands has profound affects on the stability and spectrochemistry of the resulting complexes. Further work is needed to elucidate these factors in more detail.

Acknowledgement

We are grateful to the Science Research Council for the award of Research Studentships to W. L. and S.G.M.

References

1 Part VII: S.T. Chow and C.A. McAuliffe, *J. Organomet Chem., 77,* 401 (1974); Part VIII: W. Levason, C.A. McAuliffe and S.G. Murray, *J.C.S. Dalton,* 1556 (1975); Part IX: W. Levason, C.A. McAuliffe and S.G. Murray, *J.C.S. Dalton,* in press.

2 B. Chiswell, *Aspects of Inorg. Chem., 1,* 271 (1973).

3 R.B. King, *Accs. Chem. Res., 5,* 177 (1972).

4 C.A. McAuliffe, *Adv. Inorg. Chem. Radiochem., 17,* 165 (1975).

5 M.J. Norgett, J.H.M. Thornley and L.M. Venanzi, *Coord. Chem. Rev., 2,* 99 (1967).

6 T.D. DuBois and D.W. Meek, *Inorg. Chem., 8,* 146 (1969).

7 T.L. Blundell and H.M. Powell, *J. Chem. Soc. A,* 1650 (1967).

8 R.D. Cannon, B. Chiswell and L.M. Venanzi, *J. Chem. Soc. A,* 1277 (1967).

9 R.W. Hardy, R.C. Burns and G.W. Parshall, in "Inorganic Biochemistry", ed. G.L. Eichorn, Elsevier, New York, 1973.

10 R.H. Holm, *Endeavour,* 38 (1975).

11 T.N. Lockyer, *Aust. J. Chem., 27,* 259 (1974).

12 C.A. McAuliffe, *Inorg. Chem., 12,* 2477 (1973).

13 W. Rosen and D.H. Busch, *J. Am. Chem. Soc., 91,* 4694 (1969).

14 R.L. Dutta, D.H. Busch and D.W. Meek, *Inorg. Chem., 9,* 2098 (1970).

15 R.L. Dutta, D.M. Busch and D.W. Meek, *Inorg. Chem., 9,* 1215 (1970).

16 R.L. Dutta, D.H. Busch and D.W. Meek, *Inorg. Chem., 10,* 1820 (1971).

17 L. Baracco and C.A. McAuliffe, *J.C.S. Dalton,* 948 (1972).

18 C.A. McAuliffe, *D. Phil. Thesis,* Oxford Univ., 1967.

19 B.C. Lane, J. Dawson, R.J. Mynott and L.M. Venanzi, *Inorg. Chim. Acta, 5,* 25 (1971).

20 C.K. Jørgensen, *Inorg. Chem., 3,* 1201 (1964).

21 A.B.P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, London, 1968.

22 M.E. Farago and J.M. James, *Chem. Comm.,* 471 (1965).

23 B. Bosnich, R.D. Gillard, E.D. McKenzie and G.A. Webb, *J. Chem. Soc. A,* 1331 (1966).

24 D.A. Rowley and R.S. Drago, *Inorg. Chem., 7,* 795 (1968).

25 D.A. Rowley and R.S. Drago, *Inorg. Chem., 6,* 1092 (1967).

26 G.R. Brubaker and D.H. Busch, *Inorg. Chem., 5,* 2114 (1966).

27 D.C. Goodall, *J. Chem. Soc. A,* 1387 (1967).

28 G. Dyer and L.M. Venanzi, *J. Chem. Soc.,* 2771 (1965).