COMPLEXES OF OPEN-CHAIN TETRADENTATE LIGANDS CONTAINING HEAVY DONOR ATOMS

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I. Introduction 165
II. Ligand Synthesis 170
III. Studies on Coordination Complexes 173
  A. Tetraphosphine Chelates 173
  B. Diphosphine–Diarsine Chelates 174
  C. Diphosphine–Dithioether Chelates 174
  D. Diphosphine–Diimine Chelates 175
  E. Tetraarsine Chelates 176
  F. Diarsine–Dithioether Chelates 177
  G. Diarsine–Dioxygen Chelates 179
  H. Dithioether–Diarsine Chelates 179
  I. Tetrathioether Chelates 181
  J. Diaminodithioether Chelates 185
IV. Conclusion 185
References 185

I. Introduction

During the past decade there has been growing interest in the synthesis of quadridentate chelating ligands containing "heavy" donor atoms, i.e., P, As, Sb, S, and Se. Previously the coordination chemistry of multidentate chelates had been restricted to those containing class *a* donors, and the chemistry of such ligands derived, for example, from Schiff base condensation reactions has been much studied and reported upon. The multidentate chelates containing class *b* donors received sparse attention mainly because of the intricate preparative routes involved in their synthesis. Subsequently, however, largely through the work of the groups led by Venanzi, Meek, and Sacconi, and their students the complex organic chemistry associated with the preparation of intricate chelates containing phosphines, arsines, thioethers, etc., was developed leading to a whole series of ligands.

The first of these quadridentate ligands produced were of the tripod

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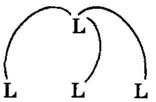
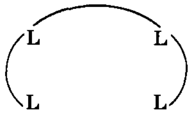
type (**I**) rather than the linear or open-chain type (**II**). The tripod ligands have been extensively studied and generally they form trigonal-bipyramidal complexes with d^7 and d^8 metal ions (*1–5*). When considering the relative crystal field stabilization energies (cfse) for low-spin d^7 or d^8 square planar or the two common pentacoordinate structures, then it is clear that on cfse grounds all quadridentate ligands should form planar

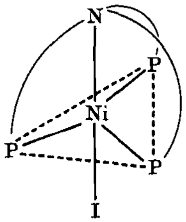


(**I**)

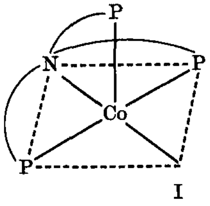


(**II**)

rather than pentacoordinate complexes. Presumably the formation of a further metal–ligand bond is energetically favorable enough to offset the loss in cfse resulting from stereochemical changes. When comparing the cfse for the trigonal bipyramidal (D_{3h}) and square pyramidal (C_{4v}) arrangements, it appears that the square pyramid should be the preferred structure (*4*, *6*). However, the overwhelming majority of pentacoordinate complexes containing tripod tetradentate ligands have been characterized as trigonal bipyramidal. Studies (*2*) of a number of these complexes have attributed this structure to factors such as steric requirements due to the trigonal symmetry of the ligands, the rigid nature of the linkage (*o*-phenylene usually) between the donor atoms, and the steric bulk of the terminal donors. Observations that tripod tetradentate ligands with the flexible trimethylene linkage replacing the rigid *o*-phenylene linkage also form trigonal bipyramidal complexes rather than square pyramidal complexes have been interpreted as showing the importance of factors such as the repulsive interaction between bonding electron pairs and the π-acceptor ability of the ligand donor atoms in determining the structure of the complex (*7*, *8*). However, mention should be made of the unusual behavior of the ligand tris-(2-diphenylphosphinoethyl)amine (tpn), which forms trigonal-bipyramidal complexes [Ni(tpn)I]$^+$ (**III**), (*9*), and [Co(tpn)Cl]$^+$ (*10*), but the square-pyramidal [Co(tpn)I]$^+$ (**IV**), (*11*). This coordination geometry

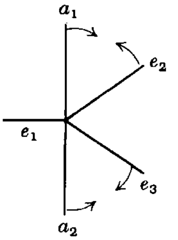


(**III**)

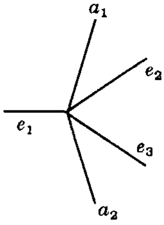


(**IV**)

transition is probably due to the influence of increased cfse (square-pyramidal) over ligand geometry (trigonal-bipyramidal), even though, in the case of cobalt(II), complications can arise from Jahn–Teller effects. It should also be pointed out that there are only quite small bond angle movements needed to convert one idealized geometry into another:



$D3_h$



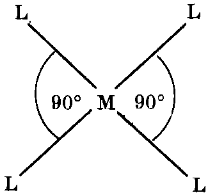
C_{4v}

That, in the absence of strong constraints such as rigid ligands, the energy difference between D_{3h} and C_{4v} structures is small has recently been demonstrated by the isolation of two distinct pentacoordinate molecules of formulation, chlorobis-(1,2-bisdiphenylphosphinoethane)-cobalt(II) trichlorostannate, [Co(diphos)Cl][$SnCl_3$] (*12*). X-Ray crystallographic work by Meek and co-workers (*13*) has shown the red isomer to have a square pyramidal structure with four basal phosphines and an equatorial chlorine, and the green isomer to be trigonal-bipyramidal with two axial phosphines, two equatorial phosphines, and an equatorial chlorine. It is thus seen that, although tripodal tetradentate ligands have contributed significantly to recent coordination chemistry, the type of complex formed by them appears to be restricted by the steric requirements of the ligand, and in order for the metal ion to exert a preference more flexible ligands are needed. This has led coordination chemists to study open-chain quadridentates, since in complexes formed from such ligands the metal atoms and donor atoms will be more free of the constraints placed upon them by the links between the donor atoms.

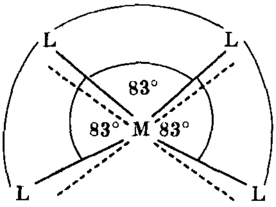
Although open-chain quadridentates do not have trigonal symmetry properties, results from X-ray structural determinations of tripod ligand complexes are of interest to chemists studying open-chain quadridentates. Crystallographic studies have shown that the metal ions in [Co(qp)Cl]BPh_4 [qp = tris-(*o*-diphenylphosphinophenyl)phosphine] (*14*), [Ni(pts)Cl]ClO_4 [pts = tris-(*o*-methythiophenyl)phosphine] (*15*), $[Ni(tpn)I]^+$ (*9*), and [Pt(qas)I]BPh_4 [qas = tris-(*o*-diphenylarsionphenyl)arsine] (*16*) reside a significant distance below the plane of the three equatorial atoms. However, in the case of [Ni(ptas)CN]ClO_4

[ptas = tris-(3-dimethylarsinopropyl)phosphine] (*17*), the metal ion lies above the plane of the three equatorial arsenic atoms. Thus, it appears that when apical and equatorial donor atoms are linked by *o*-phenylene chelate chains the equatorial donors are below the metal atom. This is, of course, due to the inability of the two-carbon and three-carbon chains to provide for an L(apical)—M—L(equatorial) angle of 90°; for the two-carbon case this L_a—M—L_e angle will be less than 90° (usually it is about 83°), and for the three-carbon case the L_a—M—L_e angle will be greater than 90° (*18*, *19*). Reflectance spectra of trigonal bipyramidal nickel(II) complexes formed by the ligands $(o\text{-}Ph_2PC_6H_4)_3L$ (L = P, As, Sb) have supported this argument. The spectrochemical series formed by changing L in $[NiL\text{-}(o\text{-}Ph_2PC_6H_4)_3X]^+$ complexes exhibited anomalous behavior, the order found being P > As < Sb (*20*) in contrast to the spectrochemical order R_3P > R_3As > R_3Sb found for monodentate ligands R_3L (*21*). This effect has been attributed to compression of the apical ligand to metal bond complexation (*20*). To a certain extent this compression is relieved by a displacement of the metal atom below the plane of the three equatorial ligands.

Although chelate ring strain interested Corey and Bailar (*22*) as long ago as 1959, it is a facet of chelates that has not attracted much attention from coordination chemists despite its obvious importance. There are indications that this state of affairs is changing, (*18–20*, *23*), and, in studying open-chain facultative quadridentates [facultative quadridentates are flexible and are able to coordinate to a metal atom in either planar or nonplanar arrangement (*24*)], the effect of chelate chain length can be shown to have important stereochemical and spectrochemical effects. Consider a square-planar structure containing monodentate ligands, L:

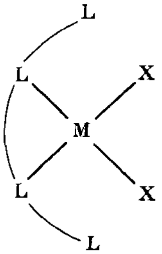


The LML is, ideally, 90°, and in this situation one might confidently expect optimum M—L orbital overlap. A planar complex containing similar donors connected by three dimethylene or *o*-phenylene linkages L—L—L—L may be altered in one of three ways (or, more likely, in a combination of these three ways): (*a*) by distorting the overall geometry of the complex (V); (*b*) as a result of the distortion caused by LML

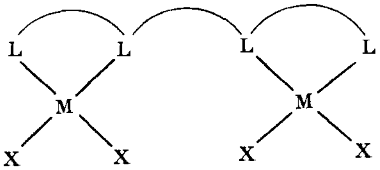


(V)

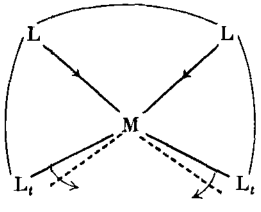
~83°, very poor orbital overlap between terminal L and the metal may be expected, resulting in a decrease in stability of complex (**V**) and the formation of a bidentate ligand complex (**VI**) or the bridging quadridentate complex (**VII**) [both (**VI**) and (**VII**) have been isolated using the S_2As_2 quadridentates of Busch and co-workers (*25*)]; (*c*) if terminal donors, L_t, do coordinate to form a mononuclear complex, then, in order to form the strongest possible L_t—M bonds, there will be a tendency for the L_t—M—L (**VIII**) to open up in order to facilitate better L_t—M orbital overlap. This will result in a shortening of the L—M bond due to compression, resulting also in an artificially high, ligand field strength of L.



(VI)

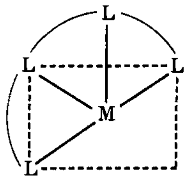


(VII)

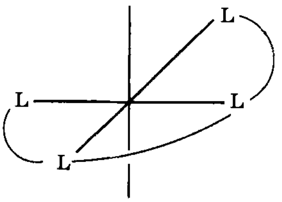


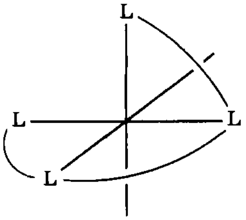
(VIII)

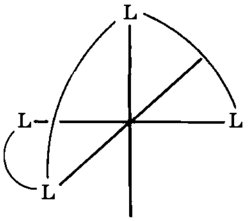
Such deviations from ideal behavior can be prohibited by varying the chelate backbone lengths. Thus, an L_t—C_2—L—C_3—L—C_2—L_t system or an L_t—C_3—L—C_2—L—C_3—L_t system might be expected to relieve strains *a*–*c*, and it has been found that altering chelate backbone can have quite startling effects on the resulting complex stereochemistry and spectrochemistry. One way in which strains *a–c* can be relieved is for the ligand to become nonplanar and adopt configuration (**IX**). The tetrahedral linkages about the donor atoms make this configuration less strained and, although these ligands do form planar complexes, it is likely that many of the pentacoordinate derivatives have configuration (**IX**) (*26*). It will be seen later in this article that low-spin pentacoordinate complexes are frequently encountered in studies with these linear quadridentates containing heavy donor atoms. However, a number of six-coordinate species have been isolated, and it should be pointed out that a number of octahedral configurations are possible:



(**IX**)







Observations that linear quadridentates form planar, trigonal-bipyramidal, square-pyramidal, and octahedral complexes testify to the flexibility of this ligand arrangement.

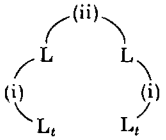
II. Ligand Synthesis

A number of linear quadridentate ligands have been made *in situ* and complexed to a metal ion without prior isolation of the ligand. However, most have been synthesized quite separately from complexation reactions, and these are listed in Table I. A number of ligand syntheses of general application will be outlined here. It must be emphasized that these are not complete syntheses and that many of the precursors used are themselves prepared by quite arduous routes.

1. Ligands with the $\mathrm{Ph\underset{|}{As}(CH_2)_{n}\underset{|}{As}Ph}$ intermediate linkage require two major steps in their preparation.

TABLE I

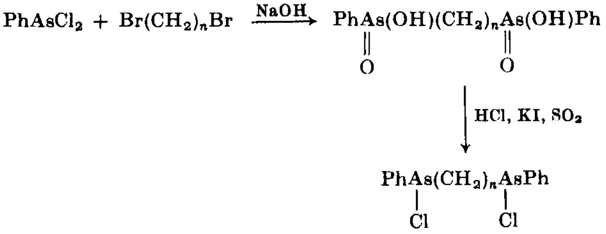
LINEAR QUADRIDENTATE LIGANDS AND THEIR ABBREVIATIONS



L_t	L	(i)	(ii)	Ligand[a]	Ref.
PPh_2	PPh	$—(CH_2)_2—$	$—(CH_2)_2—$	p_4	*(27)*
PPh_2	AsPh	o-C_6H_4	$—(CH_2)_3—$	p_2as_2	*(28)*
PPh_2	S	$—(CH_2)_3—$	$—(CH_2)_3—$	p_2s_2	*(29)*
PPh_2	N	$—(CH_2)_2—$	$=C(Me)C(Me)=$	p_2n_2	*(30)*
$AsPh_2$	PPh	o-C_6H_4	$—(CH_2)_3—$	as_2p_2	*(28)*
$AsPh_2$	$AsPh_2$	o-C_6H_4	$—(CH_2)_3—$	as_4ph	*(28)*
$AsPh_2$	S	$—(CH_2)_3—$	$—(CH_2)_3—$	as_2s_2	*(31)*
$AsPh_2$	S	o-C_6H_4	$—(CH_2)_2—$	as_2s_2e	*(32)*
$AsPh_2$	S	o-C_6H_4	$—(CH_2)_3—$	as_2s_2p	*(33)*
$AsPh_2$	S	o-C_6H_4	$—(CH_2)_4—$	as_2s_2b	*(33)*
$AsPh_2$	N	$—(CH_2)_2—$	$=C(Me)C(Me)=$	as_2n_2	*(34)*
$AsPh_2$	O	o-C_6H_4	$—(CH_2)_2—$	as_2o_2	*(32)*
$AsMe_2$	AsPh	$—(CH_2)_3—$	$—(CH_2)_3—$	qas	*(35)*
$AsMe_2$	AsMe	o-C_6H_4	o-C_6H_4	as_4me	*(26)*
$AsMe_2$	S	$—(CH_2)_3—$	$—(CH_2)_3—$	as_2s_2me	*(31)*
SMe	AsPh	o-C_6H_4	$—(CH_2)_2—$	s_2as_2e	*(25)*
SMe	AsPh	o-C_6H_4	$—(CH_2)_3—$	s_2as_2p	*(25)*
SMe	AsPh	o-C_6H_4	$—(CH_2)_4—$	s_2as_2b	*(36)*
SMe	S	o-C_6H_4	$—(CH_2)_3—$	s_4	*(31)*
NH_2	S	o-C_6H_4	$—(CH_2)_2—$	n_2s_2e	*(32)*
NH_2	S	o-C_6H_4	$—(CH_2)_3—$	n_2s_2p	*(37)*
NH_2	S	o-C_6H_4	$—(CH_2)_4—$	n_2s_2b	*(37)*

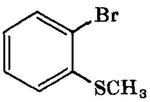
[a] The abbreviations may, in a small number of cases, appear to be somewhat cumbersome. However, in devising abbreviations for these complicated tetradentates attempts at consistency have led, inevitably, to a number of cumbersome symbols.

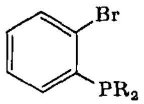
a. Preparation of the alkanebis(phenylchloroarsine):

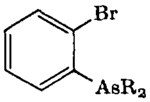


$$PhAsCl_2 + Br(CH_2)_nBr \xrightarrow{NaOH} Ph\underset{\underset{O}{\|}}{As}(OH)(CH_2)_n\underset{\underset{O}{\|}}{As}(OH)Ph \xrightarrow{HCl,\ KI,\ SO_2} Ph\underset{\underset{Cl}{|}}{As}(CH_2)_n\underset{\underset{Cl}{|}}{As}Ph$$

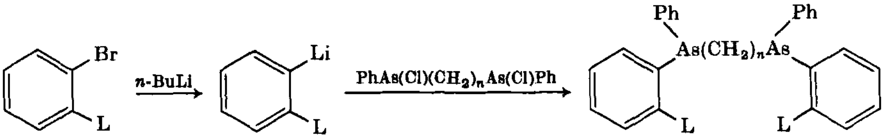
b. Preparation of the terminal ligand moiety, such as



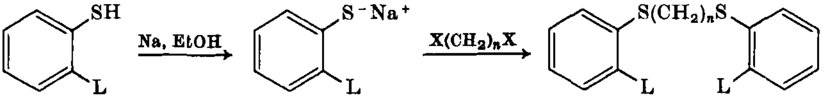




The final reaction is

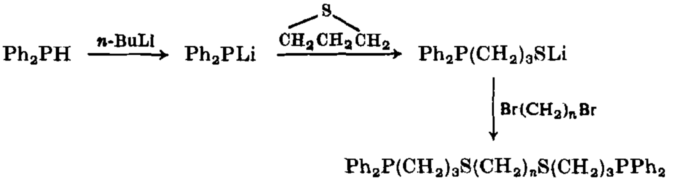


2. Ligands that have an $-S(CH_2)_nS-$ intermediate linkage are frequently prepared as follows:



(L = NH_2, PR_2, AsR_2)

or:



3. Ligands containing the $-N{=}C(CH_3)C(CH_3){=}N-$ intermediate linkage are readily synthesized:

$$Ph_2LCH_2CH_2NH_2 + CH_3C(O)C(O)CH_3 \longrightarrow Ph_2LCH_2CH_2N{=}C(CH_3)C(CH_3){=}NCH_2CH_2LPh_2$$

(L = P, As)

4. Linear tetratertiary phosphine, P_4, was obtained by King and Kapoor (*27*), by the addition of phosphorus–hydrogen bonds in 1,2-bisphenylphosphinoethane to the carbon–carbon double bonds in two equivalents of diphenylvinylphosphine, according to the following equation:

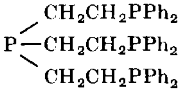
$$2Ph_2PCH{=}CH_2 + PhP(H)CH_2CH_2P(H)Ph \longrightarrow Ph_2P(CH_2)_2P(Ph)(CH_2)_2P(Ph)(CH_2)_2PPh_2$$

Most of these chelates are air stable or sufficiently stable to allow complexing reactions to be carried out with a minimum of difficulty with regard to transfer of reactants.

III. Studies on Coordination Complexes

A. TETRAPHOSPHINE CHELATES

The elegant syntheses of a whole range of polytertiary phosphines devised by King and Kapoor have been reviewed (*38*). They prepared both the tripod tetradentate, tris-(2-diphenylphosphinoethyl)phospine (qp) (**X**), and the open-chain tetraphosphine, 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (p_4) (**XI**). King (*38*) points out that these tetratertiary phosphines can bond to one or more metal atoms in ten fundamental ways: (*a*) monoligate monometallic; (*b*) biligate monometallic; (*c*) triligate monometallic; (*d*) tetraligate monometallic; (*e*) biligate bimetallic; (*f*) triligate bimetallic; (*g*) tetraligate bimetallic; (*h*) triligate trimetallic; (*i*) tetraligate trimetallic; (*j*) tetraligate tetrametallic.



(X)

$Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$

(XI)

Four of the ten possible ways of bonding the tripod chelate qp have been shown (*39*) to exist in (i) biligate monometallic $Pt(qp)Cl_2$, $M(qp)(CO)_4$ (M = Cr, Mo), $(CH_3CO)Mn(qp)(CO)_3$, $[C_5H_5Mn(qp)(NO)]PF_6$, and $[C_5H_5Fe(qp)(CO)]I$; (i) triligate monometallic $M(qp)Cl_3$ (M = Rh, Re), $M(qp)(CO)_3$ (M = Cr, MO), $CH_3Mn(qp)(CO)_2$, and $Mn(qp)(CO)_2Br$; (iii) tetraligate monometallic $[M(qp)Cl]^+$ (M = Ni, Co, Fe), and $M(qp)(CO)_2$ (M = Mo, W); (iv) tetraligate tetrametallic $[(qp)\{Mo(CO)_2(COCH_3)(C_5H_5)\}_4]$, and $[(qp)\{Fe_2(CO)_2(C_5H_5)_2\}_2]$. Significantly, the linear tetradentate P_4 ligand has produced complexes in which six of the ten possible ways of bonding are involved: (i) monoligate monometallic $CH_3COFe(p_4)(CO)(C_5H_5)$; (ii) biligate monometallic $M(p_4)(CO)_4$ (M = Cr, Mo), $CH_3Mn(p_4)(CO)_3$, $[C_5H_5Mo(p_4)(CO)_2]Cl$, $C_5H_5Mn(p_4)(CO)$; (iii) triligate monometallic $M(p_4)Cl_3$ (M = Rh, Re), $M(p_4)(CO)_3$ (M = Cr, Mo), $Mn(p_4)(CO)_2Br$, and $[C_5H_5Fe(p_4)]^+$; (iv) tetraligate monometallic $[M(p_4)]^{2+}$ (M = Ni, Pd, Pt), $[Co(p_4)Cl]^+$, and $[Rh(p_4)]^+$; (v) tetraligate bimetallic $[(C_5H_5)_2Mn_2(p_4)(CO)(NO)_2](PF_6)_2$; (vi) tetraligate tetrametallic $[(p_4)\{Mo(CO)_2(COCH_3)(C_5H_5)\}_4]$, and $[(p_4)\{Fe_2(CO)_2(C_5H_5)_2\}_2]$.

It is somewhat hard to imagine either of these two chelates forming all the possible complex types devised by King. Nonetheless, the versatility of these ligands has been amply demonstrated by King and co-workers (*39*). As well as enumerating the bonding types in the preceding, it is also worth mentioning that the same transition metal reactant forms different types of complexes with qp (**X**) and p_4 (**XI**):

(i) the linear tetratertiary phosphine reacts with nickel(II) chloride to give, after treatment with PF_6^-, the yellow planar $[Ni(p_4)](PF_6)_2$, whereas qp produces the blue pentacoordinate $[Ni(qp)Cl]PF_6$ [this complex is reported (*39*) as having $\mu_{eff} = 2.23$ BM, suggesting that reinvestigation would be desirable]; (ii) the linear p_4 does not react with ferrous chloride in boiling ethanol, whereas under the same conditions qp forms the blue pentacoordinate $[Fe(qp)Cl]^+$; (iii) the open-chain p_4 reacts with $[C_5H_5Mn(CO)_2NO]PF_6$ to form the triligate bimetallic derivative, $[(C_5H_5)_2Mn_2(p_4)(CO)(NO)_2]PF_6$, whereas the tripod tetradentate, under identical conditions, yields the biligate monometallic derivative, $[C_5H_5Mn(qp)(NO)]PF_6$.

Examining these differences King (*38*) has been tempted to suggest that of the two tetraphosphine ligands the tripod qp is the better "chelating agent" (i.e., better at forming complexes with several phosphorus atoms all bonded to a single metal atom). However, the open-chain p_4 is more adept at forming polymetallic complexes. This is exactly the behavior predicted from the considerations discussed in the Introduction.

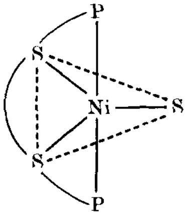
The current interest in open-chain tetradentates is such that p_4 is now commercially available, and Sacconi and co-workers (*40*) have extended the work of King *et al.* (*39*) and prepared a series of complexes of general formula $[M(p_4)X]BPh_4$ (M = Fe, Co, Ni; X = Cl, Br, I). Spectral and X-ray investigations suggest a square-pyramidal geometry for all complexes. The cobalt(II) and nickel(II) complexes are low spin, and the magnetic properties of the iron(II) complexes are consistent with a spin equilibrium between a singlet ground state and a thermally accessible low-lying triplet state. Complex $[Fe(p_4)(NCS)_2]$ is diamagnetic and probably has a trans-octahedral structure.

B. Diphosphine–Diarsine Chelates

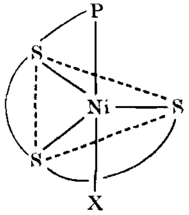
Initial studies with 1,3-bis-[phenyl-(*o*-diphenylphosphinophenyl)-arsino]propane (p_2as_2) by McAuliffe (*28*) have led to the isolation of the diamagnetic planar $[Ni(p_2as_2)](ClO_4)_2$ and the purple $[Ni(p_2as_2)X]BPh_4$ (X = Cl, Br, I) complexes. The latter have been assigned square-pyramidal coordination about the nickel atom, on the basis of electronic spectral studies.

C. Diphosphine–Dithioether Chelates

Dubois and Meek (*29*) synthesized 1,3-bis-(diphenylphosphinopropylthio)propane or $Ph_2P(CH_2)_3S(CH_2)_3S(CH_2)_3PPh_2$ (p_2s_2), a chelate with three trimethylene bridges between the donors. A series of planar d^8 complexes $[M(p_2s_2)](ClO_4)_2$ (M = Ni, Pd, Pt) and pentacoordinate $[M(p_2s_2)X]^+$ (M = Ni, Pd, Pt; X = halogen) have been prepared (*29*). The flexibility of this ligand is demonstrated by the fact that the five-coordinate nickel complexes are trigonal-bipyramidal, whereas those of palladium and platinum are square-pyramidal. This is a most important result, since it shows that the open-chain quadridentate can allow the central metal ion to dictate its stereochemical surroundings to a large degree. As discussed earlier, these considerations predict that the square-pyramidal geometry is more stable than trigonal-bipyramidal. This effect should increase in descending the triad, Ni, Pd, Pt, and is apparently demonstrated by this system. DuBois and Meek suggest that either of the isomers (**XII**) or (**XIII**) are compatible with their results.



(XII)

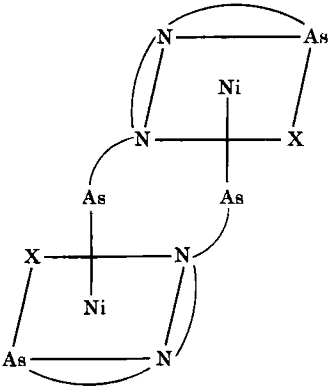


(XIII)

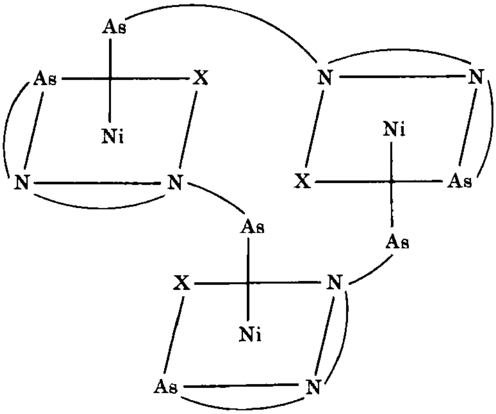
Electronic spectral results provide strong evidence, especially in the case of nickel(II) complexes, for particular pentacoordinate geometries, which is somewhat surprising in view of the fact that the ideal geometries are interchanged by relatively small bond movements. Nonetheless, it has been demonstrated conclusively that low-spin trigonal-bipyramidal nickel(II) complexes have their main *d-d* absorptions in the region of ~ 16 kK (*7*, *8*, *41–44*), whereas those with square-pyramidal geometry have visible absorptions in the region of ~ 20 kK (*45*). With p_2s_2, DuBois and Meek (*29*) also prepared the maroon pentacoordinate $[Co(p_2s_2)X]^+$ (X = Cl, Br, I) derivatives, and these were tentatively assigned a square-pyramidal structure, although it should be emphasized that this assignment is by no means as certain as that of the nickel complexes.

D. DIPHOSPHINE–DIIMINE CHELATES

Recently, DuBois (*30*) has prepared the phosphorus–nitrogen tetradentate 2,3-butanedionebis-(2-diphenylphosphinoethylimine), $Ph_2PCH_2CH_2N{=}C(CH_3)C(CH_3){=}NCH_2CH_2PPh_2$ (p_2n_2), and isolated the planar $[Ni(p_2n_2)](ClO_4)_2 \cdot 0.5EtOH$ and the square-pyramidal $[Ni(p_2n_2)X]\ ClO_4 \cdot 0.5EtOH$ (X = Cl, Br, I). Dubois argues that, because of the rigidity of the imine linkages, these pentacoordinate complexes contain the ligand chelated in the plane. However, although anionic ligands can be added to the planar $[Ni(p_2n_2)]^{2+}$ species to yield monomeric pentacoordinate complexes, DuBois and Smith (*34*) have found that planar nickel(II) derivatives of the analogous 2,3-butanedionebis-(2-diphenylarsinoethylimine) (as_2n_2), $[Ni(as_2n_2)]^{2+}$, do not add anions to produce monomeric $[Ni(as_2n_2)X]^+$ species. Pentacoordinate derivatives are, indeed, produced, but spectrometric titrations of $[Ni(as_2n_2)]^{2+}$ with $(n\text{-}C_7H_{15})_4NX$ (X = Cl, Br) indicate that ligand displacement from the planar cation takes place. These authors suggest structures (**XIV**) or (**XV**) as the most likely and also suggest that the difference in behavior between the p_2n_2 and as_2n_2 ligands is probably due to the ability of phenyl groups on the *cis*-arsines to interfere sterically with each other.



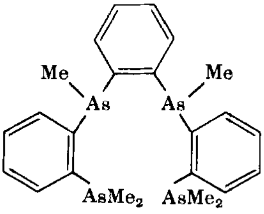
(XIV)



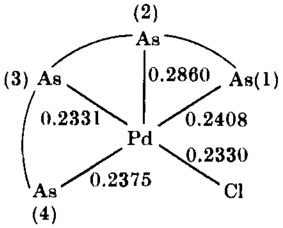
(XV)

E. Tetraarsine Chelates

The only complex of a linear quadridentate that has been studied by X-ray techniques is that of $[Pd(as_4me)Cl]ClO_4 \cdot C_6H_6$ (as_4me = *o*-phenylenebis-*o*-dimethylarsinophenylmethylarsine) (**XVI**) (*26*). The pentacoordinate complex cation crystallizes with perchlorate ions in an ionic lattice in which benzene molecules are included as a clathrate. The cation has a square-pyramidal coordination (**XVII**), with a chlorine atom in the basal plane in which the palladium atom is coplanar with the four attached atoms (the palladium, chlorine, and three arsenic as$_4$me =



(XVI)



(XVII)

atoms lie within 0.06 Å of the least-squares plane through them). The apical palladium–arsenic bond is almost 0.05 nm longer than those in the basal plane, which also differ significantly from one another. The distortions in the molecule are essentially a consequence of strain due to the *o*-phenylene linkages between the arsenic donors; this is reflected in the bond angles, as shown in Table II. One most significant distortion is seen in the As(1)—Pd—As(2) angle of 80.1°, which results from the ideal apical Pd—As bond being pulled to one side by short *o*-phenylene links.

The tetradentate arsine ligand containing three trimethylene linkages, 1,3-propanebis-(3-dimethylarsinopropylphenylarsine) (qas) forms a series of square-pyramidal nickel(II) complexes of the type [Ni(qas)X]BPh$_4$ (X = Cl, Br, I, NO$_3$) and [Ni(qas)(H$_2$O)](ClO$_4$)$_2$ (*35*, *46*). Similar results have been obtained with the tetraarsine as$_4$ph (*28*).

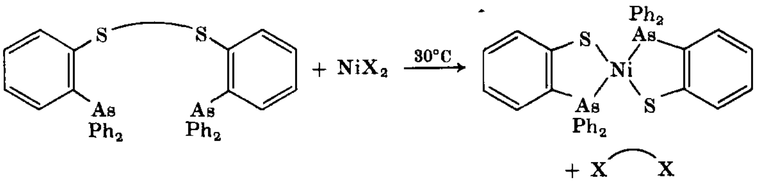
TABLE II

GEOMETRIC PARAMETERS OF [Pd(as$_4$me)Cl]ClO$_4$.C$_6$H$_6$

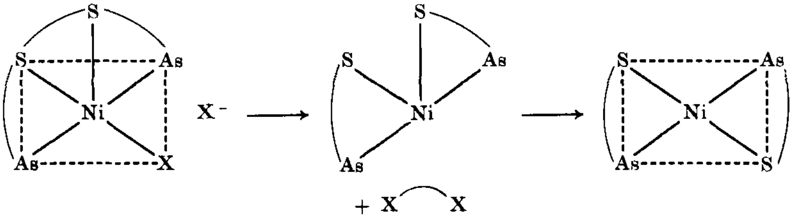
Arsenic Molecule	Bond angle
As(1)—Pd—As(2)	80.1°
As(1)—Pd—As(3)	95.9°
As(1)—Pd—As(4)	178.2°
As(1)—Pd—Cl	89.8°
As(2)—Pd—As(3)	81.9°
As(2)—Pd—As(4)	99.3°
As(2)—Pd—Cl	101.8°
As(3)—Pd—As(4)	85.7°
As(3)—Pd—Cl	173.7°
As(4)—Pd—Cl	88.6°

F. DIARSINE–DITHIOETHER CHELATES

Initial studies with as$_2$s$_2$ and as$_2$s$_2$me have led to the isolation of pentacoordinate [NiL(H$_2$O)](ClO$_4$)$_2$ complexes (*31*). The arsenic–sulfur chelates as_2s_2e (*32*) and as_2s_2b (*33*), have been investigated by Venanzi (*32*) and by McAuliffe and co-workers (*33*, *47*). A series of complexes $[Pd(as_2s_2e)X_2]$ (X = Cl, Br, I, NCS) were assigned square-planar structures in which one arsenic and one sulfur donor of the ligand was coordinated (*32*). In contrast to the reactions with palladium in which the ligand retains its integrity, reactions between as_2s_2e, as_2s_2p, and as_2s_2b with nickel(II) salts in acetone proceed as shown in reaction (1) (*47*). The trans structure has been assigned to the final complex because the visible and infrared spectra of the products of the reaction are identical with those of the $[NiL_2]$ complex formed in the reaction between nickel(II) salts and *o*-diphenylarsinophenylthiol. This suggests possible intermediate reactions of the type shown in reaction (2). The deep blue-black colors obtained when NiX_2 (X = Cl, Br, I, NO_3, ClO_4) and these ligands are mixed suggests the formation of a pentacoordinate intermediate. Interestingly, no reaction is observed when the reactants are mixed at temperatures below 30°C; at this temperature the deep blue-black color develops followed almost immediately by the precipitation of the green S-dealkylated complex. Although S-dealkylation is not uncommon for palladium–thioether complexes, there has only been one other report of a nickel-induced dealkylation reaction (*48*), and this involved boiling DMF as solvent. The facile bis-S-dealkylation of as_2s_2e, as_2s_2p, and as_2s_2b would seem to be unique. Levason *et al.* have also obtained bis-S-dealkylation in the reaction of cobalt(II) perchlorate with as_2s_2e, but the integrity of the ligand remained intact in the reaction between as_2s_2p and cobalt(II) bromide, leading to the eventual isolation of the $[Co(as_2s_2p)Br]BPh_4$ complex (*33*).



(1)



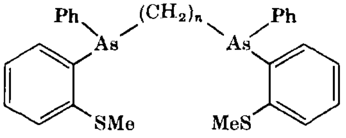
(2)

G. Diarsine–Dioxygen Chelates

Cannon *et al.* (*32*) reacted 1,2-bis-(*o*-diphenylarsinophenoxy)ethane (as_2o_2) with palladium(II) salts and obtained the complexes $[Pd(as_2o_2)X_2]$ (X = Cl, Br, I, NCS), which are nonconductors in nitrobenzene. These workers doubt that coordination of two oxygen atoms or one oxygen and one arsenic atom would occur in palladium(II) complexes of as_2o_2, as the bond between ether oxygen and palladium is expected to be very weak. Because the $[Pd(as_2o_2)Cl_2]$ complex is monomeric in methylphenyl ketone and because all the complexes of the general formula $[Pd(as_2o_2)X_2]$ have similar ultraviolet–visible spectra, therefore, there are two structural possibliities: (*a*) a bridging ligand with the two arsenic atoms in trans positions or (*b*) a bridging ligand with the two arsenic atoms in cis positions. From molecular models, Cannon *et al.* conclude that the first of these two possibilities is the most likely.

H. Dithioether–Diarsine Chelates

Dutta, Meek, and Busch (*25*, *36*) have made a thorough study of the arsenic ligands s_2as_2e, s_2as_2p, and s_2as_2b (**XVIII**) and their reactions with palladium(II) salts and, more recently, have studied the reactions of s_2as_2e and s_2as_2p with potassium tetrachloroplatinite (*49*). The following complexes were isolated.



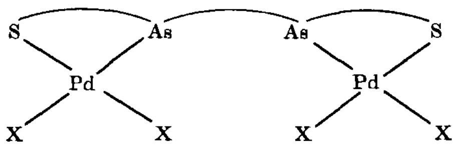
(**XVIII**)

n = 2; s_2as_2e (*25*)
n = 3; s_2as_2p (*25*)
n = 4; s_2as_2b (*36*)

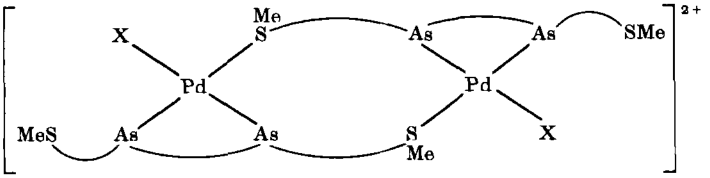
(i) Compounds $PdLX_2$ (L = s_2as_2e, X = Cl, Br, I; L = s_2as_2p, X = Cl, Br, I, SCN), which contain coordinated arsenic groups; NMR studies indicated uncoordinated —SMe groups. However, in nitromethane and acetonitrile, the $Pd(s_2as_2p)I_2$ complex behaves as a 1:1 electrolyte.

(ii) Compounds Pd_2LX_4 (L = s_2as_2e, X = Cl, I) in which two halides and one thioether plus one arsenic atom attached to the same benzene ring are coordinated to each palladium(II) ion in a probable structure of type (**XIX**).

(iii) The $Pd_2L_2X_2^{2+}$ species formed probably from $PdLX_2$ on displacement of a coordinated halide ion by a thiomethyl group accompanied by dimerization, and having suggested structure (**XX**).

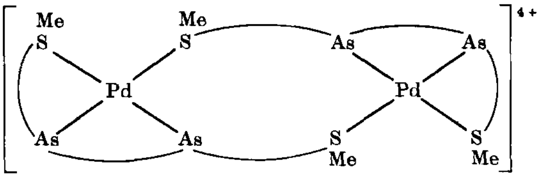


(XIX)



(XX)

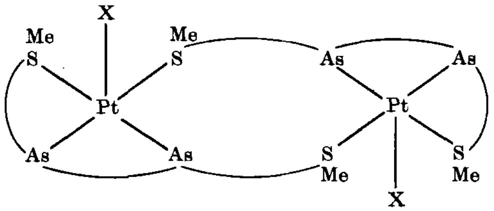
(iv) The $[Pd_2L_2]^{4+}$ complexes (L = s_2as_2e, s_2as_2p) obtained as the perchlorate salts, having square-planar structures with the ligands functioning as bridging quadridentates (**XXI**).



(XXI)

Some of the reactions carried out in this comprehensive study are illustrated in Fig. 1.

The platinum complexes formed (*49*) were (i) $[Pt_2L_2X_2]^{2+}$ (L = s_2as_2p, X = Cl, I) of which the proposed structure is (**XXII**), and



(XXII)

(ii) $[PtLI_2]$ (L = s_2as_2e, s_2as_2p) formed by the reaction of MeI with the dealkylated complexes, as for the palladium analogs. The structure suggested for the dealkylated complexes (**XXIII**) is dimeric, whereas the MLI_2 complexes are monomeric.

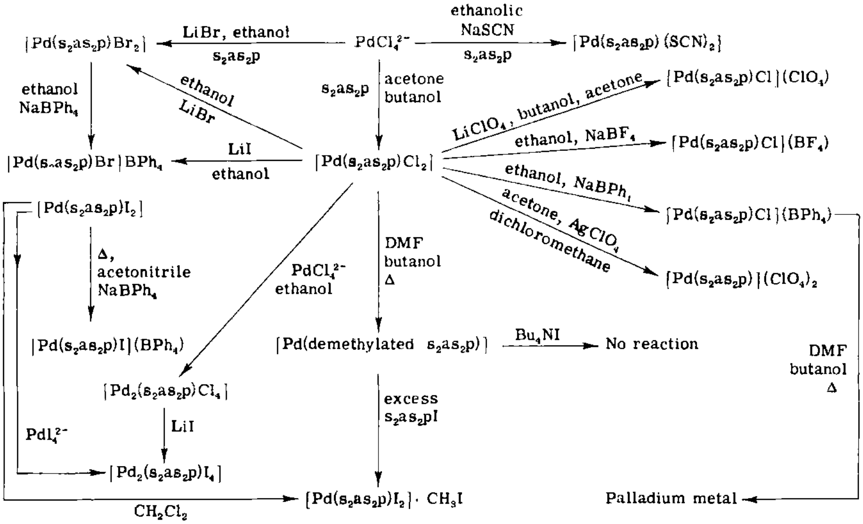
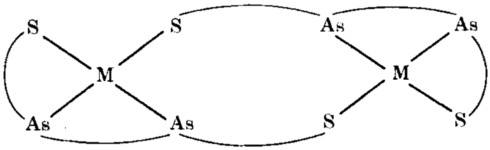


FIG. 1. Methods of preparation of the palladium(II) complexes of s_2as_2p. [From Dutta *et al.* (*25*).]

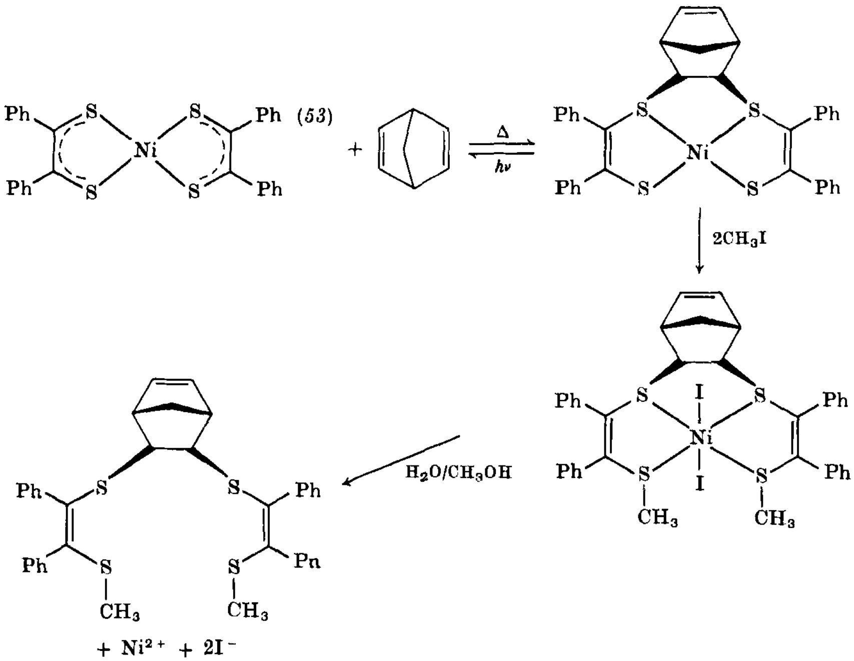
The complexes formed by palladium with s_2as_2b were (i) $[Pd_2LX_4]$ (X = Cl, I) having a proposed structure of type (**XIX**), and (ii) a dimeric series $[Pd_2L_2X_2](BPh_4)_2$ containing two arsenic atoms, one exchanging thiomethyl group, and one halide ion coordinated to each palladium(II) ion.



(**XXIII**)

I. TETRATHIOETHER CHELATES

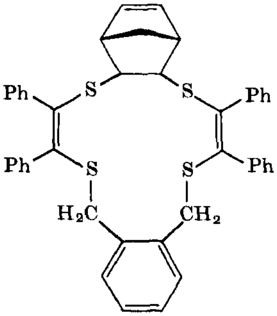
A number of metal ions in biological situations are bound essentially by sulfur donor groups (*50*), and thus chelates of type 1,3-bis-(*o*-methylthiophenylthio)propane (s_4) (*31*) have added interest. Apparently this ligand does not form monomeric complexes; the only species isolated thus far are the dimeric $[Pd_2(s_4)X_4]$ (X = Cl, Br, I) and $[Pt_2(s_4)X_4]$ (X = Cl, I), and the trimeric $Rh_3(s_4)_2Cl_9$.



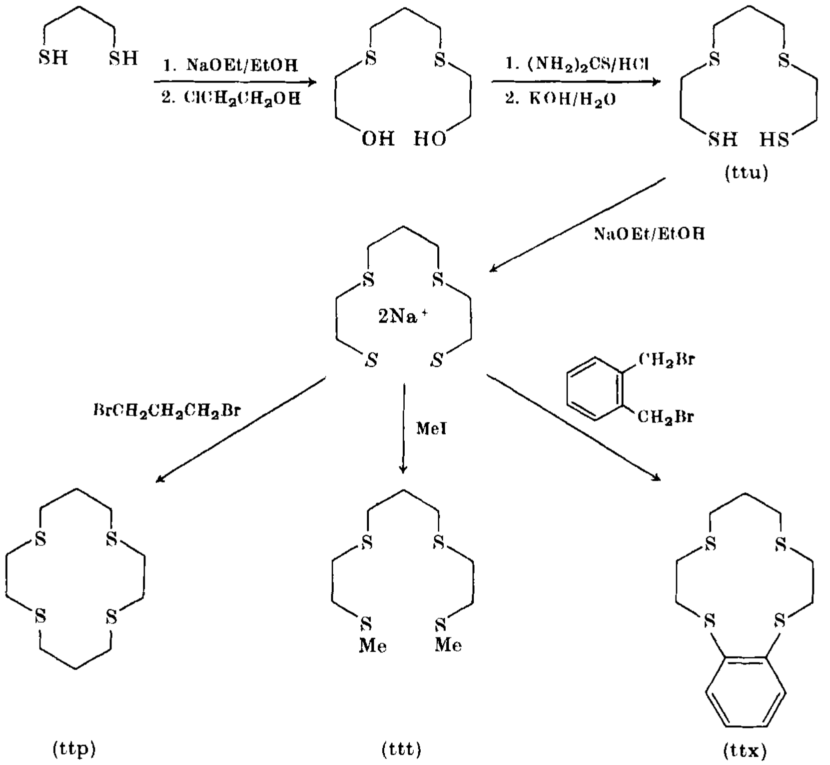
SCHEME 1

A novel method of preparing sulfur quadridentate ligands by a template type reaction has been reported (*51, 52*) Schrauzer *et al.* (*52*) isolated the free ligand by the sequence shown in reaction Scheme 1. However, it appears that this rather incomplete work on a very interesting system has not been pursued further.

Schrauzer (*52*) also found that a macrocyclic sulfur quadridentate (**XXIV**) could be formed by the sequence of Scheme I if the iodomethane is replaced by α,α′-dibromo-*o*-xylene. This type of ligand is of interest



(XXIV)



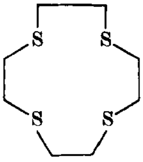
SCHEME 2

since it contains four thioether donors, and, although S^{2-} and RS^- donors have been well studied (*54*), comparatively little has been done on the RSR-type donors. Rosen and Busch have studied multidentate sulfur ligands and have synthesized the quadridentate macrocycles ttp, ttx, and the open-chain ttt (*55*) (Scheme 2). Complexation of these ligands was accomplished by reaction with the hexaacetic acid derivative of nickel(II) as the tetrafluoroborate salt in nitromethane. These complexes are red-orange and soluble in nitromethane; they react immediately with solvents of good class a-type donor ability, e.g., water, ethanol, and dimethyl sulfoxide, to give the free ligand and $Ni(solvent)_6(BF_4)_2$. This is why the preceding method of complexation was used instead of using a more standard source of nickel(II) ions.

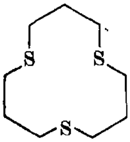
It was shown that the tetrafluoroborate anions could be replaced in metathetical reactions to produce some tetragonal species in which the anions were coordinated. Thus, two types of complex were reported for $NiLX_2$: for $X = BF_4^-$ or ClO_4^-, the complexes were diamagnetic 2:1

electrolytes and the electronic spectra were typical of square-planar nickel(II) complexes; for X = NCS^-, Cl^-, Br^-, or I^-, the solids were all paramagnetic and had four bands in their diffuse transmittance spectra. From the spectra of these tetragonal complexes, a value of Dq^{xy} for the ligand ttp was calculated as 1070 cm^{-1} which is the weakest field yet observed for a symmetrical tetradentate macrocycle. The case in which X = I^- was anomalous in that the iodide had a conductivity in nitromethane which was concentration-dependent, whereas the complexes in which X = NCS^-, Cl^-, and Br^- were non-electrolytes at all concentrations. Equilibria of the species $Ni(L)I_2$, $Ni(L)(I)^+$, and $Ni(L)^{2+}$ was postulated to explain the existence of both 2:1 and 1:1 electrolyte types.

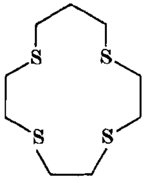
Rosen and Busch (*56*) also prepared the macrocycles ttc (**XXV**), ttd (**XXVI**), and tte (**XXVII**) by methods similar to those described in the foregoing, and the nickel(II) complexes were prepared as before. In this study the metal-to-ligand ration of the complexes was determined by a simple procedure utilizing the reaction of these complexes with water. The macrocycle was displaced from a known amount of complex and isolated quantitatively; the metal ion was then precipitated by dimethylglyoxime and isolated quantitatively. From the quantitative amounts of ligand and metal complex, the stoichiometry of the compounds was afforded. For the terdentate ttd, the complex formed was formulated as $NiL_2(BF_4)_2$, but the complexes of the tetradentate macrocycles, ttc and tte, were formulated as $Ni_2L_3(BF_4)_4$. These latter complexes gave the remarkable conductivity value of over 300 mhos in nitromethane solution which appears reasonable for such a complex if it were a dimer having the postulated structure (**XXVIII**), by analogy to that



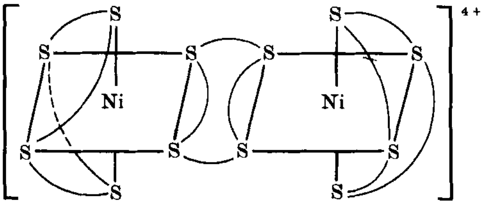
(XXV)



(XXVI)



(XXVII)



(XXVIII)

proposed for $Ni_2(trien)_3Cl_4 \cdot 2H_2O$ (*57*). The magnetic moments of these dimers were typical for octahedral high-spin nickel(II).

J. DIAMINODITHIOETHER CHELATES

With n_2s_2e, Venanzi's group (*32*) prepared the six-coordinate $[Co(n_2s_2e)Cl_2]Cl$ complex, and the high-spin six-coordinate $[Ni(n_2s_2e)X_2]$ (X = Cl, Br, I, NCS, NO_3, ClO_4). McAuliffe and co-workers (*37*) reinvestigated the nickel complexes and confirmed the earlier conclusions, but showed that the trans-octahedral complexes are tetragonally distorted. The $10Dq^{xy}$ value lay in the range 10,530–10,750 cm^{-1}, and the $10Dq^{z}$ values, i.e., those due to the coordinate anions, could be arranged in the order $Cl^- < Br^- < I^- < NO_3^- < NCS^-$. Chow *et al.* extended the work to include complexes of n_2s_2p and prepared a series $[Ni(n_2s_2p)X_2]$ (X = Cl, Br, I, NCS) (*37*). However, only the complex in which X = Cl showed indication of tetragonal distortion in the visible spectra. The axial field in the $[Ni(n_2s_2p)Cl_2]$ complex was determined as 10,420 cm^{-1}, showing the ligand field strengths to be in the order $n_2s_2e > n_2s_2p$, and $10Dq^{z}$ was found to be 872 cm^{-1}. The $10Dq^{z}$ values for the chloro complexes containing the n_2s_2p and n_2s_2e ligands were 872 and 609 cm^{-1}, respectively, suggesting that Drago's postulation (*58*) that $10Dq^{z}$ values for halides are transferable from one complex to another is incorrect. Chow *et al.* (*37*) also synthesized $[Cu(n_2s_2e)][CuCl_4]$, and Cannon *et al.* (*32*) prepared a series of $[Pd(n_2s_2e)X_2]$ (X = Cl, Br, NCS) in which the ligand was coordinated via both sulfur donors, and the amine groups were uncoordinated.

IV. Conclusion

It is hoped that this article has helped indicate the wide number of possibilities that exist for the synthesis of open-chain quadridentate chelates and the interesting complexes which they form. There is a great paucity of X-ray structural detail on the complexes, but electronic spectra have yielded a large amount of information. The intriguing relationship between type of chelate chain and the properties of resulting coordination compounds may well be illuminated further by future work in this area.

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