Co-ordination Complexes containing Multidentate Ligands. Part XI.[1–3] Transition-metal Derivatives of 1,3-Bis(3′-dimethylarsinopropylthio)propane, a Facultative Quadridentate Ligand with Diverse Donor Properties

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The synthesis of the facultative quadridentate ligand, 1,3-bis(3′-dimethylarsinopropylthio)propane (L), is described. Twenty complexes of Co^{II}, Ni^{II}, Pd^{II}, and Pt^{II} have been prepared and the variety of the resulting stereochemistries demonstrates the utility of open-chain ligands in allowing such factors as electronic properties of the metal ions, nature of the solvent, and counter ions to also dictate structure. *trans*-Pseudo-octahedral $[NiX_2L]$ complexes are obtained for X = Cl, Br, or NCS, but for X = I the diamagnetic [NiIL]I results. The $[NiCl_2L]$ complex undergoes facile transformation to planar $[NiL]X_2$ *via* a trigonal-bipyramidal intermediate. An unusual type of *trans*-chelating bidentate behaviour is observed on dissolving $[MXL]^+$ (M = Pd or Pt) complexes, which have a MAs_2S_2X donor set in the solid state and in nitromethane, in halogeno-organic solvents to form planar $[MX_2L]$ species with the donor set MAs_2X_2.

THE co-ordination chemistry of multidentate chelate ligands of heavy Group 5B and 6B donors has attracted much interest.[4] The original work on quadridentate chelates was concerned with the tripod type,[5] but more recently linear open-chain quadridentate ligands have been examined since these form complexes with a wider variety of stereochemistries due to reduced steric constraints.[4] The chelate 1,3-bis(3′-diphenylphosphinopropylthio)propane, $Ph_2P[CH_2]_3S[CH_2]_3S[CH_2]_3PPh_2$, was prepared by Dubois and Meek [6] and forms planar $[ML]^{2+}$ (M = Ni, Pd, or Pt), five-co-ordinate trigonal-bipyramidal $[NiXL]^+$ (X = halide), and square-pyramidal $[MXL]^+$ (M = Co, Pd, or Pt). The ligand 1,2-bis(*o*-diphenylarsinophenylthio)ethane, $(o\text{-}Ph_2AsC_6H_4)S[CH_2]_2S(o\text{-}C_6H_4AsPh_2)$, forms $[PdX_2L]$ which are four-co-ordinate with an $SAsX_2$ donor set,[7] but attempts to prepare nickel(II) derivatives resulted in facile bis-S-dealkylation to yield $[NiL_2]$ ($L = o\text{-}Ph_2AsC_6H_4S$) and no nickel(II) complexes of the quadridentate ligand could be isolated.[8] Dutta *et al.*[9–11] found that the ligands (I) produced a variety of palladium(II) and platinum(II) complexes including the types $[PdX_2L]$, $[Pd_2X_4L]$, $[Pd_2X_2L_2]^{2+}$, $[Pd_2L_2]^{4+}$, and $[Pt_2X_2L_2]^{2+}$. In contrast the chelates (II) produce only planar $[M_2X_4L]$ (M = Pd or Pt) and tetragonal-octahedral $[NiX_2L]$.[1,3]

Here we report the preparation of a new all-aliphatic chelate, 1,3-bis(3′-dimethylarsinopropylthio)propane,

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[1] Part VIII, W. Levason, C. A. McAuliffe, and S. G. Murray, *J.C.S. Dalton*, 1975, 1556.

[2] Part IX, W. Levason, C. A. McAuliffe, and S. G. Murray, *J.C.S. Dalton*, 1976, 269.

[3] Part X, W. Levason, C. A. McAuliffe, and S. G. Murray, *Inorg. Chim. Acta*, 1976, **17**, 247.

[4] C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 165.

[5] B. Chiswell, *Aspects Inorg. Chem.*, 1973, **1**, 267.

[6] T. D. Dubois and D. W. Meek, *Inorg. Chem.*, 1969, **8**, 146.

[7] R. D. Cannon, B. Chiswell, and L. M. Vananzi, *J. Chem. Soc.* (*A*), 1967, 1277.

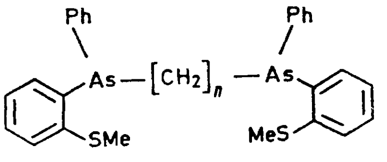
[8] C. A. McAuliffe, *Inorg. Chem.*, 1973, **12**, 2477.

[9] R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, 1970, **9**, 1215.

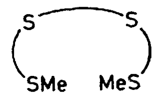
[10] R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, 1970, **9**, 2098.

[11] R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 1820.

$Me_2As[CH_2]_3S[CH_2]_3S[CH_2]_3AsMe_2$, and its complexes with Co^{II}, Ni^{II}, Pd^{II}, and Pt^{II}.



(I) $n = 2-4$



(II) ⌒ = o-C_6H_4 or $[CH_2]_n$

EXPERIMENTAL

Physical measurements were made as described previously.[2,12]

1,3-*Bis(3′-dimethylarsinopropylthio)propane* (L).—The reactions were conducted under a nitrogen atmosphere. Propane-1,3-dithiol (10.5 g, 0.097 mol) and sodium (4.6 g, 0.2 mol) in absolute ethanol (150 cm^3) were rapidly stirred for 30 min, (3-chloropropyl)dimethylarsine[13] (35.0 g, 0.194 mol) was added for 5 min, and the mixture was heated under reflux for 1 h. The solvent was distilled off and the white residue was extracted with diethyl ether (300 cm^3). Filtration, evaporation of the ether under reduced pressure, and heating the residual oil to 180 °C (0.2 Torr) * for 3 h yielded the ligand as a clear pale-yellow oil (31.6 g, 93%) (Found: C, 39.3; H, 7.5; S, 16.3. $C_{13}H_{30}As_2S_3$ requires C, 39.0; H, 7.5; S, 16.0%).

All the complexes were prepared in an inert atmosphere.

$[PdCl_2L]$.—Sodium tetrachloropalladate(II) (0.59 g, 2.0 mmol) in ethanol (15 cm^3) was stirred with the ligand (0.80 g, 2.0 mmol) in dichloromethane (15 cm^3). The mixture was warmed for 1 h, rotatory evaporated almost to dryness, and the product extracted and recrystallised from CH_2Cl_2–EtOH, yield 0.52 g (45%). The complexes $[PdX_2L]$ (X = Br, I, or NCS) were prepared similarly in the presence of a five-fold excess of the appropriate NaX, yields 60—75%.

$[PdL][ClO_4]_2$.—To $[PdCl_2L]$ (1.15 g, 2.0 mmol) dissolved in dichloromethane (15 cm^3) was added a five-fold excess of lithium perchlorate (2 g) dissolved in ethanol (10 cm^3). A precipitate formed immediately and after stirring for 1 h the solid was filtered off, washed well with dichloromethane, then with water to remove sodium salts, and finally with ethanol and diethyl ether, and dried *in vacuo*, yield 1.0 g (70%).

$[PtCl_2L]$.—The ligand (0.80 g, 2.0 mmol) in dichloromethane (15 cm^3) was stirred with bis(benzonitrile)dichloroplatinum(II) (0.96 g, 2.0 mmol) in dichloromethane (15 cm^3) and ethanol (10 cm^3) for 1 h. Evaporation almost to dryness and recrystallisation from dichloromethane produced white crystals in 50% yield. The complexes $[PtX_2L]$ (X = Br, I, or NCS) were prepared by similar methods in 50—65% yield.

$[NiX_2L]$ (X = Cl *or* Br).—The appropriate nickel(II) halide (2.0 mmol) in n-butanol (10 cm^3) and L (0.8 g, 2.0 mmol) were stirred together under gentle reflux for 1 h. The solution was cooled, filtered, and the complex precipitated by addition of excess of dry hexane. The crystals were rinsed with diethyl ether and dried *in vacuo*, yields 40—50%. The complex $[NiI_2L]$ was prepared similarly in 58% yield, except that it precipitated spontaneously on cooling.

$[Ni(NCS)_2L]$.—Hydrated nickel(II) chloride (0.48 g, 2.0 mmol) in n-butanol (10 cm^3) was stirred with sodium thiocyanate (0.8 g, 8 mmol) in n-butanol (20 cm^3) for 30 min, filtered, and L (0.8 g, 2.0 mmol) was added. The complex precipitated immediately, but stirring was continued for 30 min. After filtration the product was recrystallised from CH_2Cl_2 (0.81 g, 70%),

$[NiClL][BPh_4]$.—Hydrated nickel(II) chloride (0.48 g, 2.0 mmol) in n-butanol (20 cm^3) and the ligand (0.8 g, 2.0 mmol) were stirred together for 30 min, and then sodium tetraphenylborate (0.68 g, 2.0 mmol) dissolved in the minimum amount of n-butanol was added dropwise. After stirring for 15 min the purple solid which had precipitated was filtered off and recrystallised from dichloromethane–hexane, yield 0.95 g (60%).

$[NiXL][ClO_4]$ (X = Br *or* I).—A solution of ' $NiX(ClO_4)$ ' was prepared from hydrated nickel(II) perchlorate (0.37 g, 1.0 mmol) and the hydrated nickel(II) halide (1.0 mmol) in n-butanol (10 cm^3), and the ligand (0.8 g, 2.0 mmol) was added producing an immediate purple precipitate. After stirring for 15 min the solid was filtered off, washed with n-butanol and diethyl ether, and dried *in vacuo*, yields 80—85%.

$[ML][ClO_4]_2$ (M = Co *or* Ni).—The appropriate hydrated metal perchlorate (2.0 mmol) was stirred with the ligand (0.80 g, 2.0 mmol) in n-butanol (10 cm^3) for 1 h, after which the precipitate was filtered off and recrystallised from nitromethane–hexane, yields 55—60%. The complexes $[CoI_2L]$ *and* $[CoIL][ClO_4]$ were prepared in a manner similar to that of the nickel(II) analogues.

RESULTS AND DISCUSSION

The ligand L was obtained [equation (1)] from the reaction of the disodium salt of propane-1,3-dithiol and (3-chloropropyl)dimethylarsine in absolute ethanol.

$$HS[CH_2]_3SH \xrightarrow{2Na(OEt)} NaS[CH_2]_3SNa \xrightarrow{2Cl[CH_2]_3AsMe_2} Me_2As[CH_2]_3S[CH_2]_3S[CH_2]_3AsMe_2\ (L) \quad (1)$$

The product could not be solidified or distilled and was purified by removal of all the volatile impurities at 180 °C under high vacuum. Elemental analyses, the i.r. spectrum (which contained no bands due to S–H or As=O group, and the ^1H n.m.r. spectrum (CH_3, τ 8.96; CH_2, τ 8.35, 7.50) confirmed the purity of the ligand.

Nickel(II) *Complexes*.—The reaction of NiX_2 (X = Cl, Br, I, or NCS) with L in n-butanol produced paramagnetic ($\mu_{eff.}$ 3.0—3.12 B.M.) $[NiX_2L]$ (X = Cl, Br, or NCS) or diamagnetic $[NiIL]I$ (Table 1). The paramagnetic complexes are pseudo-octahedral in the solid state on the evidence of their electronic spectra,[14] and the appearance of only one ν(Ni–X) or ν(CN) absorption in the i.r. spectrum of the appropriate complexes points strongly to a *trans* configuration. The chloro-complex

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* 1 Torr = (101 325/760) Pa, 1 B.M. ≈ 9.27×10^{-24} A m^2.

[12] L. Baracco and C. A. McAuliffe, *J.C.S. Dalton*, 1972, 942.

[13] G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, 1964, **3**, 1544.

[14] A. B. P. Lever, ' Inorganic Electronic Spectroscopy,' Elsevier, London, 1968.

TABLE 1

Physical and spectroscopic properties and analytical data for the complexes of 1,3-bis(3′-dimethylarsinopropylthio)-ethane (L)

		Analysis (%) [a]				λ/S cm² mol⁻¹			Electronic spectra (10³ cm⁻¹)				
								$(\lambda_0 - \lambda)$ [c]					
Complex	Colour	C	H	N or halogen	$\mu_{eff.}$ [b] B.M.	*c*	*d*	c^{t}	*f*	*c*	*d*	I.r. spectra (cm⁻¹)	*M* [a,g]
$[NiClL][BPh_4]\cdot\frac{1}{2}CH_2Cl_2$	Navy	52.7 (52.5)	6.0 (6.0)	8.0 (8.3)	D	89		170	15.6	15.4 (320)	15.2 (699) [d]		
$[NiBrL][ClO_4]$	Navy	23.4 (23.5)	4.9 (4.8)		D	93		195	15.3	15.3 (693)	15.0 (745)	1 080, 620 $[ClO_4]^-$	
$[NiIL][ClO_4]$	Purple	21.9 (21.8)	4.3 (4.4)		D	95		180	25.3 (sh), 20.0, 14.7	14.9 (774)	25.3 (920), 14.6 (1 220)	1 085, 620 $[ClO_4]^-$	
$[NiL][ClO_4]_2$	Red	23.9 (23.7)	4.8 (4.6)		D	135		360	23.5, 20.6	22.3 (386)	Insol	1 085, 620	
$[NiCl_2L]\cdot CH_2Cl_2$	Pale green	27.9 (27.4)	5.8 (5.2)	11.6 (11.5)	3.0	85			24.4, 15.6, 9.8, 8.9 (sh)	15.5 (292)	Insol.	340 Ni–Cl	
$[NiBr_2L]\cdot CH_2Cl_2$	Green	24.6 (23.9)	4.8 (4.6)	22.9 (22.7)	3.0	75	1.6	172	27.0 (sh), 24.7 (sh), 15.9, 13.6 (sh), 9.1, 8.4	15.4 (690)	16.2 (69), 9.1 (18), 8.2 (4)	236 Ni–Br	
$[NiI_2L]\cdot CH_2Cl_2$	Khaki	20.7 (21.1)	4.1 (4.0)	31.7 (31.9)	D	82	20	190	25.3 (sh), 20.0 (sh), 13.8	14.9 (768)	23.3 (1 490), 14.3 (795)		
$[Ni(NCS)_2L]$	Lilac	31.0 (31.1)	5.2 (5.2)	5.0 (4.9)	3.1		3		19.1, 11.5, 9.6 (sh)	Decomp.	28.3 (4 830), 18.6 (69), 11.3 (66), 9.5 (9)	2 060 $[NCS]^-$	
$[CoL][ClO_4]_2$	Beige	24.0 (23.7)	4.4 (4.6)		3.0	137		375	20.0, 16.1 (sh), 8.2	20.9 (292), 15.8 (51)	Insol.	1 080, 620 $[ClO_4]^-$	
$[CoIL][ClO_4]$	Red–brown	22.2 (21.8)	4.4 (4.4)		2.20	91		210	22.0br, 13.6(br) 7.2	23.1 2 970	23.1 (2 970), 14.5 (155), 7.2 (65)	1 080, 620$[ClO_4]$	
$[CoIL]I$	Red–brown	20.5 (21.4)	4.0 (4.1)	35.6 (35.3)	2.25	84		195	24.8, 20.0 (sh), 13.4br, 7.3	25.0 (sh), 20.0 (1)	25.0 (sh), 20.0 (1 995), 13.7 (103), 7.1 (55)		
$[PdCl_2L]$	Yellow	26.5 (27.0)	5.0 (5.2)	12.0 (12.3)		71	0	170	24.0	23.6 (234)	28.4 (1 300)		
$[PdBr_2L]$	Orange	23.2 (23.2)	4.4 (4.5)	24.1 (24.0)		72	0	175	23.4	22.0 (544)	26.5 (1 344)		606 (666)
$[PdI_2L]$	Orange–brown	19.9 (20.5)	3.9 (3.9)	32.2 (32.4)		72	1	178	24.0, 19.1	24.1 (813), 20.2 (609)	28.5 (4 620), 23.9 (4 090)		742 (760)
$[Pd(NCS)_2L]$	Orange	28.3 (28.8)	4.8 (4.8)	4.5 (4.5)		113	3	215	25.5	22.3 (110)	25.5 (6 580)	2 076, $[NCS]^-$	
$[PdL][ClO_4]_2$	Yellow	21.0 (22.0)	4.2 (4.3)			Insol.			27.9	Insol.	Insol.	1 080, 620 $[ClO_4]^-$	
$[PtCl_2L]$	White–yellow	22.8 (23.6)	5.0 (4.6)	10.3 (10.5)		106	1	203	27.2		28.6 (3 350) (sh)		686 (666)
$[PtBr_2L]$	Yellow	20.1 (20.3)	4.4 (4.0)	21.0 (21.2)		110	2	215	25.8		26.8 (5 370) (sh)		702 (755)
$[PtI_2L]$	Orange	17.1 (17.9)	3.4 (3.4)	29.8 (30.0)		85	2	195	23.2	25.0 (360)	30.3 (sh), 24.3 (4 105)		837 (849)
$[Pt(NCS)_2L]$	Green–yellow	26.5 (25.3)	3.4 (3.4)	3.9 (3.9)		142	4	325	24.0		27.5 (sh)	2 075 $[NCS]^-$	

[a] Calculated values are given in parentheses. [b] D = Diamagnetic. [c] In nitromethane. [d] In 1,2-dichloroethane. [e] Absorption coefficients (ε/dm³ mol⁻¹ cm⁻¹) are given in parentheses. [f] Solid reflectance. [g] In chloroform.

is essentially insoluble in dichloromethane, but the bromo- and isothiocyanato-complexes remain essentially octahedral in this solvent (Table 1). The treatment of Rowley and Drago [15] has been applied to calculate the in-plane and out-of-plane ligand-field contributions (Table 2). The results of these calculations are most interesting. They show that the field strength of the bromide ligand varies significantly from the solid state to solution. (This effect may be steric in origin, as the conformation of the ligand, which contains three trimethylene linkages, makes the plane of the complex very crowded.) However, the most surprising aspect is the effect of the out-of-plane anion on the in-plane field strength of the ligand, which varies from 905 (X = Br) to 1 149 cm⁻¹ (X = NCS). It is difficult to suggest any reason for this phenomenon. Either steric (size of the

TABLE 2

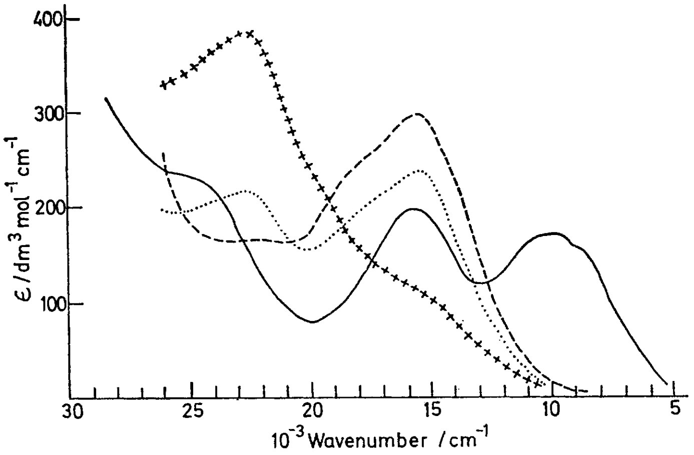
In-plane and out-of-plane ligand-field strengths in the *trans*-$[NiX_2L]$ complexes

		Dq	
Complex	State	*xy*	*z*
$[NiCl_2L]$	Solid	980	790
$[NiBr_2L]$	Solid	905	775
	CH_2Cl_2	910	730
$[Ni(NCS)_2L]$	Solid	1 149	775
	CH_2Cl_2	1 130	760

[15] D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 1967, **6**, 1092; 1968, **7**, 795.

X^- groups) or electronic (' hardness ' of the X^- groups) effects would be expected to produce similar results for $X = Cl^-$ and NCS^-; this is most obviously not the case.

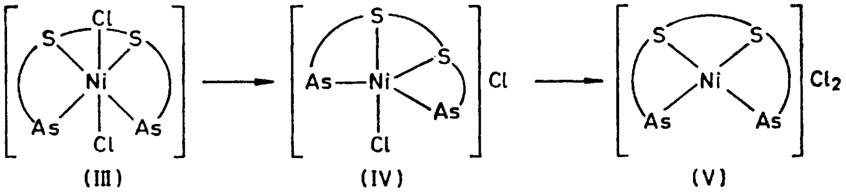
In contrast to the other $[NiX_2L]$ complexes, NiI_2L is diamagnetic, and in the solid state and in dichloromethane solution the electronic spectra are consistent with a five-co-ordinate trigonal-bipyramidal structure.[6]



Electronic spectra of $[NiCl_2L]$ in nitromethane: (——), freshly prepared (non-conducting octahedral) (· · · ·), after *ca.* 10 min (five-co-ordinate with small amount of planar species); (x x x x), after *ca.* 30 min (planar species, 1 : 2 electrolyte); and (— — — —), spectrum of five-co-ordinate $[NiClL][ClO_4]$ shown for comparison

The $[Ni(NCS)_2L]$ complex appears to decompose in nitromethane, but all three halogeno-complexes function as 1 : 1 electrolytes[6] [$\Lambda = 75$—85 S cm^2 mol^{-1}; gradient $(\lambda_0 - \lambda)c^{-\frac{1}{2}} \simeq 170$—$190$] and have visible spectra consistent with a trigonal-bipyramidal structure. On standing for *ca.* 10 min the solution of $[NiCl_2L]$ developed a new band at 23 000 cm^{-1} and Λ increased with time to 120 S cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solution after 30 min, suggesting the presence of a planar species (see Figure).

The most important reason for studying open-chain quadridentate chelate ligands is their flexible nature which, to a large extent, allows the metal ion to dictate the structure of the resulting complex.[4] This may be contrasted with the nature of the well studied ' tripod ' quadridentate ligands which tend to enforce their trigonal symmetry.[5] This flexibility property of open-chain quadridentate ligands is well illustrated by the behaviour of $[NiCl_2L]$ which undergoes facile transformation from an octahedral species (III) to a planar moiety (V) *via* a trigonal-bipyramidal intermediate (IV).



(III) (IV) (V)

Equimolar mixtures of NiX_2 and $[Ni(OH_2)_6][ClO_4]_2$ reacted with L in n-butanol to produce five-co-ordinate $[NiXL][ClO_4]$ (X = Br or I) complexes; perchlorate salt of the chloro-complex could not be obtained pure, always being contaminated with $[NiL][ClO_4]_2$. However, $[NiClL][BPh_4]$ was readily obtained. The electronic spectra of these complexes (Table 1) are essentially similar in the solid state, in dichloromethane, and in nitromethane, and thus all contain trigonal-bipyramidal $[NiXL]^+$ cations.[6] The four-co-ordinate red diamagnetic $[NiL][ClO_4]_2$ was synthesised from nickel(II) perchlorate hexahydrate in n-butanol. The i.r. spectrum confirms that the perchlorate groups are not co-ordinated[16] and no bands attributable to water were observed.

The ability of this As_2S_2 donor ligand to produce four-, five-, and six-co-ordinate nickel(II) complexes contrasts with the structurally similar tetrathioethers (S_4 donors)[3] which produce only six-co-ordinate complexes and with the four- and five-co-ordination favoured by tetra-arsines.[4,5,17] The results obtained in this study are most closely reminiscent of the properties the bidentate (*o*-methylthiophenyl)diphenylphosphine and the tridentate bis(*o*-methylthiophenyl)phenylphosphine.[18] The fact that the present complexes of Ni^{II} do not spontaneously dealkylate under the conditions employed is most notable and contrasts with the facile dealkylation observed for similar complexes of α,ω-bis(*o*-diphenylarsinophenylthio)alkanes,[8] and may be attributable to the alkyl substitution on the terminal arsine groups increasing the electron density on the sulphur (transferred *via* the nickel atom), thus reducing the tendency to undergo Zeisel-type cleavage.[19]

Cobalt(II) *Complexes.*—Cobalt(II) perchlorate afforded beige $[CoL][ClO_4]_2$, a 1 : 2 electrolyte in 10^{-3} mol dm^{-3} nitromethane, and which exhibits $\nu_3(ClO_4^-)$ at 1 080 cm^{-1} and $\nu_4(ClO_4^-)$ at 620 cm^{-1} in the i.r. spectrum in Nujol, confirming that the perchlorate groups are ionic. The magnetic moment of 3.0 B.M. is within the range reported for planar Co^{II},[20] and the spectrum resembles those of other planar cobalt(II) species.[21] On standing in air over several months this complex gradually turns pink and becomes octahedral by co-ordination of two water molecules.

Red-brown $[CoI_2L]$ and $[CoIL][ClO_4]$ were readily obtained, but repeated attempts to obtain $[CoX_2L]$ or

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[16] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 1091.

[17] E. C. Alyea, *Aspects Inorg. Chem.*, 1973, **1**, 311.

[18] M. O. Workman, G. Dyer, and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1543.

[19] P. G. Eller, J. M. Riker, and D. W. Meek, *J. Amer. Chem. Soc.*, 1973, **95**, 3540.

[20] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1954, 12.

[21] W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 1975, **14**, 127.

$[CoXL][ClO_4]$ (X = Cl or Br) in a pure state were unsuccessful, green or olive products of rather variable analysis being obtained which were essentially insoluble in common solvents and exhibited the characteristic reflectance spectra of $[CoX_4]^{2-}$ moieties.[14] The major constituents of these products are probably $[CoXL]_2[CoX_4]$, which are preferentially precipitated due to their insolubility. The complexes [CoIL]Y (Y = I or ClO_4) are 1 : 1 electrolytes in 10^{-3} mol dm^{-3} nitromethane (Table 1) and have magnetic moments of 2.1—2.2 B.M., corresponding to one unpaired electron with a small orbital contribution. In dichloromethane solution these complexes exhibited electronic spectra corresponding to five-co-ordinate Co^{II},[22-24] and the solid reflectance spectra were similar although the bands were rather broad and, especially for the case of Y = I, had ill defined maxima. The distinction between trigonal-bipyramidal and square-pyramidal Co^{II}, on the basis of electronic spectra, is uncertain at the present time [22,24] and has not been attempted here.

The complexes of L with Co^{II} exhibit fewer stereochemical variations than with Ni^{II}, especially with regard to six-co-ordination.

Palladium(II) *and Platinum*(II).—The $[PdX_2L]$ (X = Cl, Br, I, or NCS) complexes were obtained directly from the ligand and the appropriate tetrahalogenopalladates(II) in ethanol, but the analogous reactions with tetrahalogenoplatinates(II) afforded insoluble products (possibly $[PtL][PtX_4]$) in poor yield. The complexes $[PtX_2L]$ were readily obtained from L and $[PtX_2(NCPh)_2]$ in ethanol–dichloromethane.

In 10^{-3} mol dm^{-3} nitromethane solution the palladium(II) halogeno-complexes are 1 : 1 electrolytes and have spectra characteristic of five-co-ordinate Pd^{II}.[25,26] The platinum(II) complexes have slightly higher conductivities, but are still within the range expected for 1 : 1 electrolytes.[27] The difference is probably attributable to the decreased tendency to attain five-co-ordintion in the order Ni $\gg$ Pd $>$ Pt,[28] and to the greater stability on ligand-field grounds of the planar species over the five-co-ordinate species as Δ increases from 4*d* to 5*d*.[29] The reflectance spectra of the palladium(II) complexes are similar to those obtained in nitromethane solution (Table 1) and thus the complexes are also probably five-co-ordinate in the solid state. A similar comparison of the solid-reflectance and nitromethane-solution spectra for the platinum(II) complexes is not possible since the absorption of the solvent (>26 000 cm^{-1}) precludes observation of the platinum(II) spectra except for X = I, but it is not unreasonable to postulate a five-co-ordinate structure in the solid state similar to that found in solution.

The complexes $[MX_2L]$ (M = Pd or Pt; X = Cl, Br, or I) have molecular weights in chloroform solution corresponding to monomeric species and all are non-electrolytes in 1,2-dichloroethane. The ^1H n.m.r. spectra in $CDCl_3$ exhibited single methyl resonances which are sensitive to both M and X and occurred at lower field (τ 8.0—8.5) than in the free ligand (τ 8.96), proof that the terminal $AsMe_2$ groups are co-ordinated to the metal. This evidence is not inconsistent with a six-co-ordinate structure, but the electronic spectra, which are sensitive to the X group, nonetheless occur in the range expected only for four-co-ordinate species. Although little spectral information has been reported for six-co-ordination with these two metal ions, a bathochromic shift would be expected on co-ordination of a further halide to an $[MXL]^+$ chromophore,[26] and not the significant shift to higher energy which is actually observed (Table 1).

An alternative explanation,[30] completely consistent with the data, is that in halogeno-organic solvents L is behaving as a bidentate As_2 donor ligand and that the complexes are four-co-ordinate with an As_2X_2 donor set. The electronic spectra are very similar to those of other MAs_2X_2 (M = Pd or Pt) species.[31] Molecular models indicate that the ligand is under great strain to co-ordinate in a *cis*-bidentate manner, but easily affords a *trans*-bidentate structure with two sulphur atoms well removed from the metal. Further evidence for a *trans* structure is provided by the solution (CH_2Cl_2) i.r. spectra of the $[MBr_2L]$ (M = Pd or Pt) complexes which exhibited a single sharp ν(M-Br) at 285 (Pt) and 275 (Pd) cm^{-1}, within the range for *trans*-MX_2 sets.[32] Low solubility prevented us from obtaining similar spectra for the $[PtCl_2L]$ complex, but ν(Pd-Cl) occurred at 355 cm^{-1} for $[PdCl_2L]$ which is in the range expected for a *trans*-$PdCl_2$ set.[32]

Our accurate molecular models suggest that a square-pyramidal arrangement, (VI), imposes the least strain on the ligand, and a similar complex with a structurally similar tetra-arsine ligand also adopts this structure.[33] We thus propose the transformation (VI) $\longrightarrow$ (VII) in halogeno-organic solvents.* The differing behaviour in

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* A referee has suggested that we should compare the rate of alkylation of the sulphur atoms in (VI) and (VII), since facile alkylation should occur for (VII). Reaction with methyl iodide produced almost instantaneous precipitation of a completely insoluble species, and we were not able to follow the reaction by n.m.r. However, we should point out that considerable doubt has previously been cast on the application of this method to establishing co-ordination *versus* non-co-ordination of donors in solution (see, for example, ref. 9).

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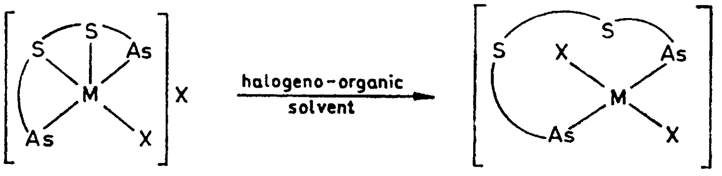
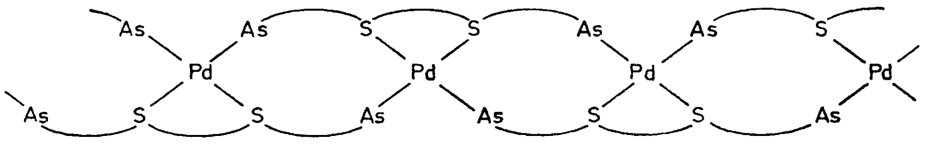
nitromethane and halogeno-organic solvents is readily rationalised, since the more polar $MeNO_2$ will favour the ionic form (VI), whereas in an halogeno-organic solvent the ions will not be stabilised by solvation and the halide displaces the thioether donors. The inability of a terminal thioether to compete with halide ions for co-ordination positions on these metal ions has been noted previously in tetrathioether [1,3] and dithioether–diarsine (RS–As–As–SR sequence) chelates.[9-11] Non-terminal thioethers will be more difficult to displace, and to our knowledge the behaviour reported here is the first example of this occurrence.



(VI) (VII)

There are a few reported examples of ligands which function as *trans*-bidentate chelates,[34-36] and a rigid backbone with the correct geometric properties [36] or a long backbone with bulky terminal groups [35] are factors which have been proposed as contributory to *trans*-bidentate behaviour. However, the results reported here suggest that when the electronic factors are suitable and the chelate chain length permits, *trans*-bidentate behaviour can occur even with a quadridentate ligand.



(VIII)

The $[Pd(NCS)_2L]$ complex exhibits behaviour intermediate between a 1 : 1 and a 1 : 2 electrolyte in nitromethane (Λ 113 S cm^2 mol^{-1}) and the i.r. spectrum of this solution contained ν(CN) bands indicative of ionic $[NCS]^-$ (2 060 cm^{-1}), N-bonded Pd–NCS groups (2 090 cm^{-1}), and a trace amount of Pd–SCN groups (2 110 cm^{-1}).[37] The electronic spectrum exhibited a weak band at 22 300 cm^{-1}, suggesting a five-co-ordinate species is present. In the same solvent the platinum(II) analogue is essentially a 1 : 2 electrolyte (Λ 142 S cm^2 mol^{-1}) and there was a strong broad ν(CN) absorption at 2 060 cm^{-1} (ionic $[NCS]^-$), although a very weak band at 2 080 cm^{-1} suggests the presence of a small amount of Pt–NCS linkages. The reduced tendency for $[NCS]^-$ to co-ordinate, compared with the halides, and the tendency for the metal to co-ordinate it being in the order Pd > Pt, is in agreement with other studies on Group 5B donors with these metals.[26]

In the solid state both $[M(NCS)_2L]$ (M = Pd or Pt) complexes exhibited one broad ν(CN) band at 2 075 cm^{-1}, probably due to *trans*-NCS groups of the MAs_2N_2 donor set. In halogeno-organic solvents four-co-ordinate *trans*-bridging-ligand structures are present analogous to the four-co-ordinate molecules of the halide complexes, on the basis of ^1H n.m.r. and electronic-spectral evidence similar to that discussed above. Furthermore, the solution i.r. spectrum contained evidence for co-ordinated thiocyanate (both S- and N-bonding, with the former predominating). There is no i.r. evidence for ionic $[NCS]^-$ in halogeno-organic solvents.

The reaction of $[PdCl_2L]$ with excess of $Li[ClO_4]$ in CH_2Cl_2–EtOH produced yellow $[PdL][ClO_4]_2$. This complex is insoluble in all common organic solvents, exhibited a reflectance spectrum consistent with planar Pd^{II}, and the solid-state i.r. spectrum shows the presence of only ionic $[ClO_4]^-$ groups. The insolubility of this complex suggests the presence of a polymeric structure of type (VIII).

Conclusions.—The variety of stereochemistries reported here demonstrates once more the utility of facultative quadridentate ligands, and the subtle interplay between the electronic properties of the metal ions, solvent, and counter ions and steric properties of the ligand in determining complex structures. This variety of factors is particularly pronounced in ligands such as L containing both Group 5B and 6B donors which have differing abilities to promote a particular structure, *e.g.* whilst P or As tend to produce four- or five-co-ordination with Ni^{II}, S favours six-co-ordination; examples of four-, five-, and six-co-ordination were obtained with L. Finally, this work clearly shows that the tendency for Pd^{II} and Pt^{II} to induce *trans*-bidentate co-ordination must be much stronger than could hitherto have been predicted.

We thank the S.R.C. for the award of Research Studentships (to W. L. and S. G. M.), Johnson, Matthey Co. Ltd. for the generous loan of palladium and platinum salts, and Dr. K. P. Beaumont for $[PtX_2(NCPh)_2]$.

[6/217 *Received, 2nd February,* 1976]

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