Complexes of Nickel(II) Halides with Polymethylenebis(phenylthiourea) Compounds

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The complexing behaviour of polymethylenebis(phenylthiourea) compounds, PhNH·CS·NH·[CH$_2$]$_n$·NH·CS·NHPh (L, n = 2—10), towards Ni^{II} halides has been investigated. These new bidentate ligands give a great variety of stereochemistries with Ni^{II}. Electronic spectra, molecular weights, and conductivity values have been measured to elucidate the stereochemistry of the complexes obtained. The following complexes have been identified: [NiLX$_2$] (X = Cl, Br, or I) (tetrahedral, monomeric, paramagnetic, chromophore NiS$_2$X$_2$); [NiLX$_2$] (tetrahedral, polymeric, paramagnetic, chromophore NiS$_2$X$_2$); [NiL$_2$X$_2$] (tetragonal, monomeric, paramagnetic, chromophore NiS$_4$X$_2$); and [NiL$_2$X$_2$] (square planar, polymeric, diamagnetic, chromophore NiS$_4$).

WE have previously investigated some bidentate ligands having one, or two, thiourea groups, PhNH·CS·NH·[CH$_2$]$_n$·NH$_2$ and PhNH·CS·NH·[CH$_2$]$_n$·NH·CS·NHPh) (n = 0 or 2). These ligands give a great variety of stereochemistries with Ni^{II} as was also found for *N*-substituted thiourea compounds.[1-7] Tetrahedral, tetragonal octahedral, and, probably, distorted five-coordinate complexes of chromophores NiS$_2$X$_2$, NiS$_3$N$_2$, NiS$_4$Br$_2$, and NiS$_5$ were obtained.[8] The closely related ligands (PhNH·CS·NH·)$_2$ and (PhNH·CS·NH·CH$_2$·)$_2$, (II), were found to give very different complexes with Ni^{II}.[8] The first gave tetrahedral NiS$_2$X$_2$ chromophores in solution, analogous to those of the unidentate thiourea ligands. However, the bromide of formula [NiL$_2$Br$_2$], the only one which could be separated from solution, gave physical properties consistent with tetragonal-octahedral NiS$_4$Br$_2$. In contrast, the second ligand gave insoluble, probably polymeric, solids of formula [NiL$_2$X$_2$], having the pseudo-tetrahedral NiS$_2$X$_2$ chromophore, also present in the mother liquors. This difference in behaviour, presumably due to the presence of methylene groups in one and not in the other ligand, suggested the study of PhNH·CS·NH·[CH$_2$]$_n$·NH·CS·NPh (n = 2—10) complexes. The intention is

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to investigate stereochemical behaviour with increasing distance between the two co-ordinating sulphur atoms.

$$\text{PhNH·CS·NH·CH}_2\text{·CH(Me)·NH·CS·NHPh}$$
(I)

$$\text{PhNH·CS·NH·[CH}_2]_n\text{·NH·CS·NHPh}$$
(II—X; $n = 2$—10)

The first ligand considered in this paper, PhNH·CS·NH·CH_2·CH(Me)·NH·CS·NHPh, (I), is the only one having a branched aliphatic chain. The higher homologues, (III)—(X), studied all have linear chains, the Roman numerals showing the number of methylene groups interposed between the thiourea groups. All the ligands will be referred to as polymethylenebis(phenylthiourea) compounds. The soluble ligand (I) has the same backbone structure, $(S·C·N·C)_2$, as that for (II) reported in the preliminary study. Ligand (II) is insoluble in the common organic solvents. Since the insolubility of the Ni^{II} halide complexes formed by (II) is attributed, apart from the polymeric nature of the complexes, to the insolubility of the ligand (which increases with the number of methyl groups in the side chain), the analogous complexes of (I) have been prepared for comparison.

RESULTS AND DISCUSSION

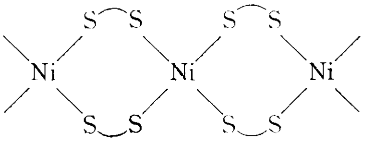
No product separated from acetone–ethanol solutions of the complexes NiX_2 (X = Cl, Br, or I) and ligand (I). Evaporation of solvent left an acetone-soluble residue. The acetone solutions of this residue gave optical spectra characteristic of the chromophore NiS_2X_2, from which the complexes $[NiLBr_2]$ and $[NiLI_2]$ [L = (I)] slowly crystallised. These two complexes gave reflectance spectra identical to the optical spectra of their solutions. The complexes are more or less soluble in acetone depending on the particular preparative conditions and number of recrystallisations used. Increasing recrystallisation led to formation of insoluble products. This suggests a change from monomeric to polymeric products, confirming the suggestions put forward for the analogous insoluble complexes of ligand (II). The monomeric nature of the soluble product was confirmed by the fact that some preparations of the complex $[NiLI_2]$ [L = (I)] gave rise (not without difficulty) to a product almost completely soluble in acetone, the molecular weight of which agreed with the formula $[NiLI_2]$. Magnetic moments, both of mixed products and completely insoluble ones, were always between 3·4 and 3·5 B.M. These data point to the existence of a pseudo-tetrahedral NiS_2X_2 chromophore in both cases.

However, this is not the only way that ligand (I) co-ordinates. On reacting $NiBr_2$ or NiI_2 with (I) in butanol, in all molar ratios, powders of composition $[NiL_2X_2]$, very soluble in acetone, separated out. The molecular weights and zero conductivity in acetone indicate that the dissociation (1) takes place for both complexes. Solution spectra support this, since they are identical to those of $[NiLX_2]$ solutions obtained as above.

$$[NiL_2X_2] \longrightarrow [NiLX_2] + L;\ L = (I) \qquad (1)$$

The structures in the solid state are more complicated. The reflectance spectra are not easily interpreted since they present characteristics common to tetrahedral, square-planar, and tetragonal chromophores. However, the most intense band at 14 500—16 000 cm^{-1} shifted in energy on varying the halogen, which excludes square-planar NiS_4 and also tetrahedral NiS_2X_2, since the shift is too small to be accounted for by the latter. The magnetic moment of 3·2 B.M. indicates a tetragonal structure NiS_4X_2. The, somewhat unlikely, structure consisting of a tetragonal chromophore with apical S and X and in-plane NiS_3X, distorted so as to give a singlet ground state, is also eliminated. In conclusion, Ni^{II} may co-ordinate up to six atoms in these complexes, although it is uncertain as to which, and how many, of these atoms make up the chromophore.

The ligand (III) gives $[NiLX_2]$ (probably tetrahedral) and $[NiL_2X_2]$ complexes under the same preparative conditions as used for (I). The former were obtained for all three halides, although the chloride is completely insoluble in all solvents and attempts at dissolution with heating led to decomposition. On the other hand, the bromide and iodide are reasonably soluble in acetone and remain so even after several recrystallisations. Molecular-weight measurements showed that the soluble products are monomeric (Table 1). The complexes $[NiL_2X_2]$ (X = Cl, Br, or I) were obtained from butanol solutions of the components in all molar ratios. They are very soluble in acetone but slowly deposit $[NiLCl_2]$ and $[NiLBr_2]$, identical to the products obtained from acetone. The ligand (IV) gives complexes very different from those above. $[NiL_2X_2]$ (X = Cl or Br) complexes were obtained from acetone or butanol. These are insoluble in acetone, high-melting, diamagnetic, bluish green powders, having spectra characterised by an intense band at *ca.* 615 nm (Table 1). These properties suggest the presence of square-planar NiS_4 chromophores, probably formed by bridging ligands. The complexes slowly dissolve in pyridine (py), decomposing to give $[Ni(py)_4X_2]$ complexes. On the other hand, NiI_2 reacts with ligand (IV) to give tetrahedral $[NiLI_2]$, insoluble in acetone, and tetragonal $[NiL_2I_2]$ soluble in acetone. The former is obtained from acetone and the latter from butanol. The same behaviour is shown by ligands (V)—(IX). In general, the most stable complexes formed are those of formula $[NiLX_2]$; these sometimes separate from acetone solutions of the tetragonal $[NiL_2X_2]$ complexes.



The complete series of complexes could not be prepared, *e.g.* the existence of tetrahedral [$NiLX_2$] [L = (X)] was suggested from solution measurements alone. Given the analogies in electronic spectra between all the complexes and those of the thiourea compounds,[6] it is deduced that the ligands bind to the metal ion *via* the sulphur atom.

The [NiL_2X_2] complexes have properties which cannot be easily rationalised and some of the analytical data were not very close to the theoretical values. Since no alternative formulation is possible, analogous selenium derivatives of ligand (VIII) with $NiCl_2$ and $NiBr_2$ were prepared. The analyses of these correspond to the formulae [NiL'_2Cl_2] and [NiL'_2Br_2] and the reflectance spectrum of [NiL'_2Br_2] was similar to that of the sulphur analogue with an intense band at 678 nm (650 nm for S). Although the data are limited, they suggest that the behaviour of the selenium complexes is similar to that of the sulphur analogues. The energy shifts in the electronic spectra on going from sulphur to selenium agree with substitution of sulphur by selenium in the co-ordination sphere.[9] The well resolved charge-transfer band at 465 nm in the selenium complexes supports this conclusion.

TABLE 1

Electronic spectra, molecular weights, and magnetic properties at 293·3 K of some significant polymethylenebis(phenylthiourea) Ni^{II} complexes

Complex [a]	L	Chromophore	10^3 Band maxima/cm^{-1} (ε/l mol^{-1} cm^{-1})	Mol. wt. Calc.	Mol. wt. Found (±4%)	Conc. (%) in acetone	μ/B.M.
[$NiLCl_2$] [b]	(III)	NiS_2Cl_2	$15\cdot5_0$, $14\cdot7_0$ (sh), $10\cdot5_5$, $9\cdot5_3$ (sh)	474·1		(insoluble)	3·54
[$NiLBr_2$] [b]	(III)	NiS_2Br_2	$23\cdot5_2$, $14\cdot9_3$, $14\cdot2_5$ (sh), $9\cdot9_5$ (sh), $9\cdot1_0$ (sh)	563·3	590	0·36	3·17
[$NiLBr_2$] [c]	(III)	NiS_2Br_2	23·8 (1 015), $15\cdot2_7$ (29_5), $14\cdot2_8$ (sh), $10\cdot0_0$ (45), $9\cdot0_9$ (53)				
[NiL_2Br_2] [b]	(III)	NiS_4Br_2	$15\cdot0_3$	907·5	504	1·15	3·30
[NiL_2Br_2] [c]	(III)	NiS_2Br_2	$23\cdot8_1$ (1 020), $15\cdot2_7$ (31_0), $14\cdot2_3$ (sh), $10\cdot0_0$ (45), 9·09 (53)				
[$NiLI_2$] [b]	(III)	NiS_2I_2	$20\cdot8_3$, $13\cdot7_9$, $9\cdot9_5$ (sh), 8·63 (sh)	657·0	570	0·27	3·23
[$NiLI_2$] [c]	(III)	NiS_2I_2	$24\cdot0_9$ (sh), 20·40 (sh), $13\cdot8_8$ (390), $13\cdot2_4$ (sh), 9·43 (60), 8·54 (45)				
[NiL_2Cl_2] [b]	(IV)	NiS_4	$16\cdot1_3$	846·6		(insoluble)	(diamagnetic)
[NiL_2Br_2] [b]	(IV)	NiS_4	$16\cdot1_3$	935·6		(insoluble)	(diamagnetic)
[$NiLI_2$] [b]	(IV)	NiS_2I_2	$13\cdot7_9$, $10\cdot0_0$, 8·62	671·0		(insoluble)	3·01
[NiL_2I_2] [b]	(IV)	NiS_4I_2	$14\cdot6_0$	1 029·5	486	0·71	3·02
[NiL_2I_2] [c]	(IV)	NiS_2I_2	$13\cdot7_5$ (370), 13·24(sh), $9\cdot5_2$ (60), 8·55 (40)				
[NiL_2Cl_2] [b]	(VII)	NiS_4Cl_2	$15\cdot9_7$	730·8	375	1·18	3·02
[NiL_2Cl_2] [c]	(VII)	NiS_2Cl_2	$16\cdot0_0$ (240), $15\cdot0_3$ (sh), $10\cdot6_0$ (40), $9\cdot5_2$ (50)				
[NiL_2Br_2] [b]	(VII)	NiS_4Br_2	$15\cdot0_5$	1 019·8	546	1·29	3·03
[NiL_2I_2] [b]	(VII)	NiS_4I_2	$14\cdot6_8$	113·7	595	1·40	3·47

[a] For composition and analytical data see Table 2. [b] Reflectance spectrum. [c] Solution absorption spectrum measured in acetone; same spectrum with ligand in excess.

Both the particular halide concerned and the solvent used must be taken into account when attempts are made to rationalise the co-ordination behaviour of the ligands. Despite this, it appears that, on the whole, the co-ordination behaviour is a function of the number of methylene groups between the two thiourea groups. Presumably the polymeric tetrahedral [$NiLX_2$] complexes are the most stable formed with ligand (I) because the two sulphur atoms are very close together. Co-ordination to a single Ni^{II} ion would cause a large distortion of the complex so formed. On the other hand, in ligand (III) the distance between the two sulphur atoms seems ideal for chelation (apparently only for Br and I, but not for Cl) and hence the stable forms are the monomeric tetrahedral complexes. Similarly the monomeric tetragonal [NiL_2X_2] forms are also stable in the solid state.

The ligand (IV) seems to have intermediate character. With $NiCl_2$ and $NiBr_2$ the polymeric square-planar forms are stabilised whilst NiI_2 gives a complex similar to those of ligand (V) upwards. From this point onwards the distance between the sulphur atoms increases, chelation is impeded, and polymeric [$NiLX_2$] forms become more stable. Hence monomeric [$NiLX_2$] forms cannot be separated and tetragonal [NiL_2X_2], having chelating ligands, are not stable in the solid state and give insoluble polymeric [$NiLX_2$] in solution.

In conclusion, polymethylenebis(phenylthiourea) compounds co-ordinate to Ni^{II} *via* the sulphur atoms, as for unidentate thioureas. Like the latter, they give a wide variety of stereochemistry: (*i*) [$NiLX_2$] (tetrahedral, monomeric, paramagnetic, chromophore NiS_2X_2); (*ii*) [$NiLX_2$] (tetrahedral, polymeric, paramagnetic, chromophore NiS_2X_2); (*iii*) [NiL_2X_2] (tetragonal, monomeric, paramagnetic, chromophore NiS_4X_2); and (*iv*) [NiL_2X_2] (square planar, polymeric, diamagnetic, chromophore NiS_4).

EXPERIMENTAL

The ligands L, of general formula $PhNH{\cdot}CE{\cdot}NH{\cdot}[CH_2]_n{\cdot}NH{\cdot}CE{\cdot}NHPh$ (n = 2—10, E = S or Se), were obtained by reacting the appropriate diamine $NH_2[CH_2]_nNH_2$ with phenyl isothiocyanate, PhNCS, or its selenium analogue, PhNCSe, in the ratio 1 : 2. The complete series of Ni^{II} halide complexes could not be obtained. Those separated

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[9] T. Tarantelli and C. Furlani, *J. Inorg. Nuclear Chem.*, 1972, **4**, 999.

in the solid state are reported in Table 2, with pertinent physical data.

TABLE 2

Analytical data for Ni^{II} polymethylenebis(phenylthiourea) complexes

Compound [a]	L	Colour	Composition	M.p. (t/°C)	Analysis (%) found (calc.) C	H	N	Halogen	Other
	(I)	White	$C_{17}H_{20}N_4S_2$	188—189	60·0 (59·25)	5·80 (5·85)	16·35 (16·25)		
[NiLBr$_2$]	(I)	Green	$C_{17}H_{20}Br_2N_4NiS_2$	210—211 [a]	36·65 (36·25)	3·60 (3·60)	10·05 (9·95)	25·5 (28·4)	Ni 10·15 (10·45) S 10·35 (11·4)
[NiL$_2$Br$_2$]	(I)	Green	$C_{34}H_{40}Br_2N_8NiS_4$	118—119	44·0 (45·0)	4·25 (4·45)	11·45 (12·35)		
[NiLI$_2$]	(I)	Brown	$C_{17}H_{20}I_2N_4NiS_2$	214—216 [a]	31·35 (31·1)	3·25 (3·05)	8·55 (8·55)	38·25 (38·65)	Ni 8·70 (8·95) S 9·90 (9·75)
[NiL$_2$I$_2$]	(I)	Brown	$C_{34}H_{40}I_2N_8NiS_4$	140—143	41·75 (40·75)	4·25 (4·05)	10·75 (11·2)		
	(III)	White	$C_{17}H_{20}N_4S_2$	130—131	59·25 (59·25)	6·85 (5·85)	15·6 (16·5)		
[NiLCl$_2$]	(III)	Green	$C_{17}H_{20}Cl_2N_4NiS_2$	168—169	42·75 (43·05)	4·70 (4·25)	11·2 (11·8)	14·2 (14·85)	Ni 11·75 (12·4) S 12·8 (13·5)
[NiL$_2$Cl$_2$]	(III)	Green	$C_{34}H_{40}Cl_2N_8NiS_4$	120—124	50·35 (49·9)	5·40 (4·90)	12·95 (13·7)		
[NiLBr$_2$]	(III)	Green	$C_{17}H_{20}Br_2N_4NiS_2$	157—159	36·25 (36·25)	4·25 (3·60)	9·40 (9·95)		
[NiL$_2$Br$_2$]	(III)	Green	$C_{34}H_{40}Br_2N_8NiS_4$	98—99	45·85 (45·0)	5·05 (4·45)	11·95 (12·35)		
[NiLI$_2$]	(III)	Brown	$C_{17}H_{20}I_2N_4NiS_2$	160—161	31·1 (31·1)	3·35 (3·05)	8·15 (8·55)		
[NiL$_2$I$_2$]	(III)	Yellow-green	$C_{34}H_{40}I_2N_8NiS_4$	103—105	40·0 (40·8)	4·30 (4·05)	10·3 (11·5)		
	(IV)	White	$C_{18}H_{22}N_4S_2$	177—179	60·5 (60·3)	6·15 (6·20)	15·35 (15·65)		
[NiL$_2$Cl$_2$]	(IV)	Blue-green	$C_{36}H_{44}Cl_2N_8NiS_4$	185—187	51·35 (51·05)	5·70 (5·25)	13·35 (13·25)	8·55 (8·35)	Ni 6·90 (6·93) S 15·0 (15·15)
[NiL$_2$Br$_2$]	(IV)	Blue-green	$C_{36}H_{44}Br_2N_8NiS_4$	183—185	45·9 (46·2)	5·05 (4·75)	11·85 (12·0)	17·3 (17·1)	Ni 6·45 (6·25) S 13·75 (13·7)
[NiLI$_2$]	(IV)	Brown	$C_{18}H_{22}I_2N_4NiS_2$	147—149	33·5 (32·2)	3·85 (3·30)	7·9 (8·55)		
[NiL$_2$I$_2$]	(IV)	Brown	$C_{36}H_{44}I_2N_8NiS_4$	120—124	43·05 (42·0)	4·65 (4·30)	10·4 (10·9)		
	(V)	White	$C_{19}H_{24}N_4S_2$	140—142	60·6 (61·25)	6·65 (6·50)	14·9 (15·05)		
[NiL$_2$Cl$_2$]	(V)	Green	$C_{38}H_{48}Cl_2N_8NiS_4$	100—101	51·8 (52·2)	5·90 (5·55)	11·65 (12·8)		
[NiLBr$_2$]	(V)	Green	$C_{19}H_{24}Br_2N_4NiS_2$	235—237	38·35 (38·6)	4·30 (4·10)	8·85 (9·50)		
[NiL$_2$Br$_2$]	(V)	Green	$C_{38}H_{48}Br_2N_8NiS_4$	105—109	46·75 (47·35)	5·35 (5·00)	10·3 (11·65)		
[NiLI$_2$]	(V)	Brown	$C_{19}H_{24}I_2N_4NiS_2$	230—233	34·6 (33·3)	3·90 (3·55)	8·20 (8·20)		
	(VI)	White	$C_{20}H_{26}N_4S_2$	140—142	61·75 (62·15)	6·35 (6·80)	14·2 (14·5)		
[NiL$_2$Cl$_2$]	(VI)	Green	$C_{40}H_{52}Cl_2N_8NiS_4$	100—102	52·85 (53·2)	6·30 (5·90)	11·4 (12·4)		
[NiL$_2$Br$_2$]	(VI)	Green	$C_{40}H_{52}Br_2N_8NiS_4$	92—95	47·9 (48·45)	5·35 (5·30)	10·75 (11·3)		
[NiL$_2$I$_2$]	(VI)	Brown	$C_{40}H_{52}I_2N_8NiS_4$	80—85	41·2 (44·25)	4·50 (4·80)	8·80 (10·3)		
	(VII)	White	$C_{21}H_{28}N_4S_2$	90—92	63·1 (62·95)	7·40 (7·05)	12·95 (14·0)		
[NiLCl$_2$]	(VII)	Green	$C_{21}H_{28}Cl_2N_4NiS_2$	190—193	48·05 (47·6)	5·45 (5·30)	10·3 (10·55)		
[NiL$_2$Cl$_2$]	(VII)	Green	$C_{42}H_{56}Cl_2N_8NiS_4$	90—94	53·9 (54·2)	6·35 (6·05)	11·45 (12·05)		Ni 5·95 (6·30)
[NiLBr$_2$]	(VII)	Green	$C_{21}N_{28}Br_2N_4NiS_2$	200—203	41·35 (40·75)	4·70 (4·55)	9·05 (9·05)		
[NiL$_2$Br$_2$]	(VII)	Green	$C_{42}H_{56}Br_2N_8NiS_4$	94—96	48·85 (49·45)	5·75 (5·55)	10·15 (11·0)		Ni 6·00 (5·75)
[NiL$_2$I$_2$]	(VII)	Brown-green	$C_{42}H_{56}I_2N_8NiS_4$	97—99	45·3 (45·3)	4·90 (5·05)	10·25 (10·05)	22·25 (22·5)	Ni 5·10 (5·25) S 11·65 (11·5)
	(VIII)	White	$C_{22}H_{30}N_4S_2$	115—117	64·05 (63·75)	7·80 (7·30)	13·95 (13·5)		
[NiL$_2$Cl$_2$]	(VIII)	Green	$C_{44}H_{60}Cl_2N_8NiS_4$	80—82	55·95 (55·1)	6·30 (6·30)	11·4 (11·7)		Ni 5·95 (6·10)
[NiL$_2$Br$_2$]	(VIII)	Green	$C_{44}H_{60}Br_2N_8NiS_4$	70—73	51·15 (50·45)	5·45 (5·75)	10·25 (10·7)		Ni 5·85 (5·60)
[NiL$_2$I$_2$]	(VIII)	Dark brown	$C_{44}H_{60}I_2N_8NiS_4$	81—85	46·85 (46·3)	5·75 (5·30)	9·35 (9·80)		Ni 4·75 (5·15)
	(VIII) [b]	White	$C_{22}H_{30}N_4Se$	110—111	51·9 (51·95)	6·50 (5·95)	11·25 (11·0)		
[NiL$_2$Cl$_2$]	(VIII) [b]	Dark green	$C_{44}H_{60}Cl_2N_8NiSe_4$	105—109	45·8 (46·1)	5·45 (5·25)	9·45 (9·75)		
[NiL$_2$Br$_2$]	(VIII) [b]	Green	$C_{44}H_{60}Br_2N_8NiSe_4$	103—106	42·3 (42·8)	5·00 (4·90)	8·95 (9·05)		
	(IX)	White	$C_{23}H_{32}N_4S_2$	102—104	63·95 (64·45)	7·90 (7·50)	12·85 (13·05)		
[NiL$_2$Cl$_2$]	(IX)	Green	$C_{46}H_{64}Cl_2N_8NiS_4$	70—72	55·85 (56·0)	7·30 (6·55)	11·5 (11·35)		Ni 5·85 (5·95)
[NiLBr$_2$]	(IX)	Green	$C_{23}H_{32}Br_2N_4NiS_2$	210—212	43·75 (42·7)	5·35 (5·00)	83·5 (8·65)	24·0 (24·7)	Ni 8·90 (9·05) S 9·80 (9·90)
[NiL$_2$Br$_2$]	(IX)	Green	$C_{46}H_{64}Br_2N_8NiS_4$	60—65	52·15 (51·35)	6·50 (6·00)	10·05 (10·4)	14·1 (14·85)	Ni 5·50 (5·45) S 11·45 (11·9)
[NiL$_2$I$_2$]	(IX)	Brown	$C_{46}H_{64}I_2N_8NiS_4$	112—115	48·1 (47·25)	5·85 (5·50)	10·0 (9·60)		Ni 5·20 (5·02)

[a] M.p. for insoluble compound. [b] Ligand containing Se instead of S.

Pseudo-tetrahedral Paramagnetic Complexes: [NiLX$_2$] (X = Cl, Br, *or* I).—These were obtained by mixing the components in 2 : 1 acetone–ethanol, evaporating to dryness, and then redissolving in acetone. If soluble the product was recrystallised from acetone. A typical preparation is described below.

[NiLBr$_2$] {L=PhNH·CS·NH·[CH$_2$]$_3$·NH·CS·NHPh, (III)}. The ligand (III) (0·69 g, 2 mmol) dissolved in anhydrous acetone (50 cm^3) was added to a solution of NiBr$_2$,3H$_2$O (0·41 g, 1·5 mmol) in ethanol (25 cm^3). A green solution was obtained which was set aside at 50 °C for 1 h. Solvent was evaporated off and the well dried residue redissolved in anhydrous acetone and the solution filtered. Light petroleum was added until the solution became slightly turbid. The product, obtained as green *crystals* (0·75 g, 88·5%), separated after 12 h. An identical product was obtained from acetone solutions of [NiL$_2$Br$_2$] and could be recrystallised from acetone.

Square-planar Diamagnetic Complexes: [NiL$_2$X$_2$] (X = Cl, Br, *or* I).—These were prepared by mixing the components in either acetone or ethanol, as below.

[NiL$_2$Br$_2$] {L = PhNH·CS·NH·[CH$_2$]$_4$·NH·CS·NHPh, (IV)}. A solution of $NiBr_2,3H_2O$ (0·55 g, 2 mmol) in ethanol (25 cm^3) was added to a solution of ligand (IV) (0·72 g, 2 mmol) in acetone (100 cm^3). The mixture was heated, filtered, and set aside for 24 h. The insoluble crystalline *product* was filtered off (0·83 g, 88·5%).

Tetragonal Paramagnetic Complexes: $[NiL_2X_2]$ (X = Cl, Br, *or* I).—These complexes were obtained by mixing the components, in any molar ratio, in n-butanol, as below.

$[NiL_2Br_2]$ {L = PhNH·CS·NH·$[CH_2]_5$·NH·CS·NHPh, (V)}. $NiBr_2,3H_2O$ (0·55 g, 2 mmol) in hot n-butanol (25 cm^3), was added to ligand (V) (0·75 g, 2 mmol) in hot n-butanol (30 cm^3). The green solution obtained rapidly became turbid. The green *product* was separated, after setting aside this solution for 48 h (0·63 g, 65%).

Conductivity measurements were carried out on a Philips PW 9501 conductivity meter, and molecular weights on a Mechrolab MP 301 A osmometer. Optical spectra, in solution and as reflectance, were obtained on a Beckman DK-1A spectrophotometer, equipped with reflectance accessory (MgO standard). Magnetic-susceptibility measurements were carried out on a Gouy balance using $Hg[Co(SCN)_4]$ and distilled water as calibrants.

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