Complexes of Nickel(II) Perchlorate with Polymethylenebis(phenylthiourea) Ligands

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The behaviour of polymethylenebis(phenylthiourea) compounds as ligands (L) towards nickel(II) perchlorate has been investigated. The ligand PhHN·CS·NH·CH_2·CH(Me)·NH·CS·NHPh, (I), gives a five-co-ordinate species of chromophore NiS_4O; PhHN·CS·NH·$[CH_2]_n$·NH·CS·NHPh (III—X; n = 3—10) give insoluble complexes $[NiL_3(ClO_4)_2]$ (n = 3—9) with octahedral stereochemistry and a soluble complex $[NiL_3(ClO_4)_2]$ (n = 3) that dissociates in solution to give square-planar $[NiL_2]^{2+}$ species (where L is a bidentate ligand). An excess of L gives rise to formation of $[NiL_4]^{2+}$ species, still square planar in stereochemistry, in which the ligand is unidentate. The ligand (X; n = 10) also gives rise to square-planar $[NiL_4]^{2+}$ species in solution but excess of ligand tends to form $[NiL_6]^{2+}$ species having an octahedral NiS_6 chromophore.

THE present paper constitutes an extension of a preceding work on complexes of nickel(II) halides with ligands containing two thiourea groups[1] and reports the behaviour of the same ligands towards nickel(II) perchlorate. The lower tendency of the perchlorate ion to co-ordinate to the metal gives the ligand greater freedom to affect the stereochemistry of the compounds by allowing co-ordination of more ligand molecules than in the halogeno-complexes. As in the preceding paper,[1] the ligands will be referred to as polymethylenebis(phenylthiourea) compounds (I)—(X). Thus for the

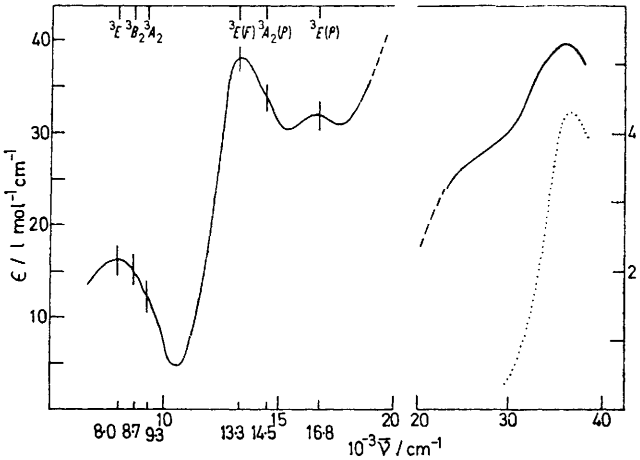
PhHN·CS·NH·CH_2·CH(Me)·NH·CS·NHPh
(I)

PhHN·CS·NH·$[CH_2]_n$·NH·CS·NHPh
(II)—(X) n = 2—10

homologues (II)—(X) the roman numerals represent the number of carbon atoms interposed between the thiourea groups. Ligand (II) is the only one that does not react with $Ni(ClO_4)_2$.

RESULTS AND DISCUSSION

With the ligand (I) no solid complex could be separated and only measurements in solution were possible. The variation of the intensity of the absorption bands in the visible electronic spectrum was followed for various (I) : $Ni(ClO_4)_2$ ratios in acetone solution. A curve was obtained with a break at (I) : $Ni(ClO_4)_2$ = 4 : 1. The conductivity of an acetone solution having this composition (4 : 1) was characteristic of a 1 : 1 electrolyte (Λ 85 S cm^2 mol^{-1} = 2×10^{-2}M; for a Ph_4AsCl solution at the same concentration, Λ 81 S cm^2 mol^{-1}).† Molecular-weight determinations gave values close to half the calculated molecular weight for $NiL_4(ClO_4)_2$. These results suggest the presence of the ions $[NiL_4(ClO_4)]^+$ and ClO_4^-. The ion $[NiL_4(ClO_4)]^+$ may be formulated as a five-co-ordinate high-spin (μ_{eff} = 3·25 B.M.) species, of chromophore NiS_4O with the perchlorate ion co-ordinated *via* an oxygen atom.[2,3] Both i.r. and electronic spectra were in agreement with this suggestion. The electronic spectrum fitted reasonably well the ligand-field diagrams for square-pyramidal geometry calculated by several authors,[4,5] assuming C_{4v} symmetry (Figure). Comparison of the i.r. spectra with those of the pure ligand suggests co-ordination by sulphur atoms[6-9] and simultaneous presence of ionic and co-ordinated perchlorate.[10] However, the possible presence of hydrogen bonding between the perchlorate oxygen atoms and the secondary amine nitrogens cannot be definitely ruled out.[11]



Absorption spectra in CH_2Cl_2 of $Ni(ClO_4)_2$ + (I) in molar ratio 1 : 4 (——), and (I) (· · · ·)

Ligands (III)—(IX) gave complexes of composition $[NiL_3(ClO_4)_2]$ in butanol solution. These are paramagnetic, insoluble in the usual organic solvents, and are characterised by electronic-reflectance spectra with bands at 14 300 and 9 000 cm^{-1}. This suggests octahedral stereochemistry, with an NiS_6 chromophore, for

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† 1M = 1 mol dm^{-3}; 1 B.M. ≃ 9·27 × 10^{-24} A m^2.

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all these complexes. In addition, polymeric character is indicated by the high insolubility.

Ligand (X), like (I), did not give rise to a well characterised crystalline solid on reaction with $Ni(ClO_4)_2$. Nevertheless, the solution behaviour was very different from that of (I). The electronic spectra in anhydrous acetone solutions, obtained as for (I), showed an intense band at 16 400 cm^{-1} which is characteristic of a square-planar NiS_4 chromophore. The band intensity increased up to a maximum (ε 230 l mol^{-1} cm^{-1}) at a ratio Ni : (X) = 1 : 4 and then decreased with further addition of ligand, an excess of which produced another low-intensity band at *ca.* 9 100 cm^{-1}. These results suggest that (X) probably behaves as a unidentate ligand giving rise to an NiS_4 chromophore which, with increasing ligand concentration, is in equilibrium with octahedral NiS_6. The magnetic moments of solutions containing 2×10^{-2}M-$Ni(ClO_4)_2$ and (X) in 1 : 3, 1 : 4, 1 : 5, and 1 : 6 ratios were between 3·0 and 3·3 B.M., with no clear correlation with the mol ratios. This appears to be in conflict with the presence of a square-planar diamagnetic species which should be present in large excess of the paramagnetic octahedral one. However, the presence of a thermally accessible triplet state in the square-planar case, as previously found for the species NiL_4X_2 (L = *NN'*-disubstituted thiourea),[12,13] satisfactorily explains all the data.

Ligand (VIII) gave similar behaviour. Besides the insoluble species obtained directly from butanol, this ligand formed complexes which are soluble in acetone and are present in the residue obtained by evaporation of acetone–ethanol solutions of the reagents. These acetone solutions are sufficiently stable to allow physical measurements, although, on standing, crystalline $[NiL_3(ClO_4)_2]$ [L = (VIII)] separates, which is identical to the complex obtained directly from butanol.

Finally ligand (III) showed a particular behaviour. This ligand is the only one of the series to give a $[NiL_3(ClO_4)_2]$ species, soluble in acetone and dichloromethane, in addition to the insoluble complex already described. The soluble complex was obtained by dissolving the residue [obtained as in the case of (VIII)] in hot acetone so as to form a saturated solution. Traces of moisture prevent formation of a soluble crystalline product; the clear crystals become opaque and insoluble when not stored under a dry atmosphere. The elemental analysis of this opaque species is still in agreement with the formula $[NiL_3(ClO_4)_2]$ [L = (III)]. The acetone solutions showed an electronic spectrum characterised by a band at 15 500 cm^{-1} (ε 70 l mol^{-1} cm^{-1}) and a very weak (ε 6 l mol^{-1} cm^{-1}) feature at *ca.* 8 300 cm^{-1}. Their conductivity indicates a 1 : 2 electrolyte (Λ 210 S cm^2 mol^{-1} in 5×10^{-4}M solution) with a magnetic moment of *ca.* 3·15 B.M. Addition of ligand caused an increase in intensity of the band at 15 500 cm^{-1}, which also moved to higher wavenumbers, while the weak band almost disappeared. The maximum intensity value (ε 200 l mol^{-1} cm^{-1}) and greatest shift (to 16 400 cm^{-1}) occurred at a ratio $[NiL_3(ClO_4)_2]$: (III) = 1 : 10. Addition of further ligand did not change the spectrum. Solutions with ligand in excess appeared to remain partially paramagnetic,[12,13] although the large diamagnetic correction due to the organic groups does not allow accurate measurement of magnetic moments. These data provide evidence for the existence of both square-planar and octahedral species in the solutions containing only $[NiL_3(ClO_4)_2]$ [L = (III)] (of chromophores NiS_4 and NiS_6, respectively), both having bidentate ligands. The ratio *M* (calc.) : *M* (obs.) of *ca.* 3·8 : 1 (acetone solutions, $2{\cdot}5 \times 10^{-3}$M, identical to those used for the electronic spectra) supports this suggestion. The fact that the most-intense band is at a lower frequency than is found in other square-planar NiS_4 chromophores may be justified by a lower ligand-field strength for these sulphur atoms. The chelating sulphur ligands probably distort on co-ordination, and give longer Ni–S distances than do unidentate sulphur ligands. Addition of excess of ligand causes progressive opening of the chelate rings, ultimately giving rise to square-planar species containing unidentate ligands. This nicely explains the appearance of the intense band at 16 400 cm^{-1}.

EXPERIMENTAL

The ligands were prepared as described previously.[1] Solid complexes of formula $[NiL_3(ClO_4)_2]$ are listed in the Table, together with their analyses and some physical properties.

Insoluble $[NiL_3(ClO_4)_2]$ *Complexes*.—These were obtained by the reaction between $Ni(ClO_4)_2,6H_2O$ and (III)—(IX) in n-butanol. Typically 0·78 g (2 mmol) of (VI), $PhHN{\cdot}CS{\cdot}NH{\cdot}[CH_2]_6{\cdot}NH{\cdot}CS{\cdot}NHPh$, in hot n-butanol (30 cm^3) was added to a hot solution of $Ni(ClO_4)_2,6H_2O$ (0·37 g, 1 mmol) in butanol (20 cm^3). The resulting greenish solution obtained quickly became turbid and a yellow-green solid separated. After standing for 12 h, this was filtered off, washed with cold n-butanol then with anhydrous acetone, and air dried, yield 0·6 g (60%).

Soluble $[NiL_3(ClO_4)_2]$ *Complexes*.—These were obtained by reaction between $Ni(ClO_4)_2,6H_2O$ and ligands (III) and (VIII). Typically 1·4 g (4 mmol) of (III), $PhHN{\cdot}CS{\cdot}NH{\cdot}[CH_2]_3{\cdot}NH{\cdot}CS{\cdot}NHPh$, in acetone solution (50 cm^3) was added to a solution of $Ni(ClO_4)_2,6H_2O$ (0·74 g, 2 mmol) in ethanol (20 cm^3). The resulting clear green solution was evaporated to dryness and the residue dried *in vacuo* over $CaCl_2$. After standing for *ca.* 2 h, the yellow crystalline product was filtered off under a dry atmosphere, washed with anhydrous acetone, and air dried, yield 0·6 g (35%).

Complexes of $Ni(ClO_4)_2$ *with* (I) *and* (X) *in Solution*.—The investigation of the complexes which could not be obtained as solids was carried out by mixing ethanol solutions of the nickel(II) salt (0·05M) and acetone solutions of the ligand (0·1M) in the required molar ratios. The solutions so obtained were evaporated to dryness and the residues dried *in vacuo* over $CaCl_2$ and then redissolved in anhydrous acetone to the required molarity.

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Analytical data and physical properties for $[NiL_3(ClO_4)_2]$ complexes [a]

L	Composition	M.p. (θ_c/°C)	Analysis (%) [b]				μ/B.M.
			C	H	N	Cl, Ni, S	
(III)	$C_{51}H_{60}Cl_2N_{12}NiO_8S_6$ [c]	135—140	47·4 (47·45)	4·75 (4·70)	12·85 (13·0)	Cl 5·40 (5·50) Ni 4·45 (4·55) S 14·9 (14·9)	3·23
(III)	$C_{51}H_{60}Cl_2N_{12}NiO_8S_6$ [d]	160—162	47·8 (47·45)	4·80 (4·70)	12·8 (13·0)		3·05
(IV)	$C_{54}H_{66}Cl_2N_{12}NiO_8S_6$	180—182	49·15 (48·65)	5·20 (5·00)	12·85 (12·6)		3·12
(V)	$C_{57}H_{72}Cl_2N_{12}NiO_8S_6$	175—178	50·2 (49·8)	5·45 (5·30)	12·2 (12·2)	Cl 5·05 (5·15) Ni 4·40 (4·25) S 14·15 (13·85)	3·11
(VI)	$C_{60}H_{78}Cl_2N_{12}NiO_8S_6$	174—177	50·8 (50·85)	6·15 (5·55)	11·75 (11·85)		3·11
(VII)	$C_{63}H_{84}Cl_2N_{12}NiO_8S_6$	168—170	51·95 (51·85)	6·15 (5·80)	11·55 (11·5)		3·18
(VIII)	$C_{66}H_{90}Cl_2N_{12}NiO_8S_6$	130—132	52·7 (52·8)	6·20 (6·05)	10·9 (11·2)		3·05
(IX)	$C_{69}H_{96}Cl_2N_{12}NiO_8S_6$	158—150	54·1 (53·7)	6·40 (6·25)	10·6 (10·9)	Cl 4·65 (4·60) Ni 3·70 (3·80) S 12·55 (12·45)	3·21

[a] All complexes are yellow-green. [b] Calculated values are given in parentheses. [c] Soluble. [d] Insoluble.

Electronic and i.r. spectra were obtained on Beckman DK-1A and I.R. 10 spectrophotometers, respectively. Reflectance spectra were run against MgO as a reference. Magnetic measurements were carried out on a Gouy balance using $Hg[Co(SCN)_4]$ as calibrant. Conductivity and molecular-weight measurements were made on a Philips PW 9501 conductivity bridge and a Mechrolab MP 301 A osmometer, respectively.

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