325. *Complexes of Bivalent Nickel with Some Compounds containing Two Sulphide Chelate Groups.*

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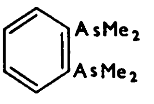
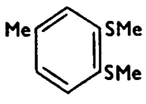
The complexes formed by the bis-sulphides (di-thioethers), 1 : 2-diethylthioethane (III) and 1 : 2-dimethylthioethane (IV), with bivalent nickel halides and with nickel perchlorate have been prepared and studied. The halides form complexes of the type $[Ni(Chelate)_2(Hal)_2]^0$ but the perchlorate gives rise to the tris-chelate complex, $[Ni(Chelate)_3][ClO_4]_2$. The compounds are not very stable, being decomposed by water, alcohol, or acetone. Measurements of conductivity (in nitrobenzene), molecular weight (in chloroform), and magnetic susceptibility indicate that in all cases the nickel atom is octahedrally co-ordinated. Attempts to obtain complexes of higher valency states of nickel were not successful. The nature of the bonding in these bivalent nickel complexes is discussed.

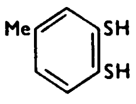
For comparison with earlier studies on the stabilisation of various valency states of nickel with an alkyl tritertiary [1] and an aryl [2-5, cf. 6] ditertiary arsine (I), the behaviour of bis-sulphide chelate groups has been investigated. It was hoped to overcome the relatively poor co-ordinating ability of sulphides towards nickel by using a bis-sulphide chelate group. Accordingly, for comparison with (I), 4-methyldithioveratrole (II) was prepared and its behaviour investigated. Only minute amounts of unstable bromo- and iodo-complexes of nickel were obtained with the latter and the use of this chelate group was therefore abandoned in favour of wholly alkyl bis-sulphides which form more stable complexes. In particular 1 : 2-diethylthioethane (III) and 1 : 2-dimethylthioethane (IV) have been prepared and studied. Complexes of chelate groups of this type have been prepared by Morgan and Ledbury [7] with salts of certain metals but the only nickel complex previously studied was the thiocyanate, which was prepared by Tschugaeff [8] and by Bennett *et al.*[9] The former assigned an octahedral configuration to the nickel atom on the basis of the analysis but no previous physical measurements have been reported.



(I)



(II)



(V)

(III) $C_2H_5\cdot S\cdot[CH_2]_2\cdot S\cdot C_2H_5$ $CH_3\cdot S\cdot[CH_2]_2\cdot S\cdot CH_3$ (IV)

The stereochemistry of nickel complexes has been discussed elsewhere,[10-12] and Table 1 is given as a basis for the interpretation of the magnetic and cryoscopic data given later. It should be emphasised that quadricovalent, spin-free complexes are rare; if tetrahedral, a large orbital contribution to the moment is expected [13,14] and hence magnetic data are useful as a guide to the stereochemistry. However, in all compounds studied here the nickel atom is sexacovalent. In the spin-free complexes the outer bonding orbitals which are required for the stereochemistry discussed are shown but the evidence for their use is presumptive,

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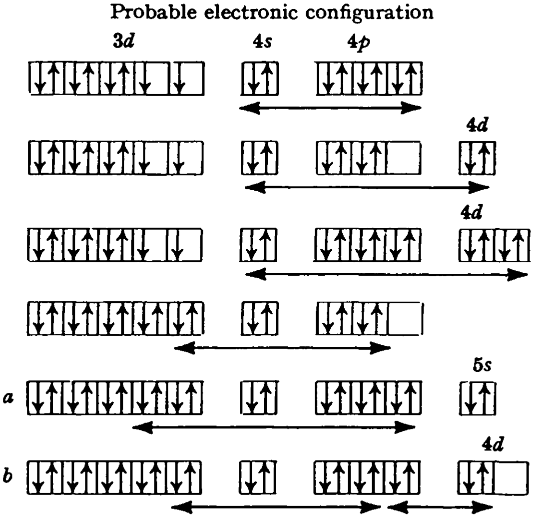
[1] Barclay and Nyholm, *Chem. and Ind.*, 1953, 378.
[2] Nyholm, *J.*, 1950, 2061.
[3] Nyholm, *J.*, 1951, 2602.
[4] Nyholm, *J.*, 1952, 2906.
[5] Nyholm and Short, *J.*, 1953, 2670.
[6] Jensen, *Z. anorg. Chem.*, 1936, **229**, 265.
[7] Morgan and Ledbury, *J.*, 1922, **121**, 2882.
[8] Tschugaeff, *Ber.*, 1908, **41**, 2222.
[9] Bennett, Mosses, and Statham, *J.*, 1930, 1668.
[10] Nyholm, *Chem. Rev.*, 1953, **53**, 263.
[11] Jörgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.
[12] Orgel, *Report to the Xth Solvay Council*, Brussels, 1956.
[13] Nyholm, *J. Proc. Roy. Soc., N.S.W.*, 1955, **89**, 1.
[14] Nyholm, *Report to the Xth Solvay Council*, Brussels, 1956.

and theoretical rather than experimental. Whether they are occupied or not is irrelevant for *this* discussion of the shape of the molecule.

The nickel(II) complexes with 1 : 2-diethylthioethane were prepared by treating a concentrated alcoholic solution of the nickel salt with the chelate group. The iodide crystallised out spontaneously and, probably owing to low solubility, is the most stable. To obtain the chloride, however, the solution had to be evaporated to a very small volume and set aside. On the other hand, the derivatives of 1 : 2-dimethylthioethane separated immediately on the addition of the chelate group. Presumably owing to their higher solubility in alcohol, the derivatives of the diethyl chelate group are obtained in analytically less pure condition than those of the dimethyl chelate. The difficulty of removing traces of nickel halide from the former is reflected in the analytical figures. The perchlorate was the most difficult of the complexes to obtain, and in this case it was necessary to remove all the alcohol by storage in a desiccator over calcium chloride. In all cases where evaporation was required the product was contaminated with the original nickel salt which is difficult to remove without partial decomposition of the complex—even in the case of the iodide. The physical properties and the experimentally determined magnetic moments of the complexes are shown in Table 2. The low solubilities of the complexes prevented any determination of molecular weights in the case of the ethyl derivatives but two measurements on methyl complexes are given which indicate six-fold co-ordination in chloroform.

TABLE 1. *Electronic arrangement, stereochemistry, and magnetic properties of bivalent nickel complexes.*

Type of complex	Co-ordination no. of Ni(II) atom
Spin	4
Free	6
Spin	4
Paired	6



Type of complex	Arrangement of bonds	Expected magnetic moment (B.M.)	Example
Spin	Tetrahedral	>3·5	$[Ni(NO_3)_2,2(C_2H_5)_3P]^0$ ($\mu_{eff.}$ = 3·05 B.M.) [a]
	Square	3·1—3·3	3·1—3·3
Free	Octahedral	3·1—3·3	$[Ni(Dipyridyl)_3][ClO_4]_2$ ($\mu_{eff.}$ = 3·10 B.M.) [b]
Spin	Square	Diamagnetic	$[NiCl_2,2(C_2H_5)_3P]^0$ ($\mu_{eff.}$ = diamagnetic) [a]
Paired	Octahedral	Diamagnetic	$[Ni(Diarsine)_3][ClO_4]_2$ (solid) ($\mu_{eff.}$ = diamagnetic) [c]

[a] See ref. 15. [b] Burstall and Nyholm, *J.*, 1952, 3570. [c] See ref. 2. ⟷ Bond orbitals.

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[15] Asmussen, "Magnetokemiske Undersogelser over Uorganiske Kompleksforbindelser," Copenhagen, 1944, p. 221.

In all cases the conductivity measurements indicate six-fold co-ordination. The magnetic measurements all indicate two unpaired electrons with a small orbital contribution. The complexes are therefore of the " outer orbital " type and, in the light of the discussion above, octahedrally co-ordinated.

All attempts to isolate complexes of the type $[Ni(Chelate)_3][Hal]_2$ were unsuccessful, only the perchlorate of the trischelate cation being isolated. In an attempt to ascertain whether any appreciable amounts of $[Ni(Chelate)_3]Br_2$ were formed in solution, the compound $[Ni(1:2\text{-dimethylthioethane})_2Br_2]^0$ in nitrobenzene was treated with excess of the chelate group. There was no change in the very low conductance of the solution, showing that electrolytes were not being formed.

It is of interest to know why these sulphur chelate groups are so much less effective than the tertiary arsine ones in effecting electron pairing and in forming complexes with strong " inner orbital " binding. It has been suggested [16] that the two factors of prime importance in strong binding to transition metals are (i) the *effective* electronegativity of the ligand donor atom and (ii) the extent of d_π bonding between the metal and ligand using d_ϵ electron pairs of the metal atom. There has been some confusion concerning the ability of sulphur to cause electron pairing; sulphur readily effects electron pairing with transition metals *provided* it is bicovalent. Thus chelate groups of the type (V) co-ordinate very strongly with transition metals [17] but with sulphides the co-ordinating ability is much less; in passing from RS^- to R·SR the proton affinity of the sulphur atom has decreased enormously, this being a rough measure of tendency to form strong σ bonds. Since chelate groups such as *o*-phenylenebisdimethylarsine (I), which have practically no basic properties, will co-ordinate strongly with transition metals, it has been suggested that it is the double bonding which in the case of the arylarsine chelate groups causes the formation of strong complexes. We conclude that both dialkyl and alkyl aryl sulphides, even if present in chelate groups, are reluctant to form d_π bonds with transition metals. It is conceivable that the reason for this is one of size, the necessary vacant *d* orbital of the bicovalent sulphur atom failing to overlap sufficiently with the filled d_ϵ orbital of the metal.

TABLE 2.

Complex *	Formula weight	Colour	*M*, in boiling $CHCl_3$	Magnetic moment (B.M.) (25°)	Molecular conductivity in $PhNO_2$ (Concn. $\approx$ 0·001M)
$Ni(ET)_2Cl_2$	430	Green	—	3·21	Non-electrolyte †
$Ni(ME)_2Br_2$	463	Green	458, 432	3·21	Non-electrolyte
$Ni(ET)_2Br_2$	519	Green	—	3·20	Non-electrolyte
$Ni(ME)_2I_2$	557	Yellow	555, 568	3·22	Non-electrolyte
$Ni(ET)_2I_2$	613	Yellow	—	3·12	Non-electrolyte
$[Ni(ME)_3](ClO_4)_2$...	708	Blue	—	3·16	41·5 mhos ‡

* ET = 1 : 2-Diethylthioethane (III); ME = 1 : 2-Dimethylthioethane (IV).

† " Non-electrolyte " means $\Lambda_M < 0{\cdot}5$ mho. ‡ Concentration is M/28,000.

EXPERIMENTAL

Chelate Groups.—1 : 2-Dimethylthioethane was prepared according to the method of Morgan and Ledbury.[7] The 1 : 2-diethylthioethane was made in a similar manner from ethanethiol and ethylene dibromide. The purified product boils at 211°.

Bis-(1 : *2-dimethylthioethane*)*dichloronickel*(II).—Nickel chloride hexahydrate (1·8 g.), dissolved in the minimum volume of alcohol, was treated with the chelating agent (1·85 g.) and the green product which separated (1·9 g.) was washed with alcohol and ether (Found : C, 25·7; H, 5·4; Ni, 15·7. $C_8H_{20}Cl_2S_4Ni$ requires C, 25·7; H, 5·36; Ni, 15·7%). On heating, the *compound* decomposes at 180° without melting. It is decomposed by cold water and boiling ethanol. The complex is slightly soluble in chloroform but practically insoluble in alcohol, benzene, ether, or nitrobenzene. Owing to decomposition in hot chloroform, ebullioscopic determination of the molecular weight was not possible.

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[16] Kabesh and Nyholm, *J.*, 1951, 3245.

[17] Sandell " Colorimetric Determination of Traces of Metals," Interscience, London, 1950, p. 130.

Bis-(1 : 2-*dimethylthioethane*)*dibromonickel*(II).—This was prepared as for the corresponding chloride by use of nickel bromide trihydrate (1·4 g.) and the chelate group (1·25 g.); yield 2·05 g. (Found: C, 21·1; H, 4·4; S, 28·0; Ni, 12·6%; *M*, ebullioscopic in $CHCl_3$ in 0·63% solution, 432, in 1·19% solution, 458. $C_8H_{20}Br_2S_4Ni$ requires C, 20·8; H, 4·32; S, 27·7; Ni, 12·7%; *M*, 463). The bright green *compound* melts at 207° (decomp.). Like the chloride, it is only slightly soluble in most solvents but in chloroform it dissolves sufficiently to permit of molecular-weight measurements.

Bis-(1 : 2-*dimethylthioethane*)*di-iodonickel*(II).—This was prepared as for the corresponding chloride and bromide from nickel iodide (1·56 g.) and the chelating agent (1·3 g.), the *compound* separating immediately as bright yellow crystals (2·2 g.) (Found: C, 17·2; H, 3·8; Ni, 10·3%; *M*, ebullioscopic in $CHCl_3$ in 0·73% solution, 555, in 0·56% solution, 568. $C_8H_{20}I_2S_4Ni$ requires C, 17·2; H, 3·6; Ni, 10·5%; *M*, 557). On heating, the compound melts at 187° (decomp.).

Iodine Oxidation Product of $[(Ni(Chelate)_2I_2]^0$.—Bis-(1 : 2-dimethylthioethane)di-iodonickel(II) (2·8 g.), prepared as above, was dissolved in chloroform (100 ml.) and treated with iodine (1·5 g.), black needles (2·9 g.) separating immediately (Found: C, 11·95; H, 2·6; Ni, 7·71. $C_8H_{20}I_4S_4Ni$ requires C, 11·8; H, 2·46; Ni, 7·21%). Since the magnetic moment indicated two unpaired electrons ($\mu_{eff.} = 2·96$ B.M.) and hence a bivalent nickel atom, the *complex* is apparently a polyiodide of bivalent nickel and hence it was not further investigated: chlorine and bromine were also tried as oxidants but caused decomposition of the complexes.

Bis-(1 : 2-*diethylthioethane*)*dichloronickel*(II).—Nickel chloride hexahydrate (1·8 g.) in alcohol was treated with the chelating agent (2·0 g.), and the green solution concentrated to 5 ml. by heating and stored in a desiccator. Green crystals separated, consisting of the *complex* contaminated with nickel chloride. These were filtered off and washed with a small amount of absolute alcohol (Found: C, 32·4; H, 6·3; Ni, 14·2. $C_{12}H_{28}Cl_2S_4Ni$ requires C, 32·4; H, 6·57; Ni, 13·7%); m. p. 116—118° (decomp.). The complex is decomposed in the cold by alcohol, acetone, and water and undergoes slow decomposition in the solid state.

Bis-(1 : 2-*diethylthioethane*)*dibromonickel*(II).—Nickel bromide trihydrate (1·4 g.) in alcohol was treated with the chelating agent (1·5 g.) and the product worked up as above. The green crystals of the *bromide* (2·0 g.) were filtered off and purified by washing with absolute alcohol (Found: C, 27·2; H, 5·25; Ni, 11·2. $C_{12}H_{28}Br_2S_4Ni$ requires C, 27·77; H, 5·44; Ni, 11·32%).

Bis-(1 : 2-*diethylthioethane*)*di-iodonickel*(II).—Nickel iodide hexahydrate (1·6 g.) in alcohol (20 ml.) was treated with the thio-ether (1·5 g.), the solution turning yellow immediately and depositing golden-yellow crystals (2·0 g.) of the required *complex*, which darkened on standing (Found: C, 23·5; H, 4·6; Ni, 9·4. $C_{12}H_{28}I_2S_4Ni$ requires C, 23·51; H, 4·60; N, 9·58%). The compound melts at 177·9° (decomp.). It is more stable than the bromide and chloride, presumably owing to its lower solubility.

Tris-(1 : 2-*diethylthioethane*)*nickel*(II) *Perchlorate*.—Nickel perchlorate hexahydrate (2 g.) in alcohol (10 ml.) was treated with the sulphide (2·6 g.). The green solution was stored in a vacuum desiccator over calcium chloride, to remove the alcohol. The residue, containing the blue crystals of the *complex* together with nickel perchlorate, was washed with absolute alcohol (3—4 ml.) at 0° and then with a minimum of ether (Found: C, 29·4; H, 5·5; Ni, 8·4. $C_{18}H_{42}O_8Cl_2S_6Ni$ requires C, 30·5; H, 5·98; Ni, 8·29%). On heating, the compound darkens at 154° and decomposes at 172—176°. The perchlorate is much less stable and is more soluble than the corresponding halides. It is readily decomposed by alcohol, acetone, and water.

Attempts to form the quadricovalent nickel(II) compound $[Ni(Chelate)_2][ClO_4]_2$ by treating nickel perchlorate with two mols. of chelate group were unsuccessful. The product always consisted of the tris-form contaminated with large amounts of nickel perchlorate, and most of the complex decomposed before all the nickel perchlorate could be removed by washing with alcohol.

Analysis.—Nickel was determined by destroying the organic material of the complex with concentrated sulphuric acid containing 70% perchloric acid (0·1 ml.), the nickel then being estimated electrolytically. An alternative method used in some cases involving simple ignition to nickel oxide gave similar results. Some carbon, hydrogen, and sulphur microanalyses were carried out by Dr. E. Challen. Magnetic susceptibilities were determined by the Gouy method.

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