

215. Complexes of Nickel and Cobalt with Certain Chelate Compounds.

By S. E. LIVINGSTONE.

Four-covalent neutral complexes of bivalent nickel and cobalt with seven chelate compounds have been prepared and the magnetic moments of the crystalline products determined.

The complexes can be divided into classes: (a) those with moments corresponding to "ionic" or tetrahedral bonding (sp^3), and (b) those corresponding to "covalent" or square bonding (dsp^2). The former contain oxygen as one of the ligand atoms of the chelate group, and the latter have sulphur, together with nitrogen, sulphur, or arsenic linked to the metal atom.

In this investigation neutral complexes of bivalent nickel and cobalt with several chelate compounds have been prepared, and their stereochemistry inferred from the magnetic moments.

The quadridentate compound, 1 : 2-di-(*o*-carboxyphenylthio)ethane, $\text{HO}_2\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ gave insoluble crystalline complexes with both nickel and cobalt. *o*-Methylthio-benzoic acid appears not to co-ordinate with these metals, probably because the entropy of formation is greater with the quadridentate ligand; this has been suggested as one of the main reasons for the relatively greater stabilities of complexes containing polydentate ligands (Burkin, *Quart. Rev.*, 1951, 5, 1).

Bis-3-dimethylarsinopropane-1-thiolnickel is remarkable in that the amorphous brown product recrystallizes from alcohol as well-formed green prisms, which are very soluble in chloroform, acetone, alcohol, and nitrobenzene, forming deep brown solutions. Moreover, the compound is diamagnetic, whereas four-covalent Ni^{II} complexes, when diamagnetic, are usually red, brown, or yellow, and when paramagnetic are green or blue (Nyholm, *Chem. Rev.*, 1953, 53, 263). The values for the molecular weight, determined cryoscopically in nitrobenzene (438, 422), correspond to that expected for the formula $\text{Ni}(\text{C}_5\text{H}_{12}\text{SAs})_2$, viz., 417.

The nickel complex of 3-ethylthiopropene-1-thiol and the cobalt complex of 3-dimethylarsinopropane-1-thiol were isolated as brown oils, the latter contaminated with excess of thiol. These oils were readily soluble in chloroform, but did not crystallize. The chelate compound, *o*-carboxyphenyldimethylarsine, $\text{AsMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, which forms a well-defined crystalline complex with palladium (Livingstone and Plowman, *J. Proc. Roy. Soc. New South Wales*, 1950, 84, 188), does not appear to co-ordinate with nickel and cobalt.

The nickel complex of *o*-aminophenol was isolated as the dihydrate (the grey crystals are stable at 120°, but in 45 min. at 145° lose the water to leave a brownish-black powder). The complex is paramagnetic in both forms (3.2 B.M.). The magnetic moment of the cobalt complex is 4.3 B.M. Mellor and Craig (*ibid.*, 1940, 74, 475, 493) reported the nickel complex as diamagnetic and the cobalt complex with a moment of 2.5 B.M.; these values must be regarded as unreliable.

The predicted magnetic moments (μ) for bivalent nickel and cobalt, calculated from the spin-only formula, i.e., $\mu = n(n + 2)$ Bohr magnetons, where n is the number of unpaired electrons, are listed in Table I.

TABLE I. Predicted magnetic moments for bivalent nickel and cobalt.

	No. of unpaired electrons	μ (B.M.)		No. of unpaired electrons	μ (B.M.)
Planar Ni^{II} (dsp^2)	0	0	Planar Co^{II} (dsp^2)	1	1.73
Tetrahedral Ni^{II} (sp^3)	2	2.83	Tetrahedral Co^{II} (sp^3)	3	3.87

The complexes prepared in this investigation and the magnetic data are listed in Tables 2 and 3. It was suggested by Mellor (*Chem. Rev.*, 1943, 33, 317; *J. Proc. Roy. Soc. New South Wales*, 1945, 79, 141) that if an element can form square complexes it will do so unless (i) it is octahedrally co-ordinated, (ii) steric effects distort the bond angles, or

(iii) the attached atom is sufficiently electronegative to favour ionic or tetrahedral bonding. When due allowance is made for the orbital contribution to the magnetic moment, which is usually high for bivalent cobalt, an examination of Tables 2 and 3 shows that where a very electronegative atom (*i.e.*, oxygen) is attached to the metal atom, the complex has a moment corresponding to a tetrahedral configuration. On the other hand, when less electronegative atoms are bonded (*i.e.*, sulphur and nitrogen, sulphur and arsenic), a

TABLE 2. *Magnetic susceptibilities of nickel complexes.*

	Colour	$10^6\chi$	$10^6\chi_m$	$10^6\chi_m$ (corr. for diamagnetism)	μ (B.M.)
1 : 2-Di-(<i>o</i> -carboxyphenylthio)ethane ...	Pale green	9.75	4151	4452	3.22
Anthranilic acid	Pale blue	12.40	4110	4327	3.20
<i>o</i> -Aminophenol	Grey	13.52	4208	445.4	3.22
<i>o</i> -Aminobenzenethiol	Greyish-yellow	-0.47	-144	—	0
<i>o</i> -Methylthiobenzenethiol	Orange	-0.25	-93	—	0
3-Dimethylarsinopropane-1-thiol	Green	-0.34	-144	—	0
3-Ethylthiopropene-1-thiol	Brown oil	-0.57	-186	—	0

TABLE 3. *Magnetic susceptibilities of cobalt complexes.*

	Colour	$10^6\chi$	$10^6\chi_m$	$10^6\chi_m$ (corr. for diamagnetism)	μ (B.M.)
1 : 2-Di-(<i>o</i> -carboxyphenylthio)ethane	Pink	27.61	10,800	11,050	5.09
Anthranilic acid	Pink	32.40	10,720	10,940	5.05
<i>o</i> -Aminophenol	Pink	26.28	7700	7907	4.03
<i>o</i> -Aminobenzenethiol	Dark blue	8.65	2660	2871	2.6
3-Ethylthiopropene-1-thiol	Dark green	6.94	2382	2566	2.44

square complex results. Nyholm (*Chem. Rev.*, 1953, 53, 263) suggested that double bonding between the ligand atom and the metal atom is also an important factor favouring the square configuration. Craig, Maccoll, Nyholm, Orgel, and Sutton (*J.*, 1954, 332) state that two strong π -bonds can be formed at right angles, using $3d$ electron pairs of a transition metal atom and vacant p or d orbitals on the ligand atom. It is interesting that ligands containing atoms or groups capable of forming double bonds with the metal atom, *e.g.*, S, As, CN, do form square planar complexes with bivalent nickel and cobalt.

EXPERIMENTAL

1 : 2-Di-(*o*-carboxyphenylthio)ethanenickel(II) Dihydrate.—1 : 2-Di-(*o*-carboxyphenylthio)ethane (1 g.) was treated with one equiv. of 0.5M-sodium hydroxide and the small amount of undissolved material removed by filtration. To the hot filtrate was added a solution of nickel acetate tetrahydrate (0.5 g.) in water (20 ml.). After some minutes at the b. p., pale green crystals were precipitated. On cooling, the *nickel complex* was filtered off, washed with a small amount of hot water, then acetone, and dried over phosphoric oxide *in vacuo*. It (0.40 g.) was practically insoluble in hot water and organic solvents (Found : C, 45.4; H, 3.6; Ni, 13.4. $C_{16}H_{12}O_4S_2Ni \cdot 2H_2O$ requires C, 45.0; H, 3.8; Ni, 13.7%).

Bisanthranilatonicel(II).—Anthranilic acid (3 g.) was dissolved in boiling water (100 ml.), and an aqueous solution (20 ml.) of nickel nitrate hexahydrate (3 g.) added. After 30 sec. a crystalline precipitate began to be formed. The mixture was kept at the b. p. for 10 min. and then filtered. The pale blue crystals (12.5 g.) were washed with hot water, then acetone. The addition of sodium acetate to the filtrate precipitated more of the *compound* (Found : C, 51.0; H, 3.7; N, 8.7. $C_{14}H_{12}O_4N_2Ni$ requires C, 50.8; H, 3.7; N, 8.5%).

Bis-o-aminophenolnickel(II) Dihydrate.—This compound was prepared by a method similar to that used by Hieber and Schnackig (*Z. anorg. Chem.*, 1936, 226, 209) (Found : C, 45.9; H, 5.1; N, 9.1; Ni, 18.9. Calc. for $C_{12}H_{12}O_2N_2Ni \cdot 2H_2O$: C, 46.3; H, 5.2; N, 9.0; Ni, 18.9%).

Bis-o-aminobenzenethiolnickel(II).—This compound has been described by Hieber and Bruck (*ibid.*, 1952, 269, 13). The yellowish-grey complex was precipitated by the addition of *o*-aminobenzenethiol to an aqueous solution of nickel nitrate (Found : C, 46.9; H, 4.1; N, 9.1; Ni, 19.4. Calc. for $C_{12}H_{12}N_2S_2Ni$: C, 46.9; H, 3.9; N, 9.1; Ni, 19.1%).

Bis-o-methylthiobenzenethiolnickel(II).—*o*-Methylthiobenzenethiol (0.5 g.) was treated with one equiv. of 0.5M-sodium hydroxide, and an aqueous solution of nickel acetate (0.3 g.) added. A yellowish-brown microcrystalline precipitate (0.53 g.) was produced, which recrystallized from 70% acetone (50 ml.) as orange cubes (0.37 g.). The *nickel complex* is readily soluble in

acetone, chloroform, and nitrobenzene producing brown solutions; it had m. p. 171° (with decomp.) (Found: C, 45.3; H, 3.6; Ni, 16.3. $C_{14}H_{14}S_4Ni$ requires C, 45.5; H, 3.8; Ni, 15.9%). Conductivity at 20°: Λ_{500} in acetone, 0.01 mho; Λ_{500} in nitrobenzene, 0.

Bis-3-dimethylarsinopropane-1-thiolnickel(II).—3-Dimethylarsinopropane-1-thiol (1.0 g.) was treated with one equiv. of 0.5M-sodium hydroxide, and an aqueous solution of nickel acetate (0.38 g.) added. An amorphous brown precipitate slowly became green and crystalline. It was recrystallized from a few millilitres of alcohol, yielding green prisms (0.35 g.), m. p. 85–86°. The compound is readily soluble in chloroform, acetone, alcohol, and nitrobenzene to deep brown solutions (Found: C, 28.6; H, 5.7; Ni, 14.0%; *M*, cryoscopically in nitrobenzene, 438 in 0.44% and 422 in 0.30% solution. $C_{10}H_{24}S_2As_2Ni$ requires C, 28.8; H, 5.8; Ni, 14.1%; *M*, 417). The molecular conductivity at 25° of a $10^{-3}M$ -solution of the compound in nitrobenzene was 0.1 mho.

Reaction of 3-Ethylthiopropene-1-thiol with Ni(II).—A suspension of the thiol (1.37 g.) in water (30 ml.) containing sodium hydroxide (0.25 g.) was treated with an aqueous solution of nickel nitrate hexahydrate (1.5 g.). There was an immediate formation of a reddish-brown oil which was extracted by chloroform (50 ml.). The extract was dried (Na_2SO_4) and evaporated, leaving a viscous dark reddish-brown oil, which was diamagnetic with $\chi_g = -0.57 \times 10^{-6}$.

1: 2-Di-(*o*-carboxyphenylthio)ethanecobalt(II).—1: 2-Di-(*o*-carboxyphenylthio)ethane (0.8 g.) was treated with one equiv. of 0.5M-sodium hydroxide, and the solution was filtered. The filtrate was poured into a warm solution of cobaltous acetate tetrahydrate (0.6 g.) in water (30 ml.), producing a purplish-pink amorphous precipitate, which was converted into pink prisms when the mixture was boiled for some time. The product (0.45 g.) was washed with boiling water, then acetone, and dried (Found: C, 48.6; H, 3.1; Co, 15.0. $C_{16}H_{12}O_4S_2Co$ requires C, 49.1; H, 3.1; Co, 15.1%).

Bisanthranylato-cobalt(II).—This compound was prepared from cobalt acetate and anthranilic acid in 50% alcoholic solution (Found: C, 49.9; H, 3.7; N, 8.4; Co, 17.6. Calc. for $C_{14}H_{12}O_4N_2Co$: C, 50.8; H, 3.7; N, 8.5; Co, 17.8%).

*Bis-*o*-aminophenolcobalt(II) Monohydrate*.—This compound was prepared from cobalt acetate and *o*-aminophenol in aqueous-alcoholic solution (Found: C, 48.5; H, 4.9; N, 9.4. Calc. for $C_{12}H_{12}O_2N_2Co \cdot H_2O$: C, 49.1; H, 4.8; N, 9.5%).

*Bis-*o*-aminobenzenethiolcobalt(II)*.—*o*-Aminobenzenethiol (2.0 g.), in alcohol (10 ml.), was added to cobaltous acetate tetrahydrate (2.0 g.) in 50% aqueous alcohol (50 ml.) at 50°. The immediate amorphous brown precipitate was filtered off and boiled with acetone (250 ml.) for 2 hr., whereupon it became dark blue and crystalline. The compound was again filtered off, washed with acetone, in which it is very sparingly soluble, and dried at 110° (yield, 2.0 g.). It slowly darkens in air owing to oxidation (Found: C, 46.7; H, 3.8; N, 9.2. $C_{12}H_{12}N_2S_2Co$ requires C, 46.9; H, 3.9; N, 9.1%).

Reaction of 3-Dimethylarsinopropane-1-thiol with Co(II).—3-Dimethylarsinopropane-1-thiol (1.52 g.) in alcohol (10 ml.) was added to cobalt acetate tetrahydrate (1.0 g.) in 50% alcohol (40 ml.). A brown oil, containing the cobalt complex dissolved in excess of the thiol, was produced. The oil is soluble in chloroform to a yellowish-brown solution. The complex could not be obtained free from the thiol.

Bis-(3-ethylthiopropene-1-thiol)cobalt(II).—Cobalt acetate tetrahydrate (1.4 g.), in warm 50% alcohol (40 ml.), was treated with the thiol (1.5 g.) in alcohol (10 ml.). An amorphous pinkish-purple product was precipitated, which crystallized when the mixture was warmed. The complex was filtered off, washed with boiling water, and boiled with acetone (50 ml.), then filtered off again and dried (yield, 0.9 g.). The dark green iridescent crystals had a reddish-purple "streak" and were only very sparingly soluble in acetone to a reddish-purple solution. They do not melt below 250° (Found: C, 37.1; H, 6.9. $C_{10}H_{22}S_4Co$ requires C, 36.5; H, 6.8%).

Magnetic Susceptibility Measurements.—The Gouy method was employed, with a balance similar to that described by Baddar, Hilal, and Sugden (*J.*, 1949, 132). The measurements were made on the compounds in powder form at room temperature (289–294° K) (except when the compound was an oil; in this instance the measurement was made on the crude oil).

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