## **1102.** Complexes of Bivalent Cobalt with 8-Hydroxyquinoline.

#### By S. LENZER.

The following 8-hydroxyquinoline (Hox) complexes of cobalt(II) have been prepared:  $[Co_2(ox)_3NO_3]$ ,  $[Co(ox)(Hox)_2](NO_3)$ ,  $[Co_2(ox)_3(Hox)_3](ClO_4)$ ,  $H_2O$ , and [H<sub>2</sub>ox]<sub>2</sub>[CoCl<sub>4</sub>]. Magnetic susceptibility measurements and solid reflectance spectra indicate an octahedral configuration about the cobalt atoms in all complexes except in the last compound, which contains the tetrahedral tetrachlorocobaltate(II) anion.  $[Co_2(ox)_3NO_3]$ , being a non-electrolyte and only sparingly soluble, probably has a polymeric octahedral structure.  $[Co(ox)(Hox)_2](NO_3)$ , on the other hand, contains a mononuclear octahedral cation in which the ligand molecule as well as its derived anion act as bidentate chelates. The perchlorate contains a binuclear cation in which the ligand molecules form bridges between two cobalt atoms. The octahedral cobalt(II) complexes  $[Co(ox)_2 2py]H_2O$  and  $[Co(ox)_2 phen]$  (where py = pyridine and phen = 1,10-phenanthroline) have also been prepared and their magnetic susceptibilities measured.

COMPLEXES of bivalent copper with 8-hydroxyquinoline which were described earlier<sup>1</sup> were assigned a binuclear structure based on their anomalous paramagnetism. This paper reports some compounds formed by bivalent cobalt and this ligand.

The familiar complex of bivalent cobalt and 8-hydroxyquinoline (I) (Hox) is the yelloworange bis-(8-hydroxyquinolato)cobalt(II) dihydrate.<sup>2</sup> The 8-hydroxyquinolato-anion (ox) has been shown to act as a bidentate chelate in the corresponding zinc(II) complex<sup>3</sup> and copper(II) complex,<sup>4</sup> for which the structures are known. The oxygen and nitrogen atoms of two anions are arranged in a square plane around the metal atoms with the two water molecules further away completing a distorted octahedron. An analogous octahedral arrangement (II) of the bivalent cobalt in  $[Co(ox)_22H_2O]$  can be inferred from its composition, magnetic moment (4.59 Bohr magnetons) (Table 1), and solid reflectance spectrum (see Fig. 1).

<sup>&</sup>lt;sup>1</sup> Harris, Kokot, Lenzer, and Lockyer, Chem. and Ind., 1962, 651.

<sup>&</sup>lt;sup>2</sup> Hollingshead, "Oxine and its Derivatives," Butterworth's Scientific Publications, London, 1954, vol. 1, p. 227. <sup>3</sup> Merrit, Cady, and Mundy, Acta Cryst., 1954, 7, 473.

<sup>4</sup> Kruh and Dwiggins, J. Amer. Chem. Soc., 1955, 77, 806.

5769

The two water molecules are not affected by drying at  $100^{\circ}$  but are removed by azeotropic distillation in benzene. The anhydrous compound is an orange-yellow powder, which closely resembles its dihydrate in colour and magnetic moment (4.55 Bohr magnetons). Obviously,



no drastic change in the stereochemical environment of the cobalt atoms has taken place, and the anhydrous compound probably has a polymeric six-covalent structure. This can readily occur by oxygen atoms from adjacent square molecules completing a polymeric octahedral arrangement about the cobalt atoms (III).

TABLE 1.

Magnetic susceptibilities of cobalt(II) complexes of 8-hydroxyquinoline.

T ......

		remp.				
Compound	Colour	(к°)	10 <sup>6</sup> χ <sub>g</sub>	10 <sup>6</sup> ∆*	10 <sup>6</sup> χm	μ B.M.
$[Co(ox)_2 2H_2 O]$	y-orange	300	22.47	110	8722	4.59
Co(ox)2]	pale orange	290.5	$25 \cdot 23$	84	8844	4.55
$[Co(ox)_2 2pv], H_2O$	orange	299	17.73	193	9483	4.78
[Co(ox) <sub>2</sub> phen]	bright red	299	16.04	<b>34</b> 0	9098	4.69
$\left[Co_{2}(0x)_{3}NO_{3}\right]$	red flakes	298	27.16	142	8457	4.51
Co(ox) (Hox) 2](NO3)	orange-red	291.5	17.47	267	9968	4.84
$[Co_2(o_X)_3(Ho_X)_3](ClO_4)H_2O$	orange-red	298	17.77	<b>275</b>	9917	<b>4</b> ⋅88
Cos(ox)s(Hox)Cl <sub>4</sub> ]	bluish-black	298	29.15	147	8857	4.61
[H <sub>2</sub> ox] <sub>2</sub> [CoCl <sub>4</sub> ]	bright blue	297	19.55	<b>279</b>	10,209	4.95

\* Including diamagnetic correction for M<sup>2+</sup>.

The water molecules in  $[Co(ox)_22H_2O]$  can be replaced by ligands that are more strongly basic: pyridine readily dissolves the otherwise very sparingly soluble compound and forms a deep-red solution; this deposits no crystals on standing, but the addition of a small quantity of water precipitates an orange compound, which has the composition  $[Co(ox)_22py]H_2O$ .



Similarly, the reaction of  $[Co(ox)_22H_2O]$  with one mole of 1,10-phenanthroline (phen) in alcohol or benzene produces the bright red  $[Co(ox)_2phen]$ . In this reaction, rearrangement of the two 8-hydroxyquinolato-anions has apparently occurred, since 1,10-phenanthroline, owing to its rigid nature, must occupy a *cis*-octahedral position (IV).

#### Lenzer: Complexes of

The reaction of 8-hydroxyquinoline with cobalt(II) salts in ethanol leads to different types of compounds. According to the conditions, the ligand can function as a bidentate or monodentate chelate or as a bridge between cobalt atoms, forming binuclear structures.

When 8-hydroxyquinoline and cobalt(II) nitrate hexahydrate reacted in the ratio of not more than one mole of ligand to one mole of salt in ethanol, a deep-red solution was formed.



When the mixture was refluxed, shiny red crystals with the composition  $[Co_2(ox)_3NO_3]$  were precipitated. The compound has a magnetic moment of 4.51 Bohr magnetons per cobalt atom; it is practically insoluble in the common solvents, and it is a non-electrolyte in nitrobenzene solution. In order to obtain further evidence for the presence of nitrato-groups, the infrared spectrum of this compound was examined. The infrared spectra of some nitratoco-ordination complexes have been previously investigated, and it has been shown<sup>5</sup> that strong absorption bands, which do not occur in ionic nitrates, appear in the regions 1530—1480,



1290—1250, and 1034—970 cm<sup>-1</sup>. These absorptions arise from the vibrations due to NO<sub>2</sub> asymmetric stretching, NO<sub>2</sub> symmetric stretching and  $-O-NO_2$  stretching, respectively. In  $[Co_2(ox)_3NO_3]$  a strong absorption maximum occurs at 1506 cm.<sup>-1</sup>, but the ligand itself absorbs in the same region, since a similarly strong maximum at 1497 cm.<sup>-1</sup> is found in  $[Co(ox)_22H_2O]$ . However, in  $[Co_2(ox)_3NO_3]$  another very strong maximum occurs at 1268 cm.<sup>-1</sup>, and a medium one at 1020 cm.<sup>-1</sup>, but no corresponding absorption maxima occur in  $[Co(ox)_22H_2O]$ . These two peaks must therefore be due to the presence of nitrato-groups and exclude an ionic nitrate. The complex could be formed by a sequence of the following or similar reactions, involving the solvated (solv.) cobalt(II) ion,

<sup>&</sup>lt;sup>5</sup> Gatehouse, Livingstone, and Nyholm, J., 1957, 4222.

When the solution containing the co-ordinatively unsaturated species (V) and (VI) is refluxed, the two condense to form binuclear complexes by sharing the oxygen atoms of the 8-hydroxyquinolato-anion,



The cobalt atoms can complete their octahedral co-ordination by a polymeric arrangement, *i.e.*, by stacking the binuclear units as indicated diagrammatically (VII). The postulated octahedral environment of the cobalt atoms is compatible with their magnetic moments and solid reflectance spectrum (see Fig. 1), and the polymeric structure with the low solubility of the compound. In this structure, the nitrato-groups act as bridging groups between two cobalt atoms, as well as occupying two co-ordination positions in one cobalt atom. Bridging nitrato-groups are known to occur in anhydrous copper(II) nitrate.<sup>6</sup> The nitrato-group acts as a bidentate ligand in certain uranium(VI) nitrate complexes, *e.g.*, rubidium uranylnitrate<sup>7</sup> and bis(triethyl phosphato)uranyl nitrate.<sup>8</sup>



The reaction of 4 moles of 8-hydroxyquinoline with 1 mole of cobalt(II) nitrate hexahydrate in ethanol at room temperature produced immediately an orange-coloured crystalline precipitate with the composition  $[Co(ox) (Hox)_2] (NO_3)$ . Excess of 8-hydroxyquinoline is apparently necessary in order to accept a proton from one 8-hydroxyquinoline molecule, which then acts as an anionic ligand,  $2 \text{ Hox} \Rightarrow ox^- + \text{H}_2^+ ox$ . Two other 8-hydroxyquinoline molecules act as neutral ligands leaving the complex ion with one positive charge. In spite of the simplicity of its preparation, it was not possible to obtain the compound completely pure, because small amounts of the ligand are always coprecipitated; further purification by recrystallization was not successful. The compound is soluble in many common solvents, but the solution decomposes slowly in the cold and quickly on warming. Its colour, solid reflectance spectrum (see Fig. 1), and magnetic moment (4-84 Bohr magnetons) indicate an octahedral environment of the cobalt atoms (VIII). Its conductivity in nitrobenzene and nitromethane is much less than expected for a uni-univalent electrolyte (see Table 2). In order

- 6 Wallwork, Proc. Chem. Soc., 1959, 311.
- 7 Hoard and Stroupe, Nat. Nucl. En. Series, Div. 3, vol. 2, ch. 2, p. 15.
- <sup>8</sup> Fleming and Lynton, Chem. and Ind., 1960, 1415.

TABLE 2.

Molecular conductivities of cobalt(II) complexes of 8-hydroxyquinoline.

Compound	${\it A_{1000} \ { m in \ PhNO_2} \ { m at \ 25^{\circ} \ (mho)}}$	Λ <sub>1000</sub> in MeNO <sub>2</sub> at 25° (mho)
$[Co_2(ox)_3(Hox)_3](ClO_4), H_2O$	26.5	81.6
$[Co(ox)(Hox)_2](NO_3)$	<u> </u>	28.5
	$\Lambda_{2000}  ext{ in PhNO}_2  ext{ at } 25^\circ  ext{ (mho)}$	$egin{array}{c} arLambda_{2000}  ext{ in MeNO}_2 \  ext{ at } 25^\circ  ext{ (mho)} \end{array}$
$[Co(ox) (Hox)_2](NO_3)$	11.0	_
$[Co_2(ox)_3NO_3]$	2.4	insoluble
[H <sub>2</sub> OX] <sub>2</sub> [CoCl <sub>4</sub> ]	12.3	77

to substantiate the presence of an ionic nitrate group, the infrared spectrum of this compound was examined. Spectra of ionic nitrates including  $Co(NO_3)_2, 6H_2O$  have been reported,<sup>9</sup> and it has been shown that they are characterized by a region of very strong absorption at 1390— 1350 cm.<sup>-1</sup> and one of medium intensity at 836—815 cm.<sup>-1</sup>.  $[Co(ox) (Hox)_2](NO_3)$  has two very strong absorption peaks at 1374 and 824 cm.<sup>-1</sup>, but  $[Co(ox)_22H_2O]$  has also two very intense maxima at 1372 and 821 cm.<sup>-1</sup>, and the absorption due to the ligand masks the absorption due to the nitrate groups. However,  $[Co(ox) (Hox)_2](NO_3)$  has no absorption maxima in the regions 1290—1250 and 1034—970 cm.<sup>-1</sup>, which are indicative of the presence of a nitratogroup, and the absence of these peaks supports the presence of an ionic nitrate. The low conductivity of the compound in nitrobenzene or nitromethane may be due to ion-pair formation or hydrogen-bonding in solution.



The reaction of cobalt(II) perchlorate and 8-hydroxyquinoline, provided that the ratio of metal atoms to ligand did not exceed one to two, produced a red solution, but no crystals were obtained either at room temperature or on refluxing. When the ligand ratio was increased to four moles per cobalt atom, an orange crystalline precipitate with the composition  $[Co_2(ox)_3(Hox)_3](ClO_4),H_2O$  formed immediately at room temperature. No mononuclear perchlorate analogous to the nitrate could be obtained. The perchlorate is a uniunivalent electrolyte in nitrobenzene and nitromethane (see Table 2). Its colour, solid reflectance spectrum (see Fig. 2) and magnetic moment (4-88 Bohr magnetons) are indicative of an octahedral environment for the cobalt atoms. In the binuclear cation (IX), two cobalt atoms are probably bridged by two 8-hydroxyquinolato-anions where the oxygen atoms of the ligand could form the bridges.

The reaction products of cobalt(II) chloride hexahydrate and 8-hydroxyquinoline are more complex, since the chlorine atoms as well as the 8-hydroxyquinoline molecules can form bridges between the cobalt atoms producing compounds of higher complexity.

<sup>9</sup> Miller and Wilkins, Analyt. Chem., 1952, 24, 1253.

## [1964]

# Bivalent Cobalt with 8-Hydroxyquinoline. 5773

When one mole of cobalt(II) chloride hexahydrate was treated with 0.5—1.3 moles of 8-hydroxyquinoline in ethanol a deep-blue solution was formed, from which, deep-bluishblack crystals were deposited when it was refluxed. Several preparations obtained with ratios of ligand varied in the above-mentioned limits were identical in appearance, and gave identical analytical results, corresponding to the composition  $[Co_6(ox)_8(Hox)Cl_4]$ . The compound is practically insoluble in all common solvents. The composition suggests that the structure involves binuclear units such as  $Co_2(ox)_3$ : three such units are apparently bridged by four chlorine atoms. Its magnetic moment was determined as 4.61 Bohr magnetons per cobalt atom. From its bluish-black colour one would expect a tetrahedral environment for the cobalt atoms, but the solid reflectance spectrum (see Fig. 2) indicates a smaller maximum displaced to shorter wavelengths than that expected for tetrahedral cobalt compounds. It is possible that some of the cobalt atoms in this compound have a tetrahedral and some an octahedral arrangement.



FIG. 2. Reflectance spectra of solid compounds.

 $\begin{array}{l} IV, \ [Co_{2}(ox)_{3}(Hox)_{3}](ClO_{4})H_{2}O;\\ V, \ [H_{2}ox]_{2}[CoCl_{4}];\\ VI, \ [Co_{6}(ox)_{8}HoxCl_{4}]. \end{array}$ 

After the precipitation of the bluish-black crystals described above, the solution was still deep blue. When ether was added and the solution set aside, green crystals deposited; these were purified by fractional recrystallization with ethanol and ether to give bright bluish-green crystals, which were readily decomposed by water. They were be shown to be bis-(8-hydroxyquinolinium) tetrachlorocobaltate(II)  $[H_2ox]_2[CoCl_4]$ . The colour, solid reflectance spectrum (see Fig. 2), and magnetic moment (4.95 Bohr magnetons) of this compound are indicative of the tetrahedral arrangement of the anion; the conductivity in nitrobenzene and nitromethane is less than expected for a uni-bivalent electrolyte (see Table 2). Low conductivities were previously observed in the tetrahalogeno-complexes  $[Co(As=S)_2] [CoX_4]$  where (X = Br, I) and (As=S) is dimethyl-o-methylthiophenylarsine.<sup>10</sup> In order to explain these anomalous conductivities, it was suggested that, in nitrobenzene solution, an equilibrium existed between the ionic form and two molecules of non-electrolyte,

$$[Co(As-S)_2][CoX_4] \xrightarrow{} 2[Co(AsS)-X_2)$$

However, such an explanation is not applicable to  $[H_2ox]_2[CoCl_4]$ , and the only obvious reason for the anomaly may be the formation of ion-pairs in solution.

#### EXPERIMENTAL

Bis-(8-hydroxyquinolato)cobalt(11) Dihydrate.—To a solution of cobalt chloride hexahydrate (12 g.) in water (100 ml.), 8-hydroxyquinoline (15 g.) dissolved in ethanol (100 ml.) was added. The pinkish precipitate was filtered off, washed with water, and dried at 100° (yield, 9.5 g.) (Found: C, 56.4; H, 4.1; N, 7.5; Co, 15.4. Calc. for  $C_{18}H_{16}O_4N_2Co: C, 56.4;$  H, 4.2; N, 7.3; Co, 15.4%).

Bis-(8-hydroxyquinolato)cobalt(11).—The dihydrate (1 g.) was refluxed with benzene (50 ml.) for 1 hr., a Dean-Stark attachment being used. The fine orange-yellow powder was filtered off,

<sup>10</sup> Chiswell and Livingstone, J., 1960, 97.

washed with ethanol and ether, and dried ( $P_2O_5$ ) (yield, 0.75 g.) (Found: C, 62.0; H, 3.5; N, 8.4; Co, 16.8. Calc. for  $C_{18}H_{12}O_2N_2Co: C, 62.3; H, 3.5; N, 8.1; Co, 17.0\%$ ).

Bis-(8-hydroxyquinolato)dipyridinecobalt(II) Monohydrate.—The dihydrate (1 g.) was dissolved in pyridine (10 ml.) and water added dropwise until an orange precipitate began to form. This was filtered, washed twice with ether, and dried *in vacuo* ( $P_2O_5$ ) (yield, 1.07 g.) (Found: C, 64.4; H, 4.6; N, 10.8; Co, 11.6. C<sub>28</sub>H<sub>24</sub>O<sub>3</sub>N<sub>4</sub>Co requires C, 64.2; H, 4.6; N, 10.7; Co, 11.3).

Bis-(8-hydroxyquinolato)-1,10-phenanthrolinecobalt(11).—The dihydrate (1 g.) and 1,10-phenanthroline monohydrate (0.6 g.) were refluxed with ethanol (20 ml.) for 1 hr. The orange-yellow compound turned bright red without apparent solution. It was filtered, washed with ethanol and ether, and dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>) (yield, 1.26 g.) (Found: C, 68.0; H, 3.8; N, 10.4; Co, 11.1.  $C_{30}H_{20}O_2N_4Co$  requires C, 68.3; H, 3.8; N, 10.6; Co, 11.2%).

The Complex  $[Co_2(ox)_3NO_3]$ .—Cobalt nitrate hexahydrate (5 g.) dissolved in ethanol (100 ml.) was mixed with 8-hydroxyquinoline (2 g.) in ethanol (75 ml). The red solution was refluxed until shiny red flaky crystals were precipitated. They were filtered off, washed with alcohol and ether and dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>) (yield, 0.65 g.) (Found: C, 53.2; H, 3.3; N, 9.1; Co, 18.6. C<sub>27</sub>H<sub>18</sub>O<sub>6</sub>N<sub>4</sub>Co<sub>2</sub> requires C, 53.0; H, 2.9; N, 9.2; Co, 19.2%).

Bis-(8-hydroxyquinoline)-8-hydroxyquinolatocobalt(11) Nitrate.—To a solution of cobalt nitrate hexahydrate (3.67 g.) in ethanol (20 ml.) were added 8-hydroxyquinoline (7.5 g.) dissolved in ethanol (100 ml.). Deep orange-red crystals were precipitated from the deep red solution after several hours. They were filtered off, washed with ethanol and ether, and dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>) (yield, 2.46 g.) (Found: C, 59.4; H, 3.6; N, 9.8; Co, 10.7.  $C_{27}H_{20}O_6N_4Co$  requires C, 58.4; H, 3.6; N, 10.1; Co, 10.6%).

The Complex  $[Co_2(ox)_3(Hox)_3](ClO_4), H_2O.$ —To a solution of cobalt perchlorate hexahydrate (3.7 g.) in ethanol (20 ml.) was added 8-hydroxyquinoline (6 g.) in ethanol (50 ml.). A pale orange precipitate formed immediately. It was filtered off, washed with ethanol and ether, and dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>) (yield, 3.8 g.) (Found: C, 59.1; H, 3.6; N, 8.1; Co, 10.8. C<sub>54</sub>H<sub>38</sub>O<sub>11</sub>N<sub>6</sub>ClCo<sub>2</sub> requires C, 59.0; H, 3.5; N, 7.6; Co, 10.7%).

The Complex  $[Co_6(x)_8(Hox)Cl_4]$ .—Cobalt chloride hexahydrate (10 g.) was dissolved in alcohol (30 ml.) and treated with 8-hydroxyquinoline (8 g.) dissolved in ethanol (60 ml.). The solution turned deep blue and, after it had been refluxed for some time, deep bluish-black crystals were formed. They were filtered off, washed with ethanol and ether, and dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>) (yield, 3.65 g.). The deep blue filtrate (excluding the solvents used for washing) was retained for the preparation of  $[H_{2}ox]_2[CoCl_4]$ . Several preparations in which one mole of cobalt chloride was treated with various ratios of ligand in the range of 0.5 moles to 1.3 moles were identical in appearance and analysis, differing only in yield (Found: C, 54.2; H, 3.3; N, 7.1; Cl, 8.1; Co, 20.1.  $C_{81}H_{54}O_9N_9Cl_4Co_8$  requires C, 54.3; H, 3.0; N, 7.0; Cl, 7.9; Co, 19.7%).

Bis-(8-hydroxyquinolinium) Tetrachlorocobaltate(II).—To the deep blue filtrate from the above preparation (90 ml.) ether was added (200 ml.). Deep-green, oily droplets, which slowly changed into green crystals separated from the solution. They were filtered off and dissolved in 30 ml. of ethanol. Addition of 30 ml. of ether to the solution precipitated bright bluish-green crystals. They were filtered, washed with ether, and dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>) (yield, 1·19 g.) (Found: C, 43·8; H, 3·2; N, 6·0; Cl, 28·5; Co, 11·7. C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>Cl<sub>4</sub>Co requires C, 43·9; H, 3·3; N, 5·7; Cl, 28·8; Co, 12·0%).

Magnetic Measurements.—Magnetic measurements were made by the Gouy method on the solid compounds at room temperature. The gram susceptibility,  $\chi_g$ , the molar susceptibility,  $\chi_g$  (corrected for the underlying diamagnetism of all atoms,  $\Delta$ ), and the magnetic moment,  $\mu$ , are set out in Table 1.

Reflectance Spectra.—Reflectance spectra were obtained with a Unicam SP 500 spectrophotometer provided with a reflectance attachment. Magnesium carbonate was used as a standard.

Infrared Spectra.—Infrared spectra were obtained from Nujol mulls, sodium chloride optics being used.

*Electrical Conductivity.*—The electrical conductivity in nitrobenzene and nitromethane was measured at  $25^{\circ}$  by means of a Philips A.C. wheatstone bridge (type PR 9500). The measurements were made at 1000 c./sec., a Philips immersion cell (type GM4221/01) with platinised electrodes being used. The results are recorded in Table 2.

Analyses for carbon, hydrogen, and nitrogen were carried out by Dr. E. Challen of the Microanalytical Laboratory of this University.

DEPARTMENT OF INORGANIC CHEMISTRY, THE UNIVERSITY OF NEW SOUTH WALES, KENSINGTON, SYDNEY, AUSTRALIA. [Received, August 31st, 1964.]