

CXCV.—*Cobalt with a Covalency of Four: A New Series of Complex Compounds.*

By EDMUND GEORGE VINCENT PERCIVAL and WILLIAM WARDLAW.

It is well known that a red aqueous solution of cobaltous chloride turns blue on the addition of concentrated hydrochloric acid or a concentrated solution of an alkali or alkaline-earth chloride. On the other hand, the blue alcoholic solution of cobaltous chloride becomes red when mercuric chloride or zinc chloride is added. Of the theories put forward to account for these striking colour changes, none has received greater attention than that of Donnan and Bassett (J., 1902, **81**, 939), who concluded from the colour move-

ment in their electrolytic experiments and from other physico-chemical data "that it appears highly probable that the blue colour is largely due to complexes such as CoCl_4'' and CoCl_3' ." But they continue: "On the other hand, the colour due to the cobalt atom when outside the immediate sphere of the chlorine atoms appears to be red. Thus the colour produced by the free cobalt kation in aqueous solution is red whilst the red colour of the solid hexahydrate is doubtless due to the fact that the water molecules intervene between the cobalt and chlorine atoms. The colours exhibited by the complex chlorides admit of a simple explanation from this point of view. Thus owing to the greater tendency of zinc to form negative complex groups the zinc double chloride will have the constitution $\text{Co}[\text{ZnCl}_4]$ whilst the calcium double chloride will have the constitution $\text{Ca}[\text{CoCl}_4]$ since cobalt has a greater tendency to form negative complexes than calcium. In agreement with this the former double salt is red whilst the latter is blue."

Corroborative evidence for these views has been furnished by various investigators, e.g., Denham (*Z. physikal. Chem.*, 1909, **65**, 641) and Howell (J., 1927, 158, 2039, 2843; this vol., p. 162).

In a recent communication, Gr6h and Schmid (*Z. anorg. Chem.*, 1927, **162**, 326) state that their physicochemical experiments indicate that cobalt chloride in acetone or propyl alcohol does not form, with lithium chloride or calcium chloride, a series of complex ions but only one, viz., CoCl_4'' . Nevertheless, certain workers have doubted the existence of such complex ions (Kotschubei, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1055; Hantzsch, *Z. anorg. Chem.*, 1927, **159**, 273; **166**, 237), and it is not without interest to find that evidence from phase-rule investigations is opposed to the idea of complex-ion formation.

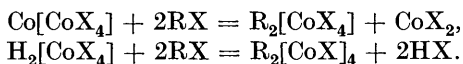
For instance, Mazzetti (*Gazzetta*, 1926, **56**, 601) had shown that for the systems NaCl , KCl , or $\text{BaCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ no double salts are formed which can exist in equilibrium with their saturated aqueous solutions at 20° , and Foote (*Amer. J. Sci.*, 1927, **13**, 158) has confirmed this conclusion for sodium and potassium chlorides in systems at 25° . Benrath (*Z. anorg. Chem.*, 1927, **163**, 396), dealing with the equilibria in the ternary systems $\text{CoCl}_2\text{-MCl}$ (or $\text{MCl}_2\text{-H}_2\text{O}$ at 25°), concludes from his own results and those of Mazzetti and Foote that the blue colour of cobalt solutions containing chlorides of sodium, potassium, ammonium, or alkaline-earth metals "is not in most cases due to double salt formation."

The double salts which have so far been isolated with certainty from solutions of cobaltous chlorides are very limited in number and give no clear indication as to whether the complex anion CoCl_4'' exists. For example, the blue lithium salt has the com-

position $\text{CoCl}_2, 4\text{LiCl}, 10\text{H}_2\text{O}$, and the red compounds the formulæ $2\text{ZnCl}_2, \text{CoCl}_2, 12\text{H}_2\text{O}$ and $2\text{CdCl}_2, \text{CoCl}_2, 12\text{H}_2\text{O}$ (Benrath, *loc. cit.*). Ferrari (*Atti R. Accad. Lincei*, 1928, 7, 848) has shown, however, that the melting-point curve for mixtures of lithium and cobalt chlorides shows a maximum corresponding to the formation of the double salt $2\text{LiCl}, \text{CoCl}_2$.

Definite evidence that the complex ion CoX_4'' does exist has now been obtained by the isolation of crystalline *compounds* of the type $\text{R}_2[\text{CoCl}_4]$, $\text{R}_2[\text{CoBr}_4]$, $\text{R}_2[\text{CoI}_4]$, where $\text{R} = \text{C}_5\text{H}_8\text{N}$, $\text{C}_9\text{H}_8\text{N}$, and $\text{C}_{10}\text{H}_{10}\text{N}$. These substances have been isolated in most cases by the addition of the appropriate base to a solution of the cobalt halide in concentrated hydrochloric, hydrobromic, or hydriodic acid. It was also possible to prepare the complex chlorides by the addition of the appropriate organic hydrochloride to an alcoholic solution of cobaltous chloride.

Evidence has been obtained by physicochemical measurements that these salts are definitely complex salts of the type indicated above, and not merely crystalline aggregates of simple salt molecules. It seems reasonable to conclude, therefore, that complex ions of the type CoX_4'' do exist in the blue solutions which cobalt halides form in alcohol or concentrated halogen acids, and that by double decomposition the new salts are precipitated in accordance with the equations



EXPERIMENTAL.

Salts of the Type R_2CoCl_4 .

Diquinolinium Cobaltous Chloride.—To a cold saturated solution of cobalt chloride (5 g., dried at 140°) in absolute alcohol (50 c.c.) saturated with hydrogen chloride, quinoline (10 g.) was added in portions with constant stirring and cooling. The small, bright blue crystals, which separated in excellent yield, were washed with alcohol to remove cobaltous chloride and acid, and dried in a vacuum over phosphoric oxide, sodium hydroxide, and calcium chloride; they could be recrystallised from boiling alcohol without change in composition in blue irregular leaflets, m. p. 170 — 171° [Found: Co, 12.8; Cl, 30.6; C, 46.2; H, 3.7; N, 6.1. $(\text{C}_9\text{H}_8\text{N})_2\text{CoCl}_4$ requires Co, 12.8; Cl, 30.8; C, 46.9; H, 3.5; N, 6.1%]. This *compound* can also be prepared by the addition of quinoline hydrochloride to a saturated solution of cobaltous chloride in alcohol.

A third method of preparation, carried out as follows, resulted in the isolation of the *monohydrate*. To a saturated solution of cobalt

chloride (10 g.) in hydrochloric acid (75 c.c.; d 1.16), quinoline (20 g.) was added slowly with constant stirring and cooling; the blue crystals, which separated in excellent yield, were washed and dried as before [Found: Co, 12.3; Cl, 29.6; C, 45.4; H, 3.8; N, 5.9. $(C_9H_8N)_2CoCl_4 \cdot H_2O$ requires Co, 12.3; Cl, 29.6; C, 45.1; H, 3.7; N, 5.8%]. Recrystallisation from hot alcohol yielded the anhydrous compound.

Analysis. The cobalt was estimated as the anhydrous sulphate by gentle ignition of the substance first alone and then with concentrated nitric and sulphuric acids in an air-bath of which the temperature was gradually raised to *ca.* 400°; when the conditions are standardised, this method proves both convenient and accurate and preferable to the determination by the phosphate method, which gives, as various investigators have found, low results. Chlorine was estimated gravimetrically in the usual way.

Dipyridinium Cobaltous Chloride.—The quinoline in the first preparation above was replaced by pyridine (7 g.), and a good yield was obtained of small blue crystals, which when washed and dried as before had *m. p.* 169—170°. The salt can be recrystallised from alcohol in blue needles without change in composition [Found: Co, 16.3; Cl, 39.2; C, 32.9; H, 3.5; N, 7.8. $(C_5H_6N)_2CoCl_4$ requires Co, 16.3; Cl, 39.3; C, 33.2; H, 3.3; N, 7.8%]. This *pyridinium* salt cannot be isolated from hydrochloric acid solution by the method described for the quinolinium derivative.

Diquinaldinium Cobaltous Chloride.—This *compound*, *m. p.* 239—240°, was obtained as a light blue, crystalline precipitate by substituting quinaldine (5 g.) for pyridine in the above preparation [Found: Co, 12.2; Cl, 29.0; C, 49.2; H, 4.2; N, 5.7. $(C_{10}H_{10}N)_2CoCl_4$ requires Co, 12.1; Cl, 29.0; C, 49.1; H, 4.1; N, 5.7%].

General Properties.—All the blue salts described above are readily soluble in water, giving red solutions containing the cobaltous ion. Cold alcohol dissolves the compounds to a small extent, and the diquinolinium and dipyridinium salts readily dissolve in hot alcohol and may be recrystallised from the blue solutions. The diquinaldinium compound is only slightly soluble in hot alcohol. The anhydrous compounds soften slightly within 10° of their *m. p.*'s.

Through the kindness of Professor S. W. J. Smith, a determination of the magnetism of the pyridinium derivative has been made, a provisional estimate of its paramagnetism by Miss M. Rider giving the value 37.5×10^{-6} for its susceptibility.

Diquinolinium Cobaltous Bromide.—Quinoline (10 g.) was added in portions to a cold saturated solution of cobalt bromide (5 g.) in 35 c.c. of hydrobromic acid (d 1.5). The bluish-green crystalline

precipitate, when washed with alcohol and dried in a vacuum as before, had m. p. 164—165° [Found: Co, 9.2; Br, 50.2; C, 33.7; H, 2.7; N, 4.3. $(C_9H_8N)_2CoBr_4$ requires Co, 9.2; Br, 50.1; C, 33.8; H, 2.5; N, 4.4%].

Dipyridinium Cobaltous Bromide.—To a cold saturated solution of cobalt bromide (5 g.) in fuming hydrobromic acid (25 c.c.; *d* 1.7), pyridine (7 g.) was added slowly with constant stirring and cooling. The greenish-blue crystalline precipitate which separated was washed with alcohol and dried as previously described; m. p. 165—166° [Found: Co, 10.8; Br, 59.1; C, 22.3; H, 2.3; N, 5.2. $(C_5H_6N)_2CoBr_4$ requires Co, 10.9; Br, 59.3; C, 22.3; H, 2.2; N, 5.2%].

Diquinaldinium Cobaltous Bromide.—This compound was obtained as a greenish-blue precipitate by the interaction of quinaldine (2 g.) with a saturated solution of cobaltous bromide (2 g.) in hydrobromic acid (15 c.c.; *d* 1.5); when washed and dried in the usual way it had m. p. 231—232° [Found: Co, 8.8; Br, 48.0; C, 35.6; H, 3.0; N, 4.2. $(C_{10}H_{10}N)_2CoBr_4$ requires Co, 8.8; Br, 48.0; C, 36.0; H, 3.0; N, 4.2%].

General Properties.—The new complex bromides are all very soluble in water, giving red solutions. They are appreciably soluble in cold alcohol, and the diquinolinium and dipyridinium derivatives readily dissolve in hot alcohol, producing blue solutions from which they can be recrystallised. Moreover, the diquinaldinium salt is sufficiently soluble in hot alcohol to be recrystallised from this solvent.

Diquinolinium Cobaltous Iodide.—To 50 c.c. of a cold solution of cobalt carbonate (10 g.) in hydriodic acid (50 c.c.; *d* 1.7), quinoline (8 g.) was added slowly with shaking and cooling. The green crystalline precipitate which separated in excellent yield was washed first with dry ether, then with dry alcohol, and dried in a vacuum as before; m. p. 156—157° [Found: Co, 7.1; I, 61.3; C, 26.1; H, 1.9; N, 3.4. $(C_9H_8N)_2CoI_4$ requires Co, 7.1; I, 61.4; C, 26.1; H, 1.9; N, 3.4%]. The compound is very soluble in water, giving a red solution, and forms a green solution in ethyl alcohol.

Cobaltous Iodide Dipyridine.—To 40 c.c. of a cold solution of cobalt carbonate (10 g.) in hydriodic acid (40 c.c.; *d* 1.7), 20 c.c. of pyridine were added at once. The blue product which separated in good yield was treated as described above; m. p. 196—197° [Found: Co, 12.5; I, 53.8; C, 25.4; H, 2.1; N, 5.9. $Co(C_5H_5N)_2I_2$ requires Co, 12.5; I, 53.9; C, 25.5; H, 2.1; N, 5.9%].

Physicochemical Measurements.

Although the new substances give aqueous solutions which are red and obviously contain the cobaltous ion, thus indicating dis-

sociation of the salts into their components $2RX$ and CoX_2 , nevertheless this does not necessarily invalidate the idea that they are complex salts of the type $R_2[CoX_4]$ (compare Sidgwick, "Electronic Theory of Valency," p. 118). The immediate precipitation of the salts from solutions in which the components are extremely soluble is highly suggestive of the formation of complex compounds, but evidence that this assumption is justified has been obtained from determinations of their molecular weights in alcohol, and their molecular conductivities in the same solvent.

Molecular Weights by the Ebullioscopic Method.—The ethyl alcohol used as solvent was prepared from commercial absolute alcohol by refluxing it for 4 hours over barium oxide, distilling the alcohol, and repeating the operation. The product was then twice refluxed over calcium turnings and distilled. The molecular weights of the quinaldinium derivatives could not be determined owing to their low solubility in alcohol even at the boiling point.

The Landsberger-McCoy apparatus was used in these experiments. Δ denotes the elevation of b. p., M the apparent molecular weight, and f the osmotic factor.

Weight of substance, g.	Volume, c.c.	Δ .	M .	f .
<i>Diquinolinium cobaltous chloride.</i>				
0.3654	23.6	0.135°	179	2.58
0.6636	29.6	0.200	175	2.63
0.8892	33.2	0.240	174	2.65
<i>Dipyridinium cobaltous chloride.</i>				
0.5770	26.4	0.210	162	2.23
0.6348	27.0	0.220	167	2.16
0.8062	33.0	0.225	169	2.14
<i>Diquinolinium cobaltous bromide.</i>				
0.4807	22.0	0.156	218	2.93
0.6619	24.4	0.194	218	2.93
0.9803	29.0	0.240	220	2.90
<i>Dipyridinium cobaltous bromide.</i>				
0.3018	18.0	0.110	238	2.26
0.9844	23.2	0.280	236	2.28
1.6710	30.1	0.356	243	2.22
<i>Quinolinium chloride.</i>				
0.2932	21.6	0.130	163	1.01
0.9254	28.0	0.330	156	1.06
1.374	33.0	0.410	158	1.05

The figures for quinolinium chloride are quoted for the purpose of comparison. The hemihydrate, m. p. 93° , was prepared by passing dry hydrogen chloride into an ethereal solution of quinoline. The anhydrous salt, m. p. 133° , was made from this by heating it in a vacuum over concentrated sulphuric acid at 110° .

Numerous anomalies exist in the molecular weights of electrolytes dissolved in solvents of low dielectric constant (compare Turner, J., 1914, **105**, 1751, 1777, 1786), and it is not easy to draw definite conclusions from such data as to the number of ions given by a complex salt. Yet the values obtained for the apparent molecular weights seem effectively to dispose of the idea that the compounds are double salts of the constitution $2\text{RX},\text{CoX}_2$; for the maximum value for the apparent molecular weight of such a compound would be one-third of the calculated value, since both quinolinium chloride and cobaltous chloride (Donnan and Bassett, *loc. cit.*) give normal molecular weights under the same conditions.

In all the cases investigated, the osmotic factor is between 2 and 3, indicating that the salts are ternary electrolytes of the type $\text{R}_2[\text{CoX}_4]$ which have undergone incomplete ionisation at the concentrations investigated.

Molecular Conductivity Determinations.—Although determinations of molecular conductivities in alcohol are subject to errors that are absent in the case of an aqueous solution (Partington, J., 1911, **99**, 1938), and require cautious interpretation, yet the results obtained for the new compounds give substantial support to the conclusions so clearly indicated from the molecular-weight data. The following results were obtained at 18° ; the alcohol used was prepared as described above and had a specific conductivity of *ca.* 10^{-7} mho. Dilutions (v) are given in litres per mol.

<i>Diquinolinium cobaltous chloride.</i>						
v	58.6	78.7	117.2	157.4	234.4	314.8
μ	29.9	30.2	31.2	30.8	33.5	34.4
<i>Dipyridinium cobaltous chloride.</i>						
v	61.1	75.4	122.2	150.8	244.4	
μ	30.8	33.0	38.0	38.0	43.2	
<i>Diquinolinium cobaltous bromide.</i>						
v	40.3	53.7	80.6	107.4	214.8	429.6
μ	34.4	35.4	37.7	39.9	41.0	39.3
<i>Dipyridinium cobaltous bromide.</i>						
v	43.6	85.8	87.2	174.4	348.8	
μ	36.9	42.6	43.3	45.4	49.0	
<i>Quinolinium chloride.</i>						
v	24.7	35.9	49.5	71.6	99.0	143.2
μ	15.2	17.0	17.2	18.2	17.4	17.3

If the new substances are double salts of the type $2\text{RX},\text{CoX}_2$, the molecular conductivity of the diquinolinium chloride should approximate to 53.4 when $v = 161.4$, as shown by consideration of the results of Rimbach and Weitzel (*Z. physikal. Chem.*, 1912, **79**, 279) for the molecular conductivity of cobaltous chloride in ethyl alcohol at 18°

($\mu = 18.4$ for $v = 161.4$) and the results recorded above for quinolinium chloride ($\mu = 17.5$ for $v = 80.7$). The experimental value for diquinolinium cobaltous chloride gives $\mu = 31$ when $v = 161.4$, and it does not seem unjustifiable to deduce that this low value is the result of the presence of a complex ion, and is not merely the operation of the law of mass action.

The Influence of a Slight Trace of Copper or Iron on Blue Cobaltous Chloride Solutions.—In the course of this work it was found that a small quantity of copper chloride or ferric chloride in hydrochloric acid or alcohol caused immediately a colour change of the blue cobaltous solutions to green. No other metallic chlorides gave this effect. By the addition of quinoline or pyridine to this green solution, a green salt was obtained in which copper could not be detected by the usual analytical reagents, and its presence was only proved by the flame test. The analytical figures and melting points were identical with those of the blue salts $R_2[CoCl_4]$.

This production of a green compound was found to be due to the fact that the corresponding copper compound, $(C_9H_8N)_2CuCl_4$, is bright yellow, and when less than 1% of this yellow compound was ground up with the blue diquinolinium salt in the presence of chloroform, a bright green product of the same melting point as the blue salt was obtained in which copper could only be detected by examination of the flame.

Evidently the formation of a green solution by the addition of iron and copper salts to the blue cobaltous chloride solution is the result of mixing the blue and yellowish-brown solutions, although the small quantity of the latter required seems very remarkable.

The authors wish to express their thanks for the award of a Priestley Scholarship to one of them (E. G. V. P.), and to the Chemical Society for a grant in aid of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[Received, April 4th, 1929.]
