23. *Cobaltic Acetate. Part I.*

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This paper presents some preliminary results obtained in a reinvestigation of the preparation and properties of cobaltic acetate. The substance was prepared by an electrolytic method and was found to be readily decomposed in aqueous solutions by dilute mineral acid, cobaltous acetate being produced. The behaviour of solutions of the compound in water, alcohol, and acetic acid on treatment with ion-exchange resins has been examined. Measurements have been made of the molecular weight, conductivity, absorption spectrum (visible and ultra-violet), and magnetic susceptibilities of a number of specimens. The structure of the compound is discussed in the light of the results obtained.

Little is known of the substance which has been named cobaltic acetate, the only reported work on this compound being that of Copaux (*Ann. Chim. Phys.*, 1905, **6**, 548), Schall and Markgraff (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 161), and Schall and Thieme-Wiedtmarckter (*Z. Elektrochem.*, 1929, **35**, 337). The last two papers present contradictory results, the earlier communication claiming preparation of a compound with the analysis and molecular weight required for $Co(OAc)_3$, whereas the later paper claimed preparation of a material with analysis corresponding to $Co(OAc)_3$ but with a molecular weight corresponding to $Co_3(OAc)_9$. Further, the results obtained by Copaux were quite different from either of these claims, all his products being found to contain cobalt(II), and, in fact, it is doubtful whether Copaux isolated anything except a crude product containing much unchanged cobaltous acetate. For these reasons, and also because of the possible use of cobaltic acetate as an oxidising agent in non-aqueous media, the substance appeared worthy of reinvestigation.

The methods which have been suggested for the preparation of cobaltic acetate have all been based on either (*a*) reaction of cobaltic sulphate with an acetate or (*b*) oxidation of cobaltous acetate. Of these the electrolytic oxidation method described by Schall and Thieme-Wiedtmarckter (*loc. cit.*) was selected as apparently the most satisfactory, particularly from the point of view of attempting to isolate the product. By the method of purification used by the earlier workers, namely, extraction of the crude product with a mixture of acetic acid and light petroleum (about which no details were given), we could not obtain specimens free from cobalt(II). This method was therefore discarded; attempts to purify the compound by extraction from aqueous solutions with an organic solvent had to be abandoned because no solvent could be found which was capable of extracting the material from water.

The method of purification finally used was based on the observation that solutions of the oxidation product in acetic acid did not appear to undergo ion-exchange with cation-exchange resins whereas, under similar conditions, cobalt(II) was readily removed from solution.

A number of properties of the material prepared have been examined in an endeavour to throw some light on the structure of this curious compound.

Experimental

Preparation of Cobaltic Acetate.—A saturated solution of cobaltous acetate tetrahydrate in glacial acetic acid to which had been added 2% (v/v) of water was electrolysed in a divided cell. The anode was a platinum sheet of 40 sq. cm. area and the cathode, contained in a porous pot, was a sheet of copper of approximately the same area. The cell was cooled by immersion in a large beaker through which cold water flowed continuously. The progress of the electrolysis was followed by removing 2-ml. portions of the anolyte, adding potassium iodide, and determining the amount of iodine liberated. In some preliminary experiments the effects of temperature and current density on the current efficiency were examined. Change of temperature between 10° and 20° was without effect, but the influence of current density was profound. The current efficiency at 100 min. fell from 66% at a c.d. of 13·7 amp./sq. m. to 2·1% at a c.d. of 100 amp./sq. m. It was thus evident that a low current density and prolonged electrolysis would be necessary. All preparations were therefore carried out at a c.d. of ~20 amp./sq. m., the volume of anolyte being 500 ml., and the duration of the electrolysis 20 hours. The temperature was kept at 10—20° during electrolysis.

After electrolysis, the anolyte was passed slowly (*ca.* 3 ml./min.) through a 2·5 × 30 cm. column of the ion-exchange resin Zeo-Karb HI. The column was freshly regenerated to the hydrogen form, according to the manufacturers' instructions, before each run and then well washed with glacial acetic acid. The dark green oxidation product passed through the column, which was washed with glacial acetic acid until the effluent was no longer green. The acetic acid solution was then evaporated *in vacuo*, at *ca.* 35°, to a syrup; this was transferred to a dish and kept in a vacuum-desiccator over phosphoric oxide until a dry product was obtained. The material thus produced was an almost black powder and will be subsequently referred to as the crude product.

Analytical Methods.—To determine Co(III), the solid compound (or a solution) was added to an excess of standard acidified ferrous ammonium sulphate solution, and the excess of ferrous iron titrated with permanganate, the end-point being determined potentiometrically. Determinations of total cobalt were made by conversion of Co(III) into Co(II) by treatment of the compound with dilute aqueous mineral acid followed by determination of the Co(II) by the volumetric oxine method.

Acetate determinations were made by distillation from solutions containing phosphoric acid, as described by Sutton (" Volumetric Analysis," 1935, p. 92) for calcium acetate.

Ion-exchange Experiments.—The ion-exchange resins used were: (1) Zeo-Karb HI, (2) Zeo-Karb 225, (3) De-Acidite " F," supplied by the Permutit Co., and (4) Amberlite IR-120-(H), supplied by B.D.H.: (1), (2), and (4) are cation-exchange resins, (2) and (4) being monofunctional (SO_3H) resins based on polystyrene, and (3) is a strongly basic anion-exchange resin.

Before use all resins were freshly regenerated, in the form required, according to the makers' instructions, and then well washed with the solvent with which they were to be used. Experiments were carried out either by shaking resin and solution in a stoppered flask, or by allowing solutions to flow through columns of the resin. The columns used were prepared in 50-ml. burettes, as this provided a convenient method of measuring bed volumes and checking flow rates.

Spectroscopy.—Absorption spectra in the range 200—1000 mμ were determined by using a Unicam S.P. 500 spectrophotometer.

Molecular-weight Determinations.—These were made by the freezing-point method. A Standard Telephones and Cables Ltd. " Thermistor " type F 2311/300 was used for temperature measurement. Temperature changes were calculated by using the approximate expression $\Delta T = k(\log R_2 - \log R_1)$, the value of the constant k being determined by separate calibration experiments. With water as solvent, urea was used for calibration. The thermistor resistance was measured by the standard bridge method and could be determined to 0·1 ohm.

Conductivity.—Conductivities were measured by means of a conventional A.C. bridge, the cell being kept at 25° ± 0·05°. The solvent was brought to bath-temperature, and a weighed quantity of solute added to a known volume; as soon as dissolution was complete, measurements could be started.

Magnetic Susceptibility.—A Curie–Chéneveau balance of the type described by Wilson (*Proc. Roy. Soc.*, 1919, *A*, **96**, 429) was employed for measurements of magnetic susceptibility. The design was modified by replacing the electromagnet by a " Magnetron "-type permanent magnet. The instrument was calibrated by using ferrous ammonium sulphate, ferric ammonium sulphate, cobaltous sulphate, cupric ammonium chloride, and potassium ferricyanide. The mass susceptibilities of these substances at room temperature were taken from International Critical Tables. All experiments were made at room temperature (17—22°).

Results.

Analysis of Solid Material.—Specimens of the crude product prepared by the method described on p. 110 had a variable Co(III) content (between 10 and 15%). The following are typical analyses.

	Co(III), %	Co(II), %	OAc, %	Unaccounted for, %
(1)	11·3	19·8	54·8	14·1
(2)	10·5	13·0	51·0	25·5

Further treatment of the crude product in acetic acid solution by ion exchange on Zeo-Karb HI (see later) gave products of an enhanced Co(III) content as the following typical figures show :

	Co(III), %	Co(II), %	OAc, %	Unaccounted for, %
(3)	17·4	12·0	39·5	31·1
(4)	16·8	8·2	50·5	25·5

On treatment of similar solutions with the ion-exchange resins Zeo-Karb 225 and Amberlite IR-120-(H), solids of much lower Co(II) content were obtained, thus :

	Co(III), %	Co(II), %	OAc, %	Unaccounted for, %		Co(III), %	Co(II), %	OAc, %	Unaccounted for, %
(5)	18·2	4·6	57·6	19·6	(7)	27·9	0·1	44·7	27·3
(6)	21·8	1·7	31·6	45·0	(8)	24·9	0·8	44·4	30·0

The significance of these figures will be discusssed later, the specimens (1)—(8) being referred to by means of these numbers in the rest of the text.

Ion-exchange Behaviour.—The behaviour of the crude product towards various ion-exchange resins has been examined in water, acetic acid, and ethyl alcohol. In all three solvents, Co(II) was found to be readily removed from cobaltous acetate solutions by the three cation exchangers in their hydrogen, sodium, and potassium forms. The Co(II) could readily be recovered from the resins by treatment with 4N-sulphuric acid. There was also found to be a slight uptake of Co(II) when cobaltous acetate solutions were run through the anion exchanger in its chloride form. The Co(II) thus taken up was removed on treatment with aqueous sodium chloride.

Prolonged contact of solutions of the crude product in any of the three solvents with any of the three cation exchangers was found to lead to a decrease in Co(III) content, and ultimately its complete disappearance. However, treatment of the exchangers, after these experiments, with sodium or potassium salt solutions or dilute mineral acid solutions failed to recover from the resin anything except Co(II). It must therefore be concluded that in contact with these resins Co(III) is reduced to Co(II). The rate of this decomposition depends markedly on the solvent and exchanger and on whether the latter is in the hydrogen or some other form. In general, reduction was rapid in aqueous solutions and much slower in the other two solvents; further, the hydrogen form of the resins was found to promote more rapid reduction than did the sodium form. The resins themselves also varied widely in their power to bring about this change, the relative rates of reduction being Zeo-Karb HI $\gg$ Amberlite IR-120-(H) $>$ Zeo-Karb 225. The readiness with which the first of these resins causes reduction when compared with the other two is understandable, for the first is a phenolic type while the others are based on a sulphonated polystyrene and hence would be expected to be very resistant to oxidation.

The behaviour of both anolyte and solutions of the crude product on ion-exchange treatment, however, showed some unexpected features. For instance, in an experiment in which the anolyte from an electrolysis was allowed to flow through the " preparative " column of Zeo-Karb HI, the following results were obtained, Co$_t$ representing the total cobalt :

	Anolyte	After 1 run through column	After 2nd run through column
Co$_t$, M/100	8·0	1·78	0·57
Co(III), M/100	1·47	0·88	0·29
Co(III)/Co$_t$	0·018	0·49	0·50

It will be seen that, although the first ion-exchange treatment brought about a great reduction in the Co(II) content, a second treatment under identical conditions did not cause any significant variation in the Co(III)/Co$_t$ ratio; but each treatment has caused considerable decomposition of the Co(III) compound. A similar experiment carried out with the resin Amberlite IR-120-(H) in the sodium form and a solution of the crude product in ethyl alcohol gave the following results :

	Original compound	Compound recovered after 1 treatment	2 treatments
Co(III), %	13·6	14·6	13·8
Co$_t$, %	23·4	21·0	23·3
Co(III)/Co$_t$	0·58	0·69	0·59

Repetition of the experiment with water as solvent, again with the sodium form of the resin, gave : Initial compound, Co(III)/Co$_t$ 0·58; after one ion-exchange run the solution had Co(III)/Co$_t$ 0·9. No solid could be recovered from aqueous solutions owing to rapid hydrolysis when attempts were made to remove the solvent by vacuum-distillation.

In contrast to this behaviour, when Zeo-Karb 225 or Amberlite IR-120-(H), in the hydrogen form, is used with acetic acid as solvent there appears to be no barrier to the eventual removal of all the Co(II) from solutions of the crude product, as the following results demonstrate :

	Co(III), %, in : original material	Co(III), %, in : solid recovered	
Amberlite IR-120-(H), hydrogen form	12·3	23·5	
	13·0	19·1	
	13·0 *	21·8	[Co(II), 1·7; OAc, 31·6%]
	14·0	20·9	
Zeo-Karb 225, hydrogen form	17·0	24·8	
	16·0 †	27·9	[Co(II), 0·1; OAc, 44·7%]
	12·0 ‡	17·3	[Co(II), 12; OAc, 39·5%]
	11·0	18·2	[Co(II), 4·6; OAc, 57·6%]

* Two runs through column; all others, one. † Resin shaken with solution in flask for 6 hrs. ‡ Resin shaken with solution in flask for 24 hrs.

All these experiments were performed by allowing an acetic acid solution (40 ml.) of crude product (1·5 g.) to flow through a 50-ml. bed of resin at *ca.* 0·3 ml./min. In all experiments the Co(II) present in the original solution was <20% of the amount required to saturate the resin.

The behaviour of solutions of the crude product on treatment with the anion-exchange resin De-Acidite " F " yields further information. With the resin in the hydroxide form, passage of an aqueous solution of the crude product through a column of the resin gave a colloidal solution of cobaltic hydroxide. With the resin in the chloride form, an aqueous solution again being used, the following results were obtained :

Original material, %	No. of passages	OAc content of soln. as % of original value
Co(III) 21·8	1	64
Co(II) 1·7		
OAc 31·6	2	38·5
Co(III) 19·1		
OAc 41·0	5	20·5

Solutions (50 ml.) contained *ca.* 2 g. of crude material and flowed through a 50-ml. column at *ca.* 0·5 ml./min. No change could be found in the Co(III) or Co(II) content of the solutions.

Properties and Reactions of Cobaltic Acetate.—The experiments described in this section were for the most part carried out with crude material containing 15—16% of Co(III).

The solubility of cobaltic acetate in a number of solvents was examined. The compound was readily soluble in acetic acid, water, and ethyl alcohol, and soluble with some difficulty in *n*-butyl alcohol, to give in all cases a very deep green solution. Solutions in acetic acid, ethyl alcohol, and *n*-butyl alcohol appeared to be stable for several months at room temperature, but a solution in ethyl alcohol on immersion in a water-bath at 95° rapidly decomposed, giving a pink precipitate and a colourless supernatant liquid. Aqueous solutions appear to hydrolyse slowly at room temperature, a brown precipitate being formed after several days; when they are heated to 60—70°, hydrolysis and formation of a precipitate occur very rapidly.

Attempts to extract the dark green Co(III) compound by shaking its aqueous solution with *n*-butyl alcohol were completely unsuccessful.

The brown precipitate produced by hydrolysis in aqueous solutions either at room temperature or on boiling retains the full oxidising power of the original solution, for on treatment with dilute sulphuric acid containing potassium iodide the theoretical quantity of iodine is liberated. Addition of sodium hydroxide to an aqueous solution also gives a brown precipitate which retains the full oxidising power and is presumably cobaltic hydroxide.

Solutions in water, acetic acid, or ethyl alcohol slowly liberate iodine from potassium iodide, the reaction taking several hours to go to completion. If the solutions are acidified, reaction is complete in a few minutes. Solutions in these solvents also rapidly oxidise acidified ferrous sulphate solutions, the Co(III) reverting to Co(II).

Addition of ethylenediamine to an aqueous solution of the compound gives a bright red colour, whereas addition of the same reagent to cobaltous acetate solution gives a brown solution which slowly becomes bright red. The addition of ammonia (*d* 0·88) to an acetic acid solution gives a bright red colour; with an aqueous solution a brown colloidal precipitate is obtained.

Aqueous solutions of the compound are rapidly decomposed on addition of mineral acid, the colour changing from deep green to pink. The reaction with *ca.* 2N-acid at room temperature is complete in a few minutes, but in 0·1—0·2N-acid it may take 2—3 hours.

Spectroscopy.—The visible and ultra-violet absorption spectrum of the crude product was examined in water, ethyl alcohol, and acetic acid as solvents, the results being presented in Fig. 1. In Fig. 2 is shown the result of an experiment in which an excess of potassium oxalate was added to an aqueous solution of the crude product, the absorption spectrum being recorded before, and 5—10 min. after, the addition. Included in Fig. 2 is the absorption spectrum of potassium tetraoxalato-μ-dihydroxodicobalt(III), prepared by Percival and Wardlaw's method (*J.*, 1929, 2628), and it will be noticed that after addition of the potassium oxalate the absorption spectrum of the cobalt(III) acetate becomes identical with that of the oxalato-compound.

FIG. 1.

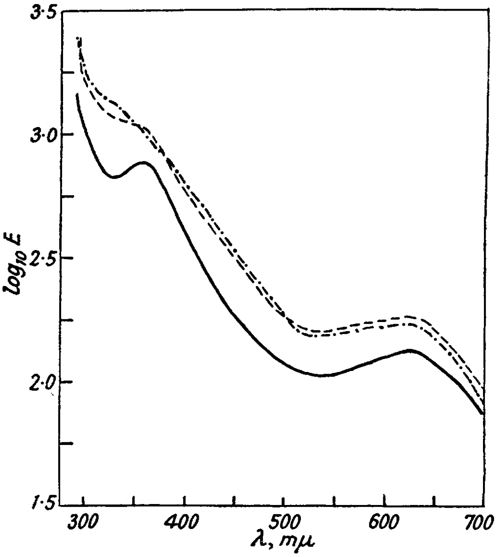


FIG. 2.

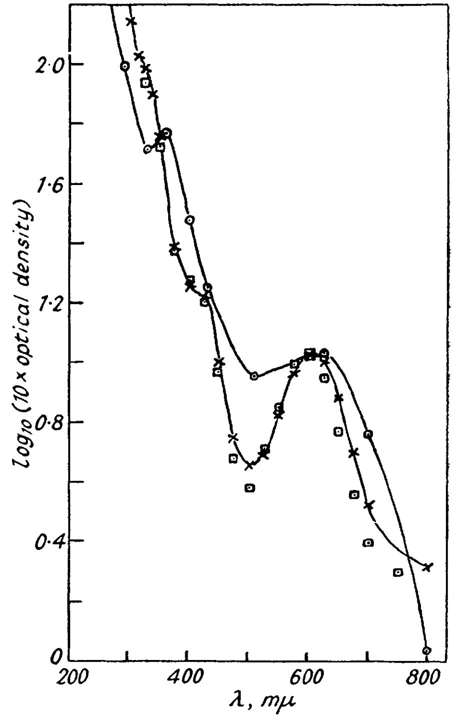


FIG. 1. *Absorption spectra of cobalt*(III) *acetate in :* ——, *water ;* — . —, *ethyl alcohol ;* — — — *acetic acid. The extinction coefficient* E *is calculated for* 1 *g.-atom of* Co(III) *per litre.*

FIG. 2. *Absorption spectra of :* ○ *cobalt*(III) *acetate;* □ *cobalt*(III) *acetate* 5—10 *min. after addition of potassium oxalate ;* × *potassium tetraoxalato-μ-dihydroxodicobalt*(III) *; all in water.*

The optical density was recorded with a 1-*cm. cell, both solutions being adjusted to contain* 7·75 × 10^{-3} *g.-atom of* Co(III) *per litre.*

Molecular weight and conductivity. Experiments were carried out on two specimens (Nos. 5 and 6) obtained by further ion-exchange treatment of the crude product, in which the molecular weight and, in one case, the conductivity, were determined at various intervals after the solutions had been prepared. The results are presented in the following tables :

Specimen (6) : 8·04 g./1000 g. of H_2O

Age of soln., min.	Apparent *M*
34	201
67	182
165	169
1460	135
1670	129

Specimen (5) : 14·6 g./1000 g. of H_2O

Age of soln., min.	Apparent *M*
62	112
1170	99
4200	94

Specimen (5) : 4·14 g./1000 g. of H_2O

Age of soln., min.	Apparent *M*
18	140
44	133
116	127
172	124
1320	123

Specimen (6) was used for all the following conductivity measurements, where κ is recorded in units mho/g.-ion of Co(III)/ml. and concentration in terms of g.-ions of Co(III)/l.

Concn.	308×10^{-5}		213×10^{-5}		532×10^{-6}		380×10^{-5}			
Age of soln. (min.)	9	1560	27	1200	21	1200	1·4	8·9	34·0	170·0
κ	61·5	83·7	85·5	92·0	100·6	107·0	58·1	71·1	80·7	84·4

Magnetic susceptibility. The magnetic susceptibilities of specimens (1), (2), (3), (5), (7), and (8) have been determined. In all cases a fairly large paramagnetic susceptibility was found, the results being presented in the following table:

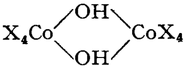
Specimen	$Co(OAc)_2,4H_2O$	(1)	(2)	(3)	(5)	(7)	(8)
$\chi \times 10^6$, c.g.s.u./g.	48·0	42·7	36·5	37·7	24·2	15·3	9·5
$\chi \times 10^3$, c.g.s.u./g.-atom of Co(III) *	—	1·39	5·73	4·57	4·83	3·19	1·87

* Corrected for Co(II), see p. 116.

DISCUSSION

The analytical results for the specimens of cobalt(III) acetate so far obtained demonstrate clearly that not all of the compound can be accounted for in terms of Co(III), Co(II), and OAc. The discrepancy is 14—45% depending on the specimen examined. Only three samples have so far been produced in which the Co(II) content is low enough for the material to be regarded as substantially free from cobalt(II) acetate. These are Nos. (6), (7), and (8) and in none of these cases does the OAc : Co(III) ratio have the value required by $[Co(OAc)_3]_x$, and neither are the analyses of the specimens concordant. Treatment of both (5) and (6) with an excess of standard sodium hydroxide has shown that 3·09 and 2·95 equivalents, respectively, are required for precipitation of 1 atom of cobalt.

The readiness with which the compound decomposes in acid solution, the similarity of its absorption spectrum to that of potassium tetraoxalato-μ-dihydroxodicobalt(III), and the ready production of the spectrum of the latter on addition of potassium oxalate seem to indicate a close structural similarity between the two. If this hypothesis is correct, it is not improbable that cobalt(III) acetate is a binuclear complex containing the μ-dihydroxo-bridge grouping, as inset. A number of compounds of this type are already known (Werner, *Annalen*, 1910, **375**, 1; Percival and Wardlaw, *loc. cit.*) and all show a breakdown of the hydroxo-bridge on treatment with mineral acid.



The determinations of molecular weight and conductivity show that the compound reacts readily with water. Although its reactions show that hydrolysis to $Co(OH)_3$ will take place if the compound is left in water for several days, yet the rapidity with which the molecular weight falls and the conductivity increases seem to indicate the occurrence of a rapid aquotisation reaction rather than hydrolysis. This would imply great lability of the acetate groupings, and in this connection support is given by the ready production of the oxalato-compound spectrum on treatment with potassium oxalate, the rapid production of a red colour with ethylenediamine in water or ammonia in acetic acid, and the ready removal of acetate from the complex on treatment with the chloride form of an anion exchanger. Further, Werner (*loc. cit.*, p. 119) found that an acetato-group in a binuclear dihydroxy-bridged complex was readily replaced, provided that it was not acting as a bridge, by treatment with salt solutions.

The nature of that part of the compound which has not been accounted for by analysis remains obscure. If a hydroxo-bridged binuclear structure be accepted, then Co(III), Co(II), and OAc would not in any case be expected to account for the whole of the material, and, as the electrolyte used in the preparation contained 2% (v/v) of water, the presence of H_2O or OH groupings in the compound is not unlikely. However, there is some ground for the belief that a further organic grouping may occur. The ready reversion of the Co(III) to the Co(II) state in acid solution implies that either the solvent (H_2O) or some part of the compound itself is oxidised. No gas evolution can be detected, and in acid solution the reaction of the cobaltic ion with water is known to be slow (*e.g.*, Bawn and White, *J.*, 1951, 331); hence an attack on the acetate groupings appears more likely. The experimental evidence, however, does not bear out this supposition. In parallel experiments with specimen (5), acetate has been determined by (i) the normal method and (ii) after reduction of the Co(III) with ferrous ammonium sulphate solution, and in both cases the same value is obtained. If the acetate were oxidised during the acid decomposition of the compound, then the two determinations would be expected to yield different values.

After decomposition with mineral acid in aqueous solution and precipitation of cobalt with sodium hydroxide, the solution gives a green fluorescence with β-naphthol in concentrated sulphuric acid, the intensity increasing on heating. This coloration is specific for glycollic and tartaric acids, although the latter does not give a positive test in the cold. If the compound is decomposed by treatment with ferrous salt solution and the metals are precipitated with sodium hydroxide solution before the β-naphthol test is applied, a green fluorescence is again obtained. This evidence suggests that glycollic acid may be present in the initial material, and in this connection it is significant that Schall and Thieme-Wiedtmarckter (*loc. cit.*) reported glycollic acid as a by-product of the electrolytic oxidation by which cobalt(III) acetate was prepared. The addition of sodium glycollate to acidified aqueous solutions of the compound was found to cause a marked increase in the rate of decomposition, and this indicates that glycollate, if present, would readily be oxidised.

If the compound contains a dihydroxo-bridge grouping, only 2 equivalents of sodium hydroxide per atom of cobalt should be required for precipitation of $Co(OH)_3$, whereas with samples (5) and (8) *ca.* 3 equivalents are required. As, in (8), the OAc/Co ratio is 1·7, then at least 1 equivalent of some other acid must be present, and in the case of (5) with OAc/Co *ca.* 2·5, then 0·5 equivalent of other acid is required per cobalt atom. This acid could presumably be glycollic acid, which might act as a chelating agent. The analytical results and the ready lability of the acetate (or other) groupings as indicated by the molecular weight, conductivity, and experiments with anion exchangers make it very doubtful whether any single pure compound has yet been isolated. Further, the difficulty, in some cases, of removing all the Co(II) from an apparently impure specimen by treatment with cation exchangers, under conditions in which free Co(II) is readily taken up, appear to favour the existence of some trinuclear compounds containing Co(II) (cf. Werner, *loc. cit.*, p. 40). For these reasons it seems possible that the so-called "cobaltic acetate" may in fact be a mixture of several multinuclear complexes of basically similar structure.

Finally, the measurements of magnetic susceptibility must be considered. These results are difficult to interpret, as most of the specimens contain considerable quantities of Co(II) the state of which is uncertain. However, if it is assumed that this is present as cobaltous acetate, then a deduction can be made from the observed value, based on the susceptibility found for cobaltous acetate, to allow for this. This has been done in the third line of the table in which these results were presented, and all the specimens are still found to possess a large paramagnetic susceptibility. That this paramagnetism is not a property of the cobalt(II) is clearly demonstrated by the values for (7) and (8) which contain virtually no cobalt(II). The magnetic properties of some binuclear complexes of cobalt(III) have been examined previously (Rosenbohm, *Z. physikal. Chem.*, 1919, **93**, 693; Berkman and Zocher, *ibid.*, 1926, **124**, 318) and all have been found to be diamagnetic as would be expected from the structures proposed. The only binuclear compounds of cobalt so far shown to possess paramagnetic properties are the μ-peroxo-cobalt(IV)–cobalt(III) complexes (Malatesta, *Gazzetta*, 1942, **72**, 287). The presence of Co(IV) in our samples seems unlikely in view of the facts (i) that Co(IV) has been found only in binuclear complexes with Co(III) and (ii) that these complexes all contain a peroxo-bridge (Sidgwick, "The Chemical Elements," Oxford, 1950, p. 1420). These measurements, although their interpretation must be treated with reserve, do seem to cast doubt on the validity of the postulate of a μ-dihydroxo-grouping in cobalt(III) acetate, although this might still be possible if the Co–OAc bonding possessed a largely ionic character.

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