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On Cobaltic Acetate

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The methods suggested for the preparation of cobaltic acetate, either by reaction of cobaltic sulphate with an acetate, or oxidation of cobaltous acetate, have both lead to controversy [1–4]. We are reporting here a different route for the preparation of cobaltic acetate.

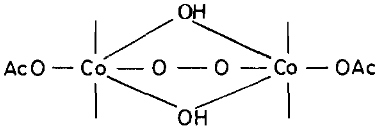
The cobalt metal (2.3 g) is reacted with an acetate (acetic acid or its anhydride 0.1 ml) under reflux in the presence of the oxidizing nitrate group (0.2 mole). The violet cobalt(II) solution obtained, accompanied with evolution of nitrogen dioxide, was partially crystallized until no further sodium acetate was obtained. The finally washed and dried product was tentatively formulated as $Co(O_3C{\cdot}CH_3)_2$. *Anal.* Found: Co, 28.9; H, 2.9; C, 22.9. Calc.: Co, 28.22; H, 2.87; C, 22.96%. Its visible spectrum is typical of octahedral cobalt(II) and its infrared suggests a peroxydic group [4] (band at 750 cm^{-1}).

When the product was hydrolyzed with water a green cobalt(III) acetate was obtained and gas was evolved (Found: Co, 31.0; H, 2.93; C, 12.27%). The visible spectrum was conclusively that of a low-spin octahedral cobalt(III) species [5], (bands at 15300 cm^{-1}, ${}^1T_{1g} \leftarrow {}^1A_{1g}$; 19200 cm^{-1}, ${}^1T_{2g} \leftarrow {}^1A_{1g}$ and 27800 cm^{-1}, ${}^1E_{1g} \leftarrow {}^1A_{1g}$). The infrared spectrum was indicative of unidentate coordinated acetate groups, where $\Delta^*(\nu_{as}(COO) - \nu_s(COO))$ is 190 cm^{-1} (see Table I). In addition, the band at 750 cm^{-1} was persistent and the (OH) stretch showed as a broad band at 3480 cm^{-1}.

TABLE I. Symmetric (ν_s(COO)) and Asymmetric (ν_{as}(COO)) Stretching Frequencies (cm^{-1}) of some Acetate Complexes

Acetate	Example	ν_{as}(COO)	ν_s(COO)	Δ*	Reference
Ionic	NaOAc	1575	1422	153	6
Uni	$Co(NH_3)_5OAc$	1603	1380	223	7
Bi	$Zn(OAc)_2 2H_2O$	1750	1452	118	8
Brid.	$Zn_4O(OAc)_6$	1639	1489	150	9

The product is partially soluble in acetic acid but completely soluble in oxalic acid and decomposes in aqueous mineral acids. Its oxidizing ability is tested qualitatively by KI acidic solution. Such properties indicate a close similarity of structure to that of cobaltic acetate reported by Sharp and White [2], *i.e.* a dimer with four bridging hydroxyl groups. Hence, a plausible structure of the product obtained could be a dimer in which a peroxydic group as well as hydroxyl groups are bridging the two cobalt atoms, e.g.



which fits the analysis and properties observed.

The following speculative mechanism is in support of such a structure. The envisaged steps are

$$CH_3CO_3 + H_2O \longrightarrow CH_3CO_3H + OH^-$$

$$CH_3CO_3H + Co^{2+} \xrightarrow{\text{fast}} Co^{3+} + CH_3COO + OH^-$$

and/or

$$2CH_3CO_3 + 2Co^{2+} \xrightarrow{\text{fast}} (Co_2O_2)^{4+} + 2CH_3COO^- + 2H^+$$

$$CH_3CO_3H + Co^{3+} \longrightarrow Co^{2+} + CH_3CO_3 + H^+$$

and CH_3CO_3 decomposes to give oxygen.

A detailed study is now in progress.

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