A New Route to the Formation of Cobaltic Acetate

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Abstract

A new route for the preparation of cobaltic acetate has been investigated in which the metal is reacted with acetic acid or acetic anhydride, under reflux in the presence of an oxidizing nitrate group. Cobaltous peroxy-acetate is first obtained which on hydrolysis yields a green precipitate of cobaltic acetate. Some of its properties such as solubility, oxidizing ability, infrared and visible spectra are reported. The reaction mechanism is illucidated and the most probable structure is inferred.

Introduction

The methods which have been suggested earlier for the preparation of cobaltic acetate have all been based on, (a) reaction of cobaltic sulphate with an acetate, (b) oxidation of cobaltous acetate.

Both methods have lead to controversy. While it has been claimed [1] that $Co_3(OAc)_9$ is formed in the electrolytic oxidation of cobaltous acetate, later workers [2] were only able to prepare samples contaminated with cobalt(II). Cobaltic acetate is also reported [3] to be present in dilute acetic acid solutions of cobaltous acetate which have been oxidized with ozone. The catalytic decompositions of peroxyacetic acid has yielded cobalt(III) acetate [4]. Mutasim [5] has observed that cobalt(III) acetate is obtained by the reaction of cobalt(III) nitrate with acetic anhydride and suggested an incorporated trinuclear (Co_3O) species which is a known feature of the acetate chemistry of tripositive 3d metals [6–8].

In this paper we are reporting a modification of the nitrate–acetic anhydride reaction so as to establish a new route for the preparation of cobalt(III) acetate.

Experimental

Sodium nitrate (0.2 mol), dissolved in the minimum amount of water, was added to acetic anhydride (0.1 mol) and weighed cobalt granules (2.3 g) were then inserted. The mixture was refluxed for several days with occasional shaking. Nitrogen dioxide evolved and a deep pink solution was obtained, which was filtered hot and partially crystallized until no white (sodium acetate) crystals separated out. The concentrated deep violet filtrate was allowed to settle, filtered, washed several times with chloroform and ether and then dried.

Analysis of cobalt is done by complexometric titration, and sodium by atomic absorption.

Spectroscopic measurements: the electronic spectra were obtained using an Acta MV 11 Beckman spectrophotometer.

The infrared measurements were made using an IR 4240 Beckman spectrophotometer.

Difficulty was encountered in the molecular weight determination by the usual freezing point depression method. Suppercooling was observed and a depression of ~6.0° was evident.

Results and Discussion

On addition of water to the dry pink cobalt(II) crystalline product, an instantaneous liberation of gas was observed accompanied by a colour change from violet into blue and finally a deep green gellatinous precipitate with a pink supernatant liquid separated out. This was filtered, washed with ether and dried.

The microanalytical data on two separate samples suggest an empirical formula of the form: $Co_1C_2O_6H_6$. *Anal.* Found: H, 3.29; C, 12.42; Co, 31. Calc.: H, 3.2; C, 12.9; Co, 31.8%.

The visible spectrum of the pink product solution is typical of an octahedral cobalt(II) species. The infrared spectrum of the solid exhibited a band at 750 cm^{-1} suggesting the presence of a peroxidic group [4]. On this basis and the microanalytical data obtained, the product is tentatively formulated as a peroxyacetato cobalt(II), $Co(O_3CCH_3)_2$. *Anal.* Found: Co, 28.9; H, 2.9; C, 22.9 Calc.: Co, 28.22; H, 2.87; C, 22.96%.

On the other hand, the diffuse reflectance and the visible spectra of the green product solution are con-

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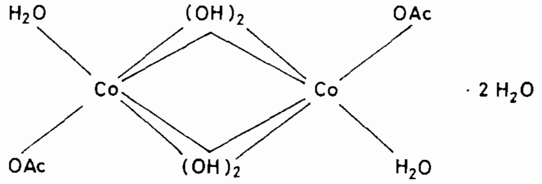
clusively that of a low spin octahedral cobalt(III) species (bands at 15 300, 19 200 and 27 800 cm^{-1}) respectively assigned to $^1T_{1g} \leftarrow {}^1A_{1g}$; $^1T_{2g} \leftarrow {}^1A_{1g}$ and $^1E_g \leftarrow {}^1A_{1g}$. These were compared with some energies of electronic absorption maxima for some cobalt(III) complexes (Table I).

The infrared spectrum showed the presence of coordinated acetato groups (bands at: 2924, C–H str; 1570(s), ν_{as}COO str; 1400(s), $\nu_{as}CH_3$ deform; 1380(5), ν_sCOO str; 1340(w) ν_2CH_3 deform; 1015-(m), $\nu_{10}CH_3$ rock; 830(sh), C–C str; 510(w), Co–O str). Hence, $\Delta^*(\nu_{as}COO - \nu_sCOO)$ is 190 cm^{-1}. This is compared with (Δ^*) of known modes of acetate bonding (Table II), which suggests a unidentate type of bonding. In addition, the band at 750 cm^{-1} was persistent and the (OH) stretch showed as a broad band at 3480 cm^{-1}.

Several of the product properties have been examined. It is partially soluble in acetic but completely soluble in oxalic acid, DMS and THF. It decomposes in aqueous mineral acids, e.g. HNO_3, H_2SO_4 to give a pink cobalt(II) solution. However, HCl gives the dark blue tetrahedral species $CoCl_4{}^{2-}$. Its oxidizing power is tested qualitatively by KI acidic solution. The product is stable over a long period (~3 months) at room temperature, but changes to pale green colour on longer aging.

On the other hand, if the green product is precipitated from the peroxyacetate by sodium or ammonium hydroxide solutions, it changes to a brown precipitate over three days. The latter retains an oxidizing power, and is presumably $Co(OH)_3$.

Such properties indicate a close similarity of structure between the product obtained and that of cobaltic acetate reported by Sharp and White [2]; *i.e.* a dimer with four bridging hydroxyl groups is a probable structure (*cis* or *trans*):



However, on the basis of solubility properties and hydrogen analysis such a formulation, *i.e.* $[Co_2(OAC)_2(OH)_4 \cdot 4H_2O]$, could be ruled out.

A possible assignment of the weak 510 cm^{-1} band to a trinuclear (M_3O) or tetranuclear (M_4O) assymetrical vibrational mode is also considered (Table III). However, the formulations incorporating such species are completely ruled out on the basis of great discrepancies with the analytical data obtained.

Hence, a more plausible structure could be a dimer in which a peroxydic as well as hydroxyl groups are bridging the two cobalt atoms:

TABLE I. Energies (cm^{-1}) of Electronic Absorption Maxima of some Cobalt(III) Complexes [9]

	Complex							Assignment
	$[CoF_6]^{3-}$	$[Co(OH_2)_6]^{3+}$	$[Co(CO_3)_3]^{3-}$	$Co(OAc_3)$ [2]	$[Co_2(C_2O_4)_4(OH_2)]^{4-}$ [2]	$[Co(NO_3)_6]^{3-}$	Product	
High spin	11800 14000							$^5E_g \leftarrow {}^5T_{2g}$
Low spin		16500	15700	15300	15300	15200	15300	$^1T_{1g} \leftarrow {}^1A_{1g}$
	24950	24950	22800	21350	21350	22500	19200	$^1T_{2g} \leftarrow {}^1A_{1g}$
					27500	25500	27800	$^1E_g \leftarrow {}^1A_{1g}$

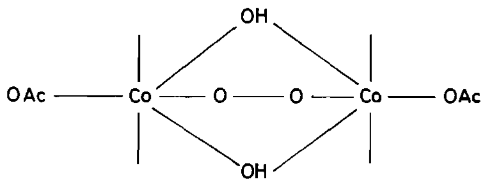
TABLE II. Symmetric (ν_s) and Assymetric (ν_{as})[COO] Stretching Frequencies (cm^{-1}) of some Acetato Complexes

Type of acetate	Example	ν_{as}[COO]	ν_s[COO]	Δ^{*a}	References
Ionic	NaOAc	1575	1422	153	10
Uni	$Co(NH_3)_5OAc$	1603	1380	223	11
Bi	$Zn(OAc)_2 2H_2O$	1570	1452	118	12
Brid	$Zn_4O(OAc)_6$	1639	1489	150	13, 14
	$[Cr(OAc)_2]_2$	1571	1422	149	15
	product	1570	1380	190	this work

$^a\Delta^* = \nu_{as}[COO] - \nu_s[COO]$.

TABLE III. Symmetric (ν_{ss}) and Assymetric (ν_{as}) [M_3O] Vibrational Bands of Tri- and Tetranuclear Oxy-complexes [6]

Description of mode		$\nu_s[M_3O]$	$\nu_{ass}[M_3O]$
D_{3h}		A_1; R	
C_{3v}		A_1; R; IR	E; R, IR
$[MeHg)_3O]ClO_4$	R	138s	549m
	IR	140vw	548m
$[Cr_3O(OAc)_6]Cl{\cdot}5H_2O$	R	180	
	IR	180w	620s
$K_2[Cr_3O(OAc)_6F_3]20H_2O$	R	186	
	IR		645m
$[Fe_3O(OAc)_6]Cl{\cdot}H_2O$	R	181	
	IR	180w	588s
$K_{10}[Ir_3O(SO_4)_4]$	R	233	
	IR		615s
Product	IR		510w
Miscellaneous trinuclear complexes			
mode (approximate)		$\nu_s[M_3O_2]$	$\nu_{as}[M_3O_2]$
$[Ru_3O_2(NH_3)_{14}]Cl_6$	IR		813s
$[Ru_3O_2Cl_6(H_2O)_n]$	IR		810w
Tetranuclear species			
Zn_4O	I	$\nu_s[M_4O]$	$\nu_{as}[M_4O]$
	IR		526w



A speculation on the mechanism of the reaction which would explain both the formation of the product and liberation of the gas may be in support of structure eqn. (2b).

The invisaged steps are:

$$CH_3CO_3^- + H_2O \longrightarrow CH_3CO_3H + OH^- \quad (1)$$

$$CH_3CO_3H + CO^{2+} \xrightarrow{fast} Co^{3+} + CH_3COO + OH^- \quad (2a)$$

$$\text{or } 2CH_3CO_3H + 2Co^{2+} \xrightarrow{fast} (Co_2O_2)^{4+} + 2CH_3COO^- + 2H^+ \quad (2b)$$

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

Step (2a) and (2b) lead to the formation of the green cobalt(III) product. The partial reduction of it, through step (3), would explain the cobalt(II) supernatant liquid obtained. This is followed by the CH_3CO_3 decomposition to given oxygen, *i.e.*

$$CH_3CO_3 \longrightarrow CH_3COO + \tfrac{1}{2}O_2$$

which is in accordance with the observed gas liberation.

The reaction products of chromium, iron, and copper are under investigation.

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