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SYNTHESIS AND THERMAL DECOMPOSITION OF COBALT(II) BIS (TARTRATO) COBALTATE(II) TRIHYDRATE

S. Sarmah and N. N. Dass[*]

Department of Chemistry, Dibrugarh University, Dibrugarh – 786 004, ASSAM, India

Abstract

The paper describes the synthesis and characterization of cobalt(II) bis (tartrato) cobaltate(II) trihydrate $Co[Co[C_4O_6H_4)_2]\cdot 3H_2O$. The complex was characterized on the basis of elemental analysis, infrared, electronic, e.s.r. spectra and X-ray powder diffraction studies. The thermal decomposition of the complex led to a mixture of Co_2O_3 and Co_3O_4 in air at about 400°C, whereas in nitrogen it was decomposed to a mixture of CoO and C at about 384°C. A tentative reaction mechanism is suggested for the thermal decomposition of the complex in air and nitrogen.

Keywords: complexes

Introduction

Although tartrato complexes of transition and non transition metals of various types had been studied extensively by different workers [1–4], complexes of the type $M[M(tart)_n]\cdot xH_2O$ are still unknown. The complexes of the type $M[M(C_2O_4)_n]\cdot xH_2O$ were prepared, characterized and their thermal behaviour were studied. In the present communication we report the synthesis and characterization of hitherto unknown $Co[Co(tartrato)_2]\cdot 3H_2O$. The thermal decomposition of the complex in both air and nitrogen media is also presented.

Experimental

Preparation of the complex

Cobalt(II) hydroxide, prepared from cobalt(II) chloride was made free from chloride. It was dissolved in glacial acetic acid and the mixture was heated on a steam both. A dark pink compound was precipitated by dropwise addition of a

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[*] Author to whom all correspondence shold be addressed.

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saturated solution of *L*(+) tartaric acid in glacial acetic acid. The compound was insoluble in common organic solvents, but was decomposed in presence of acid and alkali. The water content was determined gravimetrically as described earlier [5]. The cobalt content was determined gravimetrically as $CoSO_4$ and also by Perkin-Elmer AAS. Carbon and hydrogen were analysed by Thomas CH analyser.

Analysis as calculated for $Co[Co(C_4O_6H_4)_2]\cdot 3H_2O$, C=20.50%, H=2.99%, Co=25.19%, H_2O=11.54%, found C=20.90%, H=3.00%, Co=24.86% and H_2O–11.55%.

Spectroscopic and thermal measurements

The infrared spectra of the gases evolved during the complete decomposition of the complex were recorded as described earlier [5]. The IR spectra (4000–500 cm^{-1}, pellet in KBr) of the complex and of the intermediates were recorded with a Perkin-Elmer spectrophotometer. The low-frequency IR spectra (625–125 cm^{-1}) was recorded with BOMEM DA-8FT-IR spectrophotometer.

Diffuse reflectance spectra were recorded with a Shimadzu UV 240 spectrophotometer using $BaSO_4$ as the reference material. A varian E – line century series e.s.r. spectrometer was used to record the e.s.r. spectra of the complex with TCNE as marker.

The thermogravimetric analysis (TG) was carried out with Perkin-Elmer thermal analyser operating at a heating rate of 10°C min^{-1} both in air and nitrogen media taking 7.66 mg and 14.66 mg sample respectively. X-ray powder diffraction pattern was obtained using CuK_α radiation. The measuring conditions were 30 KV, 10 mA with scattering angle 2° to 100° with a step angle 0.05°.

Results and discussion

The complex $Co[Co(C_4O_6H_4)_2]\cdot 3H_2O$ was obtained as a dark pink microcrystalline compound which was insoluble in common organic solvents, but could be decomposed by strong acid or alkali.

Spectral studies

The e.s.r. spectra at room temperature did not produce any signal. So the complex was expected to be diamagnetic. The electronic spectrum (Fig. 1) of solid sample gave strong evidence for Co(II) species. In electronic spectrum, a complex multicomponent band was observed around 20000 cm^{-1} (14600; 19200; 20000 and 21500 cm^{-1}). The complexity was due to either (i) the occurrence of a weak two-electron transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ or (ii) mixing of spin forbidden band with spin allowed transitions [6].

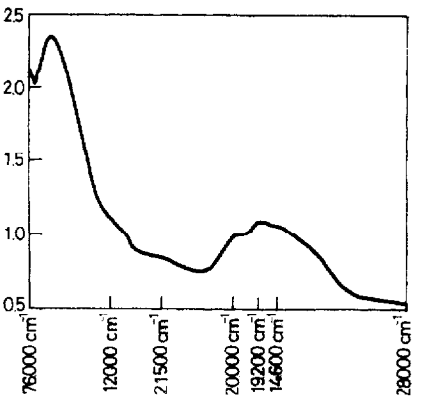

Fig. 1 Electronic spectrum (solid state) of $Co[Co(C_4O_6H_4)_2]\cdot 3H_2O$

In the present case, the complexity might be due to the presence of both distorted octahedral and tetrahedral Co(II) geometries around the two cobalt atoms [6, 7]. Both in the tetrahedral and in the octahedral geometries, the respective transitions $4A_2 \rightarrow {}^4T_1$ (P) and ${}^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P) will be expected to be around 20000 cm^{-1} [6]. Therefore, all the components could be assigned to either of the transitions. Considering the diamagnetic nature, elemental analysis and extreme insolubility, a binuclear cobalt(II) species with a strong metal-metal bond was suggested, where one metal will have tetrahedral geometry and the other octahedral geometry. In the far IR spectrum a sharp peak was observed at 180 cm^{-1} which confirmed the presence of a strong metal – metal bond [6, 14].

The presence of water molecule was indicated by a broad absorption band centered at 3200 cm^{-1}. This band was due to $\nu_{sy(O-H)}$ and $\nu_{asy(O-H)}$ of water. The peaks at 1395 cm^{-1} (S) and 1360 cm^{-1} (m) were due to $\nu_{sy(C-O)}$ and $\nu_{sy(C-C)}$ and $\nu_{sy(C-O)}$ and/or $\nu_{(O-C-O)}$ respectively [6, 16]. The single sharp peak at 1610 cm^{-1} was indicative of co-ordinated carboxylate groups. The sharp peak showed that both groups are alike (co-ordinated carboxylate groups) [2].

The carboxylate stretching absorption (1610 and 1395 cm^{-1}) strongly suggested that both oxygen atoms are co-ordinated to cobalt. If only one of the carboxylate oxygen atoms was co-ordinated to cobalt, the asymmetric frequency of the free carboxylate ion would be expected to increase as the vibration assumes more ketonic character [1].

In pure tartaric acid, a peak was observed at about 1100 cm^{-1} indicative of a secondary alcoholic group (C–O stretching) whereas cobalt complex showed a split or double peak at 1095 cm^{-1} (shifted to lower frequency). Although there was no loss of proton from –OH groups, the conversion of a single peak into a double one and the shift to lower frequencies indicated that the alcoholic hydroxyl groups are not alike in the complex. The coordination of an oxygen to the metal ion was expected to result in a reduction of the C–O stretching frequency and the fact that both peaks were at a lower frequency than the corresponding sin-

Table 1 Selected bands in the IR spectrum of the complex $Co[Co(C_4O_6H_4)_2]\cdot 3H_2O$

IR bands/cm^{-1}	Assignments
2800–3800(b)	$\nu_{sy(O-H)}+\nu_{asy(O-H)}$
1610(s)	$\nu_{asy(C=O)}$
1395(s)	$\nu_{(C-O)}$ and/or $\nu_{(C-C)}$ $\nu_{(C-O)}$ and/or $\nu_{(O-C=O)}$
1360(m)	
1250(w)	
1095(m)	Alcoholic C–O streching vibration
1035(m)	
750(m)	Co-ordinated water
620(m)	$\nu_{(CO-O)}$ and/or $\nu_{(C-C)}$
300(m)	Out of plane bending
475(m)	Ring deformation and/or $\nu_{(C-C=O)}$
375(s)	$\nu_{(O-C=O)}$
180(s)	$\nu_{(Co-Co)}$

gle peak in tartaric acid indicated that there was an attraction between the hydroxyl groups and the cobalt ion. However, the split peak indicated a much stronger attraction for one hydroxyl group by the cobalt ion than for the second. The co-ordination of a metal ion by the carboxylate groups was expected to reduce the C–O stretching frequency which was observed [2]. The sharp peak observed at 620 cm^{-1} might be due to $\nu_{(Co-O)}$ or $\nu_{(C-C)}$ [6]. The sharp peak at 180 cm^{-1} indicated metal-metal bonding in the complex. All these bands indicated the presence of co-ordinated tartrato group. Selected bands in the IR spectrum of the complex are shown in Table 1.

From XRD results four peaks were identified at 22.20°, 27.90°, 32.60° and 37.65°. The corresponding edge distances were 4.006 Å, 3.199 Å, 2.748 Å and 2.390 Å respectively. From these data, it could be suggested that there were two Co atoms-one at octahedral centre and the other was at tatrahedral centre. The slight deviation from actual value of b.c.c. (1:1.414:0.577) indicated that the complex was a distorted body centred cube. The far IR studies also indicated metal-metal bonding.

From these observation a tantative structure of the complex was proposed as indicated in Fig. 3.

Thermal studies

The TG curve in air [Fig. 2(a)] atmosphere showed the beginning of mass loss at 35°C which continued up to 220°C with mass loss 7.90% (calculated 7.69%)

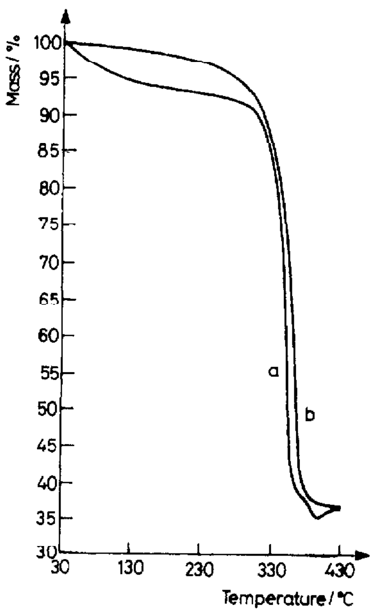

Fig. 2 TG in (a) air medium and (b) nitrogen medium

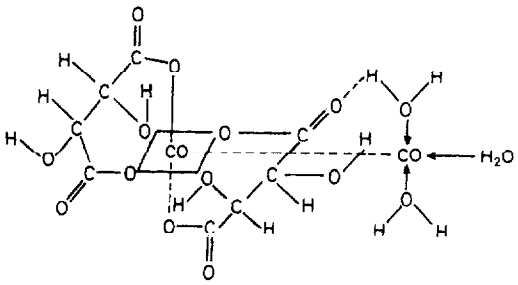

Fig. 3 Tentative structure of $Co[Co(C_4O_6H_4)_2]\cdot3H_2O$

indicating the loss of two molecules of water. The resulting compound was almost stable up to 290°C and it was isolated by temperature arrest technique. The IR spectra of the compound was similar to that of the parent compound indicating the retention of chelated tartrato group [1]. The presence of a relatively small band at 3400–3200 cm^{-1} in IR spectrum of the compound preheated to 220°C indicated the presence of trace amount of water [7].

The faint pink compound as produced absorbed moisture immediately on exposure to humid atmosphere resulting in the reformation of the original compound as evidenced by the reappearance of the broad band int he region

Table 2 TG and chemical analysis data of $Co[Co(C_4O_6H_4)_2]{\cdot}3H_2O$ in air and nitrogen media

Medium	Sample mass/mg	Step No.	$T_{\mathrm{rang(TG)}}$/ °C	Mass loss/%			Loss of molecules in the step	Reaction
				found	calc.	from independent pyrolysis		
Air	7.6556	1	35–220	7.90	7 .69	7.60	$2H_2O$	dehydration (endo)
		2	290–360	48.00	48.71	48.60	H_2O, 3CO, $2CO_2$ $1/2C_2H_4$	decomposition (exo)
		3	360–400	65.00	65.21	65.31	CO, CO_2	decomposition (exo)
Nitrogen	14.66	1	50–232	7.40	7.69	–	$2H_2O$	dehydration (endo)
		2	232–350	33.00	33.40	–	H_2O, CO	decomposition (exo)
		3	350–384	64.00	63.30	–	$2H_2O$, $2CO_2$, CO	decomposition (exo)

2800–3800 cm^{-1}. The mass loss was gradual from 50°C in nitrogen Fig. 2(b). An inflexion at 232°C with the mass loss 7.40% (calculated 7.69%) indicated the loss of two molecules of water. The third molecule of water was lost with the decomposition of the complex. The partly dehydrated complex was almost stable up to 290°C in air, beyond it, the complex lost mass up to 360°C. The last molecule of water was lost at about 290°C with the decomposition of the complex [8]. It was not possible to isolate the complete anhydrous form as the last trace of water was removed with the decomposition of the complex [7]. The removal of water at higher temperature supported the formation of metal-oxygen co-ordinate bond with water as well as the presence of hydrogen bonding [8, 19]. After removal of the last water molecule, the compound was decomposed through several steps. The first step was between 290–345°C corresponding to the mass loss 39% (calculated 38.9%) at 345°C. The mass loss data corresponded well to the formation of a mixture of CoO and $CoC_4H_2O_5$ (Cobalt meso oxalate). The formation of this type of intermediate was reported for some tartrate compounds [4, 16]. The formation of CoO and $CoC_4H_2O_5$ indicated that the outer cobalt in the complex produced CoO while the inner cobalt produced $CoC_4H_2O_5$ [5].

At 360°C, TG indicated 48% mass loss which corresponded well with the formation of CoC_2O_4 (calculated 48.71%). At 400°C, the mass loss in TG (found 65%, calculated 65.21%) indicated the formation of a compound like Co_2O_3 or a mixture of Co_2O_3 and Co_3O_4, the black amorphous compound on analysis gave Co, 69.95%, compared to the calculated values of 71.06% and 73.60% for Co_2O_3 and Co_3O_4 respectively. The IR spectrum of the compound showed band at 660 (strong), 560 and 390 cm^{-1} similar to those reported for Co_3O_4 [6]. The e.s.r. spectrum showed the paramagnetic nature of the compound. From those observation, it was confirmed that the compound might be a mixture of Co_2O_3 and Co_3O_4. The rise in TG curve beyond 400°C and stabilization around 410°C might be due to the presence of carbon formed during the disproportionation of some Co(g) to Co_2(g) [6, 8]. It was not possible to isolate CoC_2O_4 as it was decomposed immediately at about 394°C [6]. After removal of two molecules of water at 232°C, the complex was decomposed through two stages in nitrogen atmosphere. The first stage was between 232–350°C corresponding to the mass loss 33.00% (calculated 33.40%) indicated the formation of an intermediates $Co(C_4O_6H_4)CoCO_3$. The formation of such type of intermediates was reported by some workers [19, 20]. The intermediate could not be isolated as it was decomposed just above 350 °C. At 384°C, the mass loss in TG (found 64% calculated 63.3%) indicated the formation of a mixture of CoO and C.

The olive green compound on analysis gave Co; 78.30% compared to the calculated value 78.38% for CoO. The thermal analysis results are summarised in Table 2.

Depending upon the results obtained above, the following thermal decomposition process may be suggested:

In air:

$$Co[Co(C_4O_6H_4)_2]\cdot 3H_2O \xrightarrow[-2H_2O]{50^{o}C-220^{o}C} Co[Co(C_4O_6H_4)_2]\cdot H_2O$$

$$\xrightarrow[\substack{-H_2O\\-CO, CO_2}]{290-220^{o}C} CoO + CoC_4H_2O_5 + 2C \xrightarrow[\substack{-2CO, CO_2\\-1/2C_2H_4}]{345-360^{o}C} CoO+CoC_2O_4+2C$$

$$\xrightarrow[{[O]}]{360-400^{o}C} 1/3(Co_3O_4)+1/2(Co_2O_3)+mCO_2+nCO \xrightarrow{\sim 410^{o}C} 1/3(Co_3O_4)+1/2(Co_2O_3)+C$$

In nitrogen:

$$Co[Co(C_4O_6H_4)_2]\cdot 3H_2O \xrightarrow[-2H_2O]{50-232^{o}C} Co[Co(C_4O_6H_4)_2]\cdot H_2O$$

$$\xrightarrow[\substack{-H_2O\\-CO}]{232-350^{o}C} Co(C_4O_6H_4)CoCO_3+2C \xrightarrow[\substack{-2H_2O\\-2CO_2\\-CO}]{350-384^{o}C} 2CoO+2C$$

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