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SYNTHESIS AND THERMAL DECOMPOSITION OF COBALT(II) BIS(OXALATO)COBALTATE(II) TETRAHYDRATE

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Cobalt(II) bis(oxalato)cobaltate(II) tetrahydrate ($Co[Co(C_2O_4)] \cdot 4H_2O$) was synthesized and characterized on the basis of elemental and spectral analysis. The thermal decomposition of the complex was investigated in air and nitrogen media. In air, complete dehydration of the complex occured at 251°, followed by rapid decomposition to a mixture of Co_2O_3 and Co_3O_4 at 300°; in nitrogen, dehydration occurred at 206°, followed by decomposition to a mixture of Co and CoC_2O_4, and finally to Co + CoO, at 394° and 420°, respectively. The activation energies for the dehydration and decomposition reactions in nitrogen and air media were evaluated and a tentative reaction mechanism for the thermal decomposition of the complex was proposed.

Although the oxalato complexes of transition metal have been known for a long time [1–8], complexes of the type $M[M(C_2O_4)_n] \cdot xH_2O$ are relatively unfamiliar. Thermal studies of potassium bis(oxalato) complexes of Co(II), Cu(II) and Ni(II) in nitrogen and air were reported by Broadbent et al. [9].

The synthesis and characterization of iron(III) tris(oxalato)ferrate(III) tetrahydrate and the mechanism of its thermal decomposition have also been described [10]. In the present communication we report the synthesis and characterization of hitherto unknown $Co[Co(C_2O_4)_2] \cdot 4H_2O$. The thermal decomposition of the compound in both air and nitrogen media is also investigated.

Experimental

Preparation of the complex

Cobalt(II) hydroxide, prepared from Cobalt(II) chloride, was freed from chloride. It was dissolved in hot glacial acetic acid and a pale-pink compound was

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precipitated by dropwise addition of a concentrated solution of oxalic acid in glacial acetic acid. The precipitate was filtered off, washed several times with distilled water and dried over calcium chloride. The water content was determined gravimetrically as described earlier [10]. The cobalt content was determined gravimetrically as $CoSO_4$. Carbon and hydrogen were analysed with a Thomas CH analyser. Analysis: calcd. for $Co[Co(C_2O_4)_2] \cdot 4H_2O$: Co, 32.21%; C, 13.16%; H, 2.2%; H_2O, 19.69%; found: Co, 32.02%; C, 13.19%; H, 2.13%; and H_2O, 19.58%.

Apparatus

The IR spectra of the gases evolved during the decomposition of the complex were recorded as described earlier [10]. The IR spectra (4000–200 cm^{-1}, pellets in CsI) of the complex and some of the intermediates were recorded with a Perkin–Elmer 781 spectrophotometer, while the low-frequency IR spectra (600–100 cm^{-1}) were recorded with a Polytec FIR 30 instrument. Diffuse reflectance spectra were recorded with a Shimadzu UV–240 spectrophotometer, using $BaSO_4$ as the reference material. The e.s.r. spectra of the complex and its decomposition products were recorded at liquid nitrogen temperature on a Varian E-line century series e.s.r. spectrometer, with TCNE as marker. The magnetic moment of the complex was measured as described earlier [10]. The thermogravimetry (TG) and derivative thermogravimetry (DTG) were carried out with a Perkin–Elmer thermal analyser, operating at a heating rate of 10 deg min^{-1}. Differential scanning calorimetric (DSC) curves were recorded with a Mettler TA 3000 in air purged at a rate of 30 cm^3 min^{-1}, at a heating rate of 10 deg min^{-1}. For decomposition, the complex was heated by a reported method [10].

Results and discussion

The pale-pink compound, $Co[Co(C_2O_4)_2] \cdot 4H_2O$, was insoluble in water or in common organic solvents. It decomposed in the presence of strong acid or alkali.

Spectral studies

The e.s.r. spectra at room and liquid nitrogen temperature did not exhibit any signal. The magnetic moment measurement indicated that the compound was diamagnetic. This result is suggestive of a cobalt(III) species. However, the elemental analysis conforms to a molecular formula $Co[Co(C_2O_4)_2] \cdot 4H_2O$. Further, the electronic spectrum of the solid sample was more compatible with that of a cobalt(II) species; it displayed a complex multicomponent band centered around 20,000 cm^{-1} (13,510, 18,520sh, 20,000 and 21,740 cm^{-1}). The complexity could be due to either (i) the occurrence of a weak two-electron transition, $^4T_{1g}(F) \rightarrow {}^4T_{2g}$, or (ii) the mixing of a spin-forbidden band with spin-allowed transitions. In the present case, considering the complexity of the spectrum a severe distortion from ideal geometry for octahedral or tetrahedral cobalt(II) can be invoked. In both the tetrahedral and the octahedral geometries, the respective transitions $^4A_2 \rightarrow {}^4T_1(P)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ are expected to occur at around 20,000 cm^{-1}. Therefore, all the components can 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 can be visualized [11, 12] where, according to the above molecular formula, one metal will have tetrahedral geometry and the other octahedral geometry. A sharp peak observed at 180 cm^{-1} in the far IR spectrum further substantiates the presence of a strong metal-metal bond [13]. The chelating character of the oxalato group and the presence of co-ordinated water can be inferred from the IR spectra [14].

Thermal studies

The TG curve in nitrogen (Fig. 1) shows the beginning of weight loss at 60°, which continues up to 206°. This corresponds to the DTG peak between 130 and 206°, and conforms to the calculated weight loss (found 18.84%; calcd. 19.69%) from the TG curve indicating the loss of four molecules of water. The weight loss is gradual from 60° in air (Fig. 2): an inflexion at 160° indicates the loss of one molecule of water, with the loss of all the associated water molecules at 206°. The resulting anhydrous compound was isolated by the temperature arrest technique. It was bluish-violet in colour. The deaquated complex is likely to be octahedral in geometry, as is evident from its electronic and IR spectra; the latter is similar to that of the parent

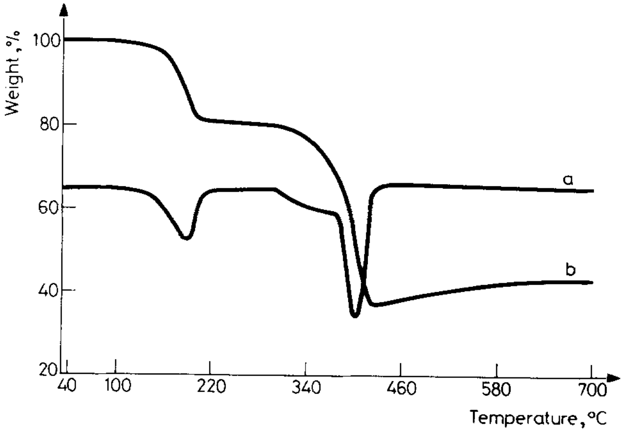

Fig. 1 (a) DTG and (b) TG curves in nitrogen compound, indicating retention of the chelated oxalato group [14, 15]. When kept in a humid atmosphere, it absorbs water. With the use of TG data, the E^+ of dehydration, calculated on the basis of the Freeman and Carroll equation [16], was found to be 92.84 and 133.8 kJ mol^{-1} in nitrogen and air, respectively; the latter compares well with the value of 142.2±2.72 kJ mol^{-1} (in air) obtained from DSC (Fig.3), in which an endothermic peak was obtained between 150 and 235° with $\Delta T_{\min} = 201°$. The enthalpy change and order of reaction obtained from DSC were 19.7×10^4 kJ mol^{-1} and 0.79±0.03, respectively. The anhydrous compound was almost stable up to 300° in nitrogen; beyond that, it lost weight up to 420°. It decomposed in two stages, the first stage corresponding to the weight loss (found 43%; calcd. 43.74%) at 394°, the mixture being assumed to be Co and CoC_2O_4. It is difficult to isolate CoC_2O_4 as it immediately decomposes just above 394°. At 420°, the weight loss in TG (found 63.15%; calcd. 63.41%) indicated the formation of a mixture of Co and CoO. The rise in the TG curve beyond 420° and the stabilization

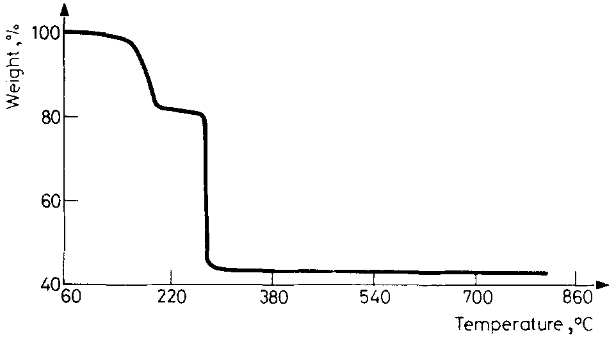

Fig. 2 TG curve in air

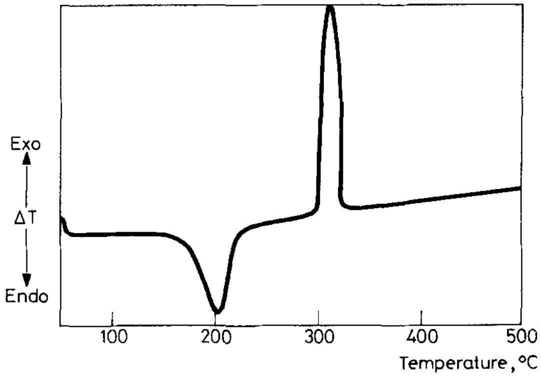

Fig. 3 DSC curve in air

around 625° may be due to the presence of carbon formed during the disproportionation of some CO(g) to CO_2(g) [19]. The E^+ values for the two decomposition stages were calculated to be 52.13 and 191.2 J mol^{-1}, respectively.

Corresponding to these stages, a broad peak was observed in the interval 300–420°, which gould be resolved into two overlapping peaks at around 342 and 404° in the DTG curve; probably due to this overlapping, the first intermediate could not be isolated. The deaquated compound (in air) was almost stable up to 251°, as indicated by the TG curve. Beyond 251° it decomposed and a steep

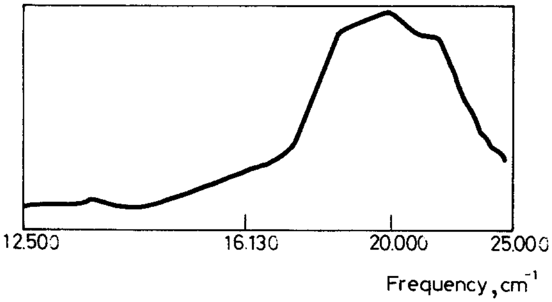

Fig. 4 Electronic spectrum (solid state) of $Co[Co(C_2O_4)_2]\cdot 4H_2O$

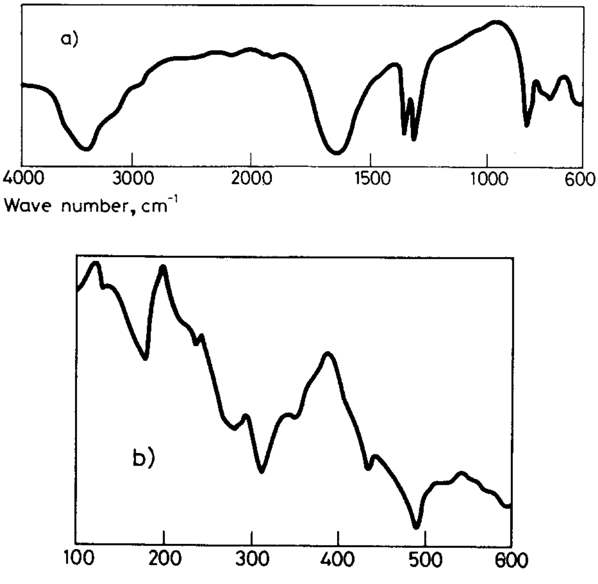

Fig. 5 Infrared spectrum of $Co[Co(C_2O_4)_2]\cdot 4H_2O$ at (a) 4000–600 cm^{-1} and (b) 600–100 cm^{-1}

slope with continuous weight loss (found 56.31%; calcd. 54.66%) was observed up to 300°, indicating the formation of Co_2O_3 or a mixture of Co_2O_3 and Co_3O_4. The black amorphous compound gave 69.84% Co on analysis, compared with the calculated values of 71.06% and 73.6% for Co_2O_3 and Co_3O_4, respectively. The IR spectrum of the compound showed bands at 660 (strong), 560 and 390 cm^{-1}, similar to those reported [17] for Co_3O_4. The e.s.r. spectrum at liquid nitrogen temperature gave three g values ($g_1 = 3.27, g_2 = 2.91, g_3 = 2.13$), indicating the paramagnetic nature of the compound. In view of the above results, the compound might be a mixture of Co_2O_3 and Co_3O_4, with both cobalt(II) and cobalt(III) in the non-stoichiometric form of both tetrahedral and octahedral interstices [18]. Corresponding to this decomposition stage, a large exothermic peak with ΔT_{max} of 312.2° was obtained between 295 and 324.7° in DSC. The corresponding enthalpy change and order of decomposition were 35.1×10^4 kJ mol^{-1} and 0.14 ± 0.01, respectively. The respective E^* values of this stage, calculated from TG and DSC, were 110.3 and 54.1 ± 1.92 kJ mol^{-1}. The water, carbon monoxide and carbon dioxide evolved during the complete decomposition in air were identified by IR spectroscopy [14].

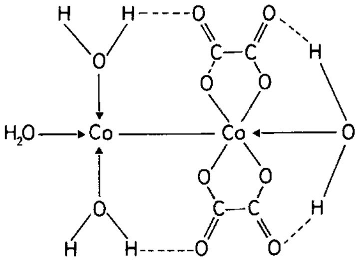

Fig. 6 Tentative structure of $Co[Co(C_2O_4)_2] \cdot 4H_2O$

In view of the results obtained above, the following tentative mechanism may be suggested for the dehydration and decomposition of the compound in nitrogen and air media.

(i) In nitrogen atmosphere:

$$Co[Co(C_2O_4)_2] \cdot 4H_2O \xrightarrow{206^\circ} Co[Co(C_2O_4)_2] + 4\,H_2O(v)$$

$$\xrightarrow{394^\circ} Co + CoC_2O_4 + 2\,CO_2(g) \xrightarrow{\text{above } 420^\circ} Co + CoO + CO_2(g) + CO(g)$$

(ii) In air atmosphere:

$$\mathrm{Co[Co(C_2O_4)_2]\cdot 4H_2O} \xrightarrow{120^\circ} \mathrm{Co[Co(O_2O_4)_2]\cdot 3H_2O + H_2O}(v)$$

$$\xrightarrow{\text{above } 206^\circ \text{ to } 251^\circ} \mathrm{Co[Co(C_2O_4)_2] + 3\,H_2O}(v)$$

$$\xrightarrow{\text{above } 300^\circ} \mathrm{(Co_2O_3 + Co_3O_4)} + m\,\mathrm{CO_2}(g) + n\,\mathrm{CO}(g)$$

* * *

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Zusammenfassung — Das Tetrahydrat von Kobalt(II)bisoxalatokobaltat(II) wurde dargestellt und mittels Elementar- und Spektralanalyse characterisiert. Die thermische Zersetzung der Komplexe wurde sowohl in Luft- als auch in Stickstoffatmosphäre untersucht. In Luft erfolgt bei 251 °C eine vollständige Dehydratierung, gefolgt von einer schnellen Zersetzung bei 300 °C in Co_2O_3 und Co_3O_4. In Stickstoff erfolgt die Dehydratierung bei 206 °C, gefolgt von einer Zersetzung bei zunächst 394 °C in Co und CoC_2O_4, anschliessend bei 420 °C in Co und CoO. Die Aktivierungsenergien für die Dehydratierung und Zersetzung in Stickstofo- und Luftatmosphäre wurden ermittelt und für die thermische Zersetzung der Komplexe ein Reaktionsmechanismus gegeben.

Резюме — Химическим и спектральным анализом охарактеризован синтезированный тетрагидрат биз-(оксалато)кобальтат кобальта ($Co[Co(C_2O_4)_2]\cdot 4H_2O$), термическое разложение которого было изучено в атмосфере воздуха и азота. В атмосфере воздуха полное разложение комплекса происходит при 251 °С с последующим быстрым разложением до смеси Co_2O_3 и Co_3O_4 при температуре 300 °С. В атмосфере азота дегидратация происходит при 260 °С с последующим разложением сначала до смеси Co и CoC_2O_4, а затем до Co и CoO при температурах, соответственно, 394 и 420 °С. Определены энергии активации реакций дегидратации и разложения, а также предложен пробный механизм реакций термического разложения.