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Synthesis, Characterization, and the Thermal Decomposition of Copper(II) Bis(oxalato)cuprate(II) Dihydrate

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Synopsis. Copper(II) bis(oxalato)cuprate(II) dihydrate, $Cu[Cu(C_2O_4)_2]\cdot 2H_2O$, has been synthesized and characterized by elemental analysis, magnetic moment measurement, and IR, electronic and ESR spectral studies. The low value of magnetic moment (1.57 B.M.) from spin-only value is indicative of the antiferromagnetic spin pairing between two paramagnetic copper(II) ions. The ESR spectrum of the powder showed a single signal with a *g* value of 2.1. The thermal decomposition in air and nitrogen media was investigated by TG, DTG, and DSC. Some of the decomposition products were identified by spectral, analytical and X-ray powder diffraction studies.

There has been a considerable interest in the study of oxalato complexes of transition metals[1-10] and much of the work have been periodically reviewed.[11] Binuclear complexes of Cu(II) with oxygen donor ligands involving metal-metal bonding have been reported.[12-16] However, studies on the compounds of the type $M[M(C_2O_4)_n]\cdot xH_2O$, [where M=same metal] are still rare.[17] The synthesis of copper(II) bis(oxalato)-cuprate(II) dihydrate, has not been reported so far. Here we are reporting the synthesis and characterization of copper(II) bis(oxalato)cuprate(II) dihydrate, $Cu[Cu(C_2O_4)_2]\cdot 2H_2O$. The thermal decomposition was also investigated and a tentative mechanism of thermal decomposition has been proposed.

Experimental

Materials. Copper(II) hydroxide, prepared from copper(II) chloride was made free from chloride. It was dissolved in glacial acetic acid and the mixture was heated on a steam bath. A light blue compound was precipitated by dropwise addition of a saturated solution of oxalic acid in glacial acetic acid. The compound was filtered off and purified by standard procedure.[17] The compound was insoluble in common organic solvents, however, decomposes in presence of acid or alkali. The water content was determined thermogravimetrically, while copper content was determined iodometrically. The percentages of carbon and hydrogen were estimated with Thomas CH analyzer. Found: C, 14.42; H, 1.13; Cu, 37.62; H_2O, 10.56%. Calcd for $C_4H_4O_{10}Cu_2$: C, 14.17; H, 1.19; Cu, 37.48; H_2O, 10.61%.

Measurements. IR spectra of the gases evolved were recorded by the reported method[17] and those of the complex and the intermediates were recorded on a Perkin-Elmer 781 spectrophotometer in CsI as well as in Nujol. The low frequency IR spectrum (600—100 cm^{-1}) of the complex was obtained using a Polytec FIR-30 instrument. Diffuse reflectance spectrum was recorded with a Shimadzu UV-240 spectrophotometer using $BaSO_4$ as the reference material. ESR spectrum at liquid nitrogen temperature was obtained on a Varian E-line century series ESR spectrometer with TCNE as marker. The magnetic moment of the complex was measured as described earlier.[17] The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained in the range from room temperature to 800 °C with a Perkin-Elmer thermal analyzer at a heating rate of 10 °C min^{-1}. Differential scanning calorimetric (DSC) screen was performed using a Mettler TA 3000. The experiment was carried out in air purged at a rate of 30 cm^3 min^{-1} with a heating rate of 10 °C min^{-1}. X-Ray powder diffraction patterns of the decomposition products were taken using Cu $K\alpha$ radiation. The time of exposure was 4 h. The residues were identified by direct comparison with photograph of standard materials. For decomposition the complex was heated in a tube as described earlier.[17]

Results and Discussion

Spectral and Magnetic Studies. The room temperature magnetic moment of the compound was 1.57 B.M. The considerable lowering on μ_{eff} from the spin-only value may be attributed to extreme distortion or partial quenching of the spin moment of the copper ions[18] or may be due to the presence of intramolecular exchange interaction between adjacent copper atoms.[19] In the ESR spectrum of the powdered compound at liquid nitrogen temperature, a strong signal with a *g* value of 2.1 was obtained. From the above results a binuclear configuration of the compound with antiferromagnetic spin pairing between two paramagnetic copper(II) ions could be suggested.[12,20] Further, the electronic spectrum of the solid sample (Fig. 1) showed bands around 13260 sh, 15500, 20200, 33100, and 40800 cm^{-1}, of which the bands around 13000—20000 cm^{-1} are d-d transitions. The shoulder at 13260 cm^{-1} and the band at 15500 cm^{-1} are tentatively assigned to $\delta\rightarrow\sigma(d_{x^2-y^2}\rightarrow d_{z^2})$ and $\delta\rightarrow\pi$ or $\delta'[d_{x^2-y^2}\rightarrow d_{zx}, d_{yz}, \text{ or } d_{xy}]$ respectively.[16] The intense bands observed at higher frequencies are L→M or M→L charge transfer, of which the band at 33100 cm^{-1} could be possibly due to transition involving the Cu-Cu bond.[21] The two

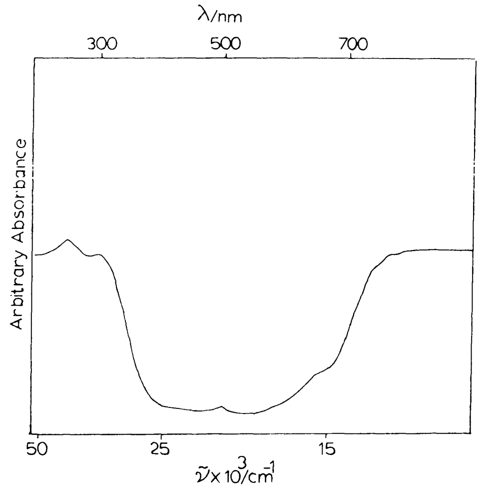

Fig. 1. Reflectance spectrum of $Cu[Cu(C_2O_4)_2]\cdot 2H_2O$.

copper atoms may be linked by either a δ bond (by lateral overlap of two $d_{x^2-y^2}$ orbitals with their lobes parallel) or σ bond due to end to end on overlap of d_{z^2} orbitals. In view of the *g* value of 2.1 and on the basis of valance bond and molecular orbital arguments[12,16] the nature of the Cu-Cu covalent bond is likely to be δ-type. The chelating character of the oxalato group was identified by IR spectroscopy[22] as shown in Table 1. In the farinfrared region a sharp peak at 188 cm^{-1} is due to Cu-Cu stretching vibrations[23] which further substantiated the presence of metal-metal bond.

TG, DTG, and DSC Studies. In the TG plot of the complex in nitrogen and air media (Fig. 2) the respective weight losses of 5.2% (at 292 °C) and 5% (at 298 °C) indicated the removal of one molecule of water. The calculated mass loss for this is 5.3%. Removal of this water at high temperature is suggestive of coordination with the metal ion with possible hydrogen bonding with the chelated oxalato group. Beyond 292 °C in nitrogen a steep slope up to 322 °C with a weight loss (Found 56.79%; Calcd 57.80%) indicated the formation of a mixture of Cu and CuO. The formation of a mixture of Cu and CuC_2O_4 as an unstable intermediate cannot be ruled out as CuC_2O_4 decomposes immediately to CuO at about 310 °C.[1,8] Corresponding to this overall decomposition a sharp peak ranging between 246—322 °C with a ΔT_{max} of 309 °C was obtained in DTG curve. The activation energy and order of reaction of the overall decomposition stage were computed on the basis of the Freeman and Carroll's equation[24] and were found to be 348.14 kJ mol^{-1} and 1.5 respectively. The rise in the TG curve beyond 322 °C and stabilization around 483 °C with a net gain of weight by 3.79% and overall weight loss (Found 53%; Calcd 53.08%) indicated the formation of a probable stable compound like 2CuO. The gain in weight may be due to the presence of carbon formed during disproportionation of some CO(g) to C and CO_2(g), due to catalytic activity of CuO.[25] The reduction of some amount of CuO to elementary copper by CO(g) cannot be ruled out.[7] In air medium beyond 298 °C a steep slope up to 310 °C in TG curve with a weight loss 84.75% apparently indicated the formation of metallic copper. This was confirmed as the positions and number of lines in the X-ray diffraction powder photograph exactly coincide with that obtained from pure copper wire. The activation energy and order of decomposition were calculated to be 503.63 kJ mol^{-1} and 1 (unity) respectively. In the DSC curve recorded in air (Fig. 3), the presence of two overlapping exotherm indicated that the complex decomposes via two stages. The first exotherm at 260.3—312 °C with a ΔT_{max} of 295.7 °C with activation energy and enthalpy change 252.79±10.38 and 155.09 kJ mol^{-1} respectively. The second exotherm at 312—329 °C with a ΔT_{max} of 323.4 °C with respective activation energy and enthalpy change 412.51±16.64 and 99.17 kJ mol^{-1}. The intermediate compound formed corresponding to first exotherm could not be identified by the temperature arrest technique as it was immediately decomposed to subsequent product and is suggestive of the removal of coordinated water molecule. The weight loss (Found 53%; Calcd 53.08%) after complete decomposition indicated the compound to be 2CuO. The residue gave an analysis, Cu, 80.15% compared to the calculated value of 79.88%. The X-ray

Table 1. Selected Bands in the Infrared Spectrum of the Complex $Cu[Cu(C_2O_4)_2]\cdot 2H_2O$

IR band/cm^{-1}	Assignment
3200—3660b	ν_{sy}(O-H)+ν_{asy}(O-H)
1610s	δ_{sy}(H-O-H)
1500—1750b	ν_{asy}(C=O)
ca. 1390m	ν(C-O) and/or ν(C-C)
ca. 1350s, ca.1305s, and ca. 1265m	ν(C-O) and/or δ(O-C=O)
810s	ν(Cu-O) and/or δ(O-C=O)
470—500b (split into two peeks)	ring deformation and/or δ(O-C=O)
365s	δ(O-C=O)
317m	out of plane bending
188 (sharp)	ν(Cu-Cu)

b=broad, m=medium, and s=strong.

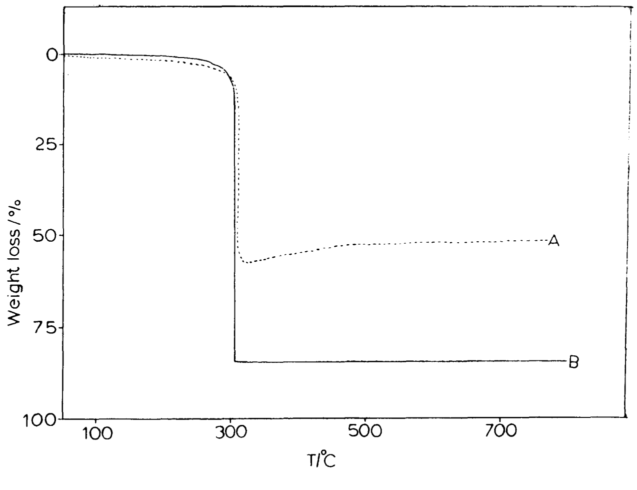

Fig. 2. A: TG curve of $Cu[Cu(C_2O_4)_2]\cdot 2H_2O$ in a flowing nitrogen atmosphere. B: TG curve of $Cu[Cu(C_2O_4)_2]\cdot 2H_2O$ in a flowing air atmosphere.

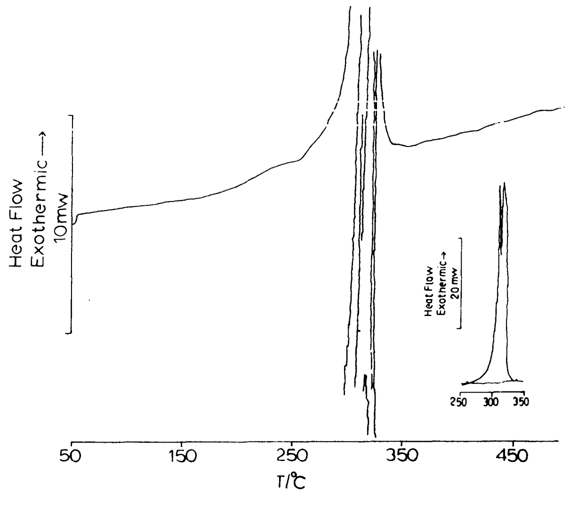

Fig. 3. DSC curve of $Cu[Cu(C_2O_4)_2]\cdot 2H_2O$ in a flowing air atmosphere.

powder diffraction photograph is similar to that of pure CuO which confirmed the black residue to be 2CuO. In the farinfrared absorption spectrum of the residue the presence of band around 600, 540, 410, and 310 (strong) $\mathrm{cm^{-1}}$ further substantiated the compound to be 2CuO.[26)] In comparison with TG in air discussed above, the corresponding weight loss in DSC is 53% instead of 84.75% and apparently this could be due to the escape of CO(g) through the pan hole before reducing CuO. X-Ray powder diffraction analysis of the product obtained on heating beyond 310 °C in a closed vessel suggested the reduction of CuO to metallic copper.[27)] The infrared spectral analysis[22)] of the gaseous products confirmed the evaluation of both carbon monoxide and carbon dioxide.

On the basis of above results the following thermal decomposition processes in nitrogen medium may be suggested.

$$\mathrm{Cu[Cu(C_2O_4)_2]\cdot 2H_2O \xrightarrow{ca.\ 292\,^{\circ}C} Cu[Cu(C_2O_4)_2]\cdot H_2O}$$
$$\mathrm{+\,H_2O(v) \xrightarrow{322\,^{\circ}C} Cu + CuO + H_2O(v) + CO_2(g)}$$
$$\mathrm{+\,CO(g) \xrightarrow{ca.\ 483\,^{\circ}C} 2CuO\ (stable).}$$

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