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Note

Reactions of Copper(II) Oxalate with Monomethylamine and Monomethylammonium Oxalate

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Two kinds of products were obtained by the reaction of copper(II) oxalate and monomethylamine: $\text{CuC}_2\text{O}_4(\text{CH}_3\text{NH}_2)$ as the major product and a very small quantity of $(\text{CH}_3\text{NH}_3)_2\text{Cu}(\text{C}_2\text{O}_4)_2$. The latter was also obtained by the reaction of copper(II) oxalate and monomethylammonium oxalate in the molar ratio of 1:2 in the presence of monomethylamine. Identification of these substances was made by X-ray powder diffraction patterns, IR-spectra, elemental and TG and DSC analyses.

INTRODUCTION

A survey of the literature shows that a number of amine complexes of bivalent metals have been prepared with virtually all possible inorganic salts. Some molecular addition compounds of cobalt(II) oxalate with primary aliphatic amines have been prepared¹ with a general formula $\text{CoC}_2\text{O}_4\text{RNH}_2$ ($\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{and } \text{C}_5\text{H}_{11}$). It has been pointed out that, irrespective of the quantity of the added amine, the ratio of cobalt(II) oxalate to amine is always 1:1 in all compounds. Magnetic susceptibility and visible absorption spectra of copper(II) oxalate with some amines have been studied.² These complexes were prepared by suspending copper(II) oxalate in chloroform and then adding a little more than the calculated quantity of the amine. In this way, $\text{CuC}_2\text{O}_4(\text{CH}_3\text{NH}_2)_2$ was obtained.

The thermal decomposition of copper(II) oxalate hemihydrate and its various compounds with different amines has been studied by thermogravimetric and differential thermal analysis (DTA) methods in nitrogen and air atmospheres.³ It was found that $\text{CuC}_2\text{O}_4(\text{CH}_3\text{NH}_2)_2$ produces copper(II) oxide as a final product, whereas $\text{CuC}_2\text{O}_4(\text{NH}_3)_2$ and $\text{CuC}_2\text{O}_4(\text{py})$ produce copper(II) oxide.

Double salts of copper(II) oxalate with monovalent cations are not well known. There are no data about double oxalates with alkylammonium, either. The aim of this work is to present the results of investigations of the products obtained by reacting

copper(II) oxalate with monomethylamine in one case, and in another case, copper(II) oxalate and monomethylammonium oxalate in the presence of monomethylamine.

EXPERIMENTAL

Chemicals

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were *p.a.* grade »Merck« and monomethylamine water solution (25%) »BDH«. $\text{CuC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$ was obtained by the reaction of an aqueous solution of copper(II) sulfate pentahydrate with oxalic acid dihydrate. A concentrated solution pentahydrate with oxalic acid dihydrate. A concentrated solution of monomethylammonium oxalate was obtained by neutralization of an aqueous suspension of oxalic acid with monomethylamine at $\text{pH} = 4$.

Preparation of the Complexes

$(\text{CH}_3\text{NH}_3)_2\text{Cu}(\text{C}_2\text{O}_4)_2$. – Water suspension of $\text{CuC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$ (0.58 g, 3.6 mmol) and monomethylammonium oxalate (1.2 g, 7.6 mmol), with addition of 6 cm^3 of monomethylamine, was slightly heated until clear solution was reached. The solution was left to evaporate at room temperature. The dark-blue crystals of $(\text{CH}_3\text{NH}_3)_2\text{Cu}(\text{C}_2\text{O}_4)_2$ that were formed overnight, were separated out, washed with water-ethanol mixture and dried in air.

Anal. Calcd. for $\text{Cu}_6\text{H}_{12}\text{N}_2\text{O}_8$: Cu 20.92, C 23.72, H 3.98, N 9.23, $\text{C}_2\text{O}_4^{2-}$ 57.96%;
found: Cu 21.01, C 23.30, H. 4.37, N 9.00, $\text{C}_2\text{O}_4^{2-}$ 57.49%.

$\text{Cu}(\text{C}_2\text{O}_4)(\text{CH}_3\text{NH}_2)$. – Suspension of $\text{CuC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$ (0.58 g, 3.6 mmol) in monomethylamine (25% water solution) was slightly heated until the copper oxalate was dissolved. The solution was left to evaporate as above. During the evaporation process, the blue powder of the composition $\text{Cu}(\text{C}_2\text{O}_4)(\text{CH}_3\text{NH}_2)$ was precipitated out. This was washed with ethanol and dried in air. Besides this substance, a very small amount (~ 2%) of (CH_3NH_2) was obtained (mechanically isolated), as well.

Anal. Calcd. for $\text{CuC}_3\text{H}_5\text{NO}_4$: Cu 34.77, C 19.73, H 2.77, N 7.67, $\text{C}_2\text{O}_4^{2-}$ 48.20%;
found: Cu 33.88%, C 20.46, H 2.93, N 7.37, $\text{C}_2\text{O}_4^{2-}$ 49.00%.

Analysis and Physical Measurements

Elemental analyses of carbon and hydrogen were carried out by Liebig's method, on CARBON-HYDROGEN-ANALYZER COLEMAN MODEL 33. Nitrogen was determined by the Dumas method. The mass percent of copper in complexes was determined by complexometric titration with murexid as indicator and that of oxalate anion by titration with a standardized solution of potassium permanganate.

TG and DSC curves were obtained on the METTLER TA 2000 SYSTEM in a flow of air with a velocity of 35 mL/min, scan speed 4 K/min. The reference substance for the DSC determination was $\alpha\text{-Al}_2\text{O}_3$; the mass of the compounds was about 20 mg; temperature range from 20 to 600 °C. IR-spectra were made on a PERKIN ELMER SPECTROPHOTOMETER M 580 in KBr pellets. X-ray powder diffraction patterns were made on a JEOL DIFFRACTOMETER MODEL JDH-7E with $\text{CuK}\alpha$ -radiation, Ni-filtered.

RESULTS AND DISCUSSION

Dark-blue crystals of the composition $(\text{CH}_3\text{NH}_3)_2\text{Cu}(\text{C}_2\text{O}_4)_2$ were obtained by the reaction of copper(II) oxalate hemihydrate with concentrated water solution of monomethylammonium oxalate in the presence of monomethylamine. Another type of compound with coordinated monomethylamine, of the composition $\text{Cu}(\text{C}_2\text{O}_4)(\text{CH}_3\text{NH}_2)$, was formed as a blue powder in the reaction of copper(II) oxalate hemihydrate with methylamine water (25%) solution. In this reaction, a small amount (~ 2%) of the former complex was also formed. According to the X-ray powder diffraction patterns (Figure 1), the isolated complexes are not isostructural solids.

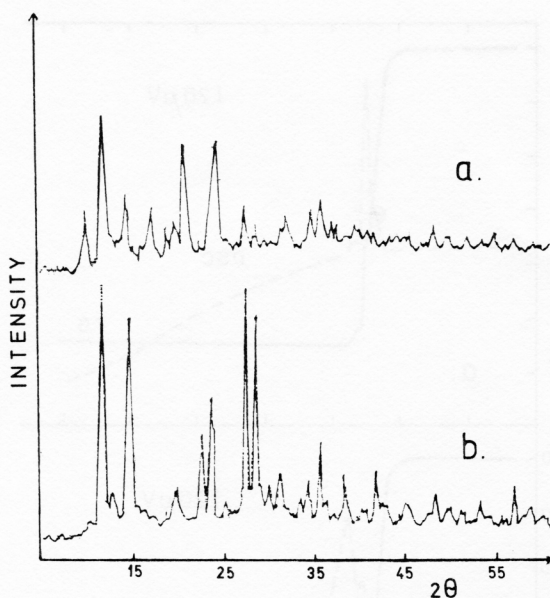


Figure 1. X-ray powder diffraction patterns of: a) $\text{CuC}_2\text{O}_4(\text{CH}_3\text{NH}_2)$ and b) $(\text{CH}_3\text{NH}_3)_2\text{Cu}(\text{C}_2\text{O}_4)_2$.

TABLE I

Observed IR frequencies (cm^{-1}) and assignments
of $(\text{CH}_3\text{NH}_3)_2\text{Cu}(\text{C}_2\text{O}_4)_2$ (1) and $\text{CuC}_2\text{O}_4(\text{CH}_3\text{NH}_2)$ (2)

	(1)	(2)
ν ($-\text{NH}_2$)		3370–3345 m,br*
ν (N–H)	3140 m,br	
ν_{as} (COO^-)	1670–1635 s	1700–1640 s
δ ($-\text{NH}_2$)		1600–1540 s
δ_{as} ($-\text{NH}_3^+$)	1498 m,sp	
δ_{as} ($-\text{CH}_3$)	1453 m,sp	1445 m,sp
ν_{s} (COO^-)	1415 s,sp	1415 s,sp
δ_{s} ($-\text{CH}_3$)	1284 s,sp	1300 s,sp
δ (COO^-)	805 s,sp	805 s,sp
ν (Cu–O)	490 s,sp	495 s,sp
ν (Cu–N)		440 m

* s - strong; m - medium; br - broad; sp - sharp

The structural and compositional differences are reflected on the spectroscopic properties of both complexes. The exact position of absorption bands in the IR spectra is given in Table I. The absorption bands located in the region 1700–1600 cm^{-1} , as well as at 1415 cm^{-1} , indicate asymmetric and symmetric stretching vibrations of COO^- groups, respectively. The strong absorption band originating from $\nu(\text{Cu}-\text{O})$ is observed at 490 cm^{-1} for $(\text{CH}_3\text{NH}_3)_2\text{Cu}(\text{C}_2\text{O}_4)_2$ and 495 cm^{-1} for $\text{CuC}_2\text{O}_4(\text{CH}_3\text{NH}_2)$. The stretching vibration $\nu(\text{Cu}-\text{N})$ observed only in $\text{CuC}_2\text{O}_4(\text{CH}_3\text{NH}_2)$ is a medium intensity band located at 440 cm^{-1} . The other absorption bands in the spectra originate from different vibrations of CH_3 or NH_2 groups, as assigned in Table I. This assignment is in agreement with the

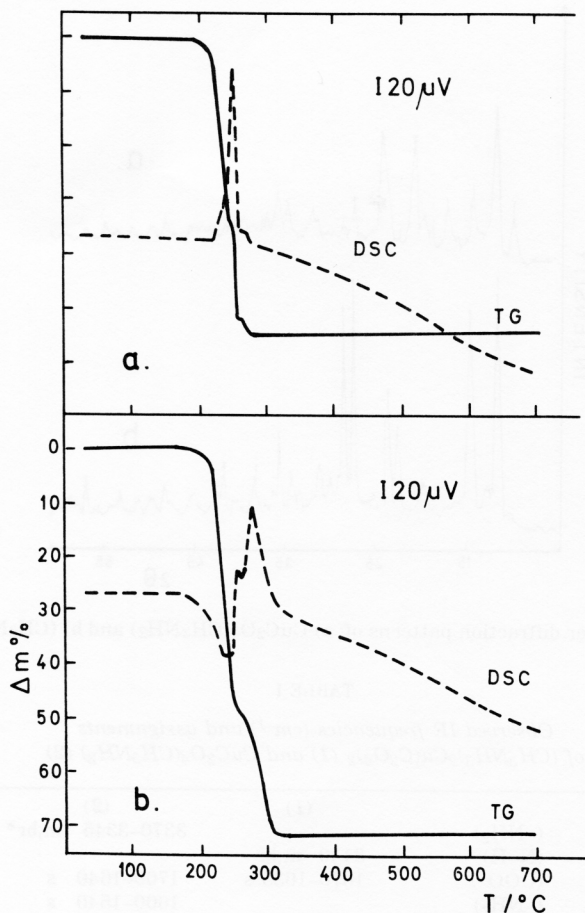


Figure 2. TG and DSC curves of: a) $\text{CuC}_2\text{O}_4(\text{CH}_3\text{NH}_2)$ and b) $(\text{CH}_3\text{NH}_3)_2\text{Cu}(\text{C}_2\text{O}_4)_2$

results found for the amine-oxalate complexes of nickel(II)⁴ and cobalt(II),⁵ as well as vanadium(IV).⁶

Thermal decomposition of these compounds occurs in two close steps in the temperature range 200–300 °C (Figure 2). Simple analysis of the TG curve of $(\text{CH}_3\text{NH}_3)_2\text{Cu}(\text{C}_2\text{O}_4)_2$ indicates that the first decomposition step could correspond to the mass loss originating from the separation of $(\text{CH}_3\text{NH}_3)_2\text{C}_2\text{O}_4$ (mass loss: calc. 50.10%; found from TG curve 52.16%) and the second to the decomposition of CuC_2O_4 to CuO , CO and CO_2 . This seems to be in accordance with the endo- and two exothermic peaks observed in the DSC curve of this compound (Figure 2b).

For the $\text{CuC}_2\text{O}_4(\text{CH}_3\text{NH}_2)$, a significant difference from the previous compound is observed in DSC curve. Only one peak (exothermic) at 250 °C in DSC curve is found (Figure 2a). This maximum could correspond to the simultaneous mass loss of CH_3NH_2 and CO (calc. 32.15%; found from TG curve 33.00%). The second step in TG curve

could originate from CuCO_3 decomposition to CuO and CO_2 (mass loss calc. 24.10%; found from TG curve 22%).

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SAŽETAK

Reakcije bakar(II)-oksalata s monometilaminom i monometilamonijevim oksalatom

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Reakcijom bakar(II)-oksalata i monometilamina dobivena su dva tipa spojeva: $\text{CuC}_2\text{O}_4(\text{CH}_3\text{NH}_2)$ kao glavni produkt i mnogo manja količina dvojnog oksalata, $(\text{CH}_3\text{NH}_3)_2\text{Cu}(\text{C}_2\text{O}_4)_2$. Posljednji je dobiven i u reakciji bakar(II)-oksalata s koncentriranom vodenom otopinom od monometilamonijeva oksalata (množinski odnos 1:2) u prisutnosti monometilamina. Za identifikaciju dobivenih produkata poslužila je elementna analiza, röntgenogrami praha, infracrveni spektri, termogravimetrija i DSC.