A CONTRIBUTION TO THE PROBLEM OF THE MODIFICATIONS OF OXALATOCOPPER(II) COMPLEXES. THE CRYSTAL STRUCTURE OF THE DIHYDRATE OF THE OXALATODIAMMINECOPPER(II) COMPLEX

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The crystal structure of the complex $Cu(COO)_2(NH_3)_2.2 H_2O$ has been determined by the method of X-ray structure analysis. The space group of symmetry is $P\bar{1}$, a 6·293(5), b 5·781(8), c 5·539(5) Å, α 77·53(6), β 100·59(9), γ 104·11(7) Å, ϱ_0 1·94 g cm^{-3}, ϱ_c 1·95 g cm^{-3}, z 1. The co-ordinates and the isotropic coefficient of thermal oscillations were refined by the least squares method using 446 independent non-zero reflections, R 0·145. Bivalent copper is co-ordinated by two nitrogen atoms (Cu—N=1·960 Å) and by four oxygen atoms from the oxalate groups (2 Cu—O=2·147 and 2 Cu—O=2·327 Å). The oxalate groups form chelates. The structure consists of infinite linear chains which are bonded to each other by hydrogen bridges. In the present paper, conclusions are made on the decomposition mechanism of the hydrate and the structure of anhydrous β-$Cu(COO)_2(NH_3)_2$, on the basis of a study using methods including thermal and infra-red analyses and electron spectroscopy.

The complex of the chemical formula $Cu(COO)_2(NH_3)_2$ is known in the literature[1-3] in several modifications. One of them, the so-called α-modification, is formed by crystallization from an aqueous solution. The other modifications are formed by decomposition of higher ammine complexes, such as $Cu(NH_3)_5(COO)_2$ (see[3]) and also $Cu(NH_3)_4(COO)_2.2 H_2O$, or by the dehydratation of the complex $Cu(NH_3)_2(COO)_2.2 H_2O$. By the decomposition of the latter complex, also the compound $Cu(COO)_2(NH_3)_2$ is formed; its powder diffraction patterns are similar to those of a complex with identical composition, which is formed by the decomposition of $Cu(NH_3)_5$.$(COO)_2$. This compound was considered in our previous papers[2,4] to be the β-modification.

In an effort to elucidate the structural differences between the modifications, the structure of $Cu(COO)_2(NH_3)_2.2 H_2O$, which crystallizes from an aqueous medium in the form of well developed single crystals, was solved. The dihydrate easily loses two water molecules (already at room temperature) and is converted into β-$Cu(COO)_2$.$(NH_3)_2$. On this fact the assumption was based that the bivalent copper is not co-ordinated with the water molecules and that, on losing water, no substantial change will occur in the Cu(II) co-ordination. To verify this assumption, other physico-chemical methods were also used, *e.g.* electron spectra and thermic methods.

EXPERIMENTAL AND RESULTS

Preparation and Analysis of the Substances

The dihydrate diaminooxalatocopper(II) complex was prepared according to the literature[5]. The complex prepared in this way, and the products of its decomposition were analyzed by determining copper (complexometrically), oxalate (by titration with permanganate), and ammonia (by the distillation method). The water content was determined from the thermogravimetric curves. For $Cu(C_2O_4)(NH_3)_2 . 2 H_2O$ (221·7), calculated: 28·68% Cu; 39·72% $C_2O_4^{2-}$; 15·05% NH_3; 16·24% H_2O, found: 28·72% Cu; 39·56% $C_2O_4^{2-}$; 15·13% NH_3; 16·30% H_2O. For $Cu(C_2O_4)(NH_3)_2$ (185·6) calculated: 34·24% Cu; 47·42% $C_2O_4^{2-}$; 18·35% NH_3, found: 34·13% Cu; 47·17% $C_2O_4^{2-}$; 18·35% NH_3. For $Cu(C_2O_4)(NH_3)$ (168·6) calculated: 37·69% Cu; 52·22% $C_2O_4^{2-}$; 10·09% NH_3, found 37·75% Cu; 52·18% $C_2O_4^{2-}$; 10·12% NH_3.

X-ray Structure Analysis

Space group and the unit cell. The crystals have triclinic symmetry. On the basis of the statistical distribution of the intensities[6], it was concluded that the crystals have a centre of symmetry; consequently, the space group is P$\bar{1}$. The approximate lattice constants, found from the Weissenberg patterns, were refined by the least squares method using the experimental data obtained from the Guinier powder patterns. The following constants were established: $a = 6·293 \pm 0·005$ Å, $b = 5·781 \pm 0·008$ Å, $c = 5·539 \pm 0·005$ Å, $\alpha = 77·53^0 \pm 0·06^0$, $\beta = 100·59^0 \pm 0·09^0$, $\gamma = 104·11^0 \pm 0·07^0$. The unit cell volume is 188·98 Å^3. The density of the crystals was found to be $\varrho_{exp} = 1·94$ g cm^{-3}, using the flotation method. The calculated value for one formula unit in the unit cell was 1·95 g cm^{-3}. The basic identification X-ray powder data are summarized in Table I.

Procedure for the solution of the crystal structure and the obtaining the diffraction data. Crystals of the approximate size of $0·1 \times 0·1 \times 0·2$ mm were photographed using the Weissenberg method and Cu K$_\alpha$ radiation. Besides the three zero layers recorded in the directions of the crystallographic axes, three more higher layers were recorded in the direction of the growth axis (the *b*-axis). The intensities were measured photometrically, and corrected for non-linearity, for the splitting factor, and the Lorentz polarization factor. The effect of absorption was neglected ($\mu R = 0·4$). The crystal structure was first solved in projections and then by means of three dimensional diffraction data. The atom co-ordinates were refined by the least squares method, taking into account individual isotropic thermal oscillations, and using the full matrix. Further, the scale factors were also refined by the Cruickshank weighting scheme[7] in which the resulting values of the constants *A* and *C* were 5·00 and 0·049, respectively.

The programme used for the parameter refinement by the least squares method, originally written by Gantzel, Sparks, and Trueblood and modified for the IBM 360/65 by Lindgren. The atomic factor values are in agreement with those of Ibers[9]. The structure found was verified by calculating the three dimensional Fourier synthesis and the differential Fourier synthesis. The highest electron density in the differential synthesis reached the value 1·5 e/Å. The programme used to compute the Fourier synthesis was written by Zalkin and modified by Lindgren. After the refinement, the R factor, defined as $\sum ||F_0| - |F_c|| . \sum |F_0|^{-1}$ for 446 independent reflections observed reached the value of 0·145. Using the co-ordinates refined in the centrally symmetrical space group, the refinement of the $Cu(C_2O_4)(NH_3)_2 2 H_2O$ structure in a noncentrally symmetrical group was attempted, but no reasonable result was obtained. The refined atomic positions and the thermal oscillation coefficients, together with their standard deviations are given in Table II. The interatomic distances and bond angles are shown in Tables III and IV. All the complexes obtained were identified by their X-ray powder patterns obtained on the GON II, diffractograph, using the Cu K$_\alpha$ radiation.

Physico-Chemical Investigation

The thermal decomposition of $Cu(C_2O_4)_2(NH_3)_2.2 H_2O$ was followed with an OD 102 derivato-graph, (MOM, Budapest). The description of the apparatus and its function is given in the literature[8]. The measuring conditions were as follows: the sample weight, 100 mg, the sensitivity: DTA, 1/10, DTG, 1/10, TG, 50 mg, the rate of temperature increase, 3 K/min, the sample grain size, $0.1-0.25$ mm. All measurements were carried out in the air under the given conditions. The kinetic parameters were calculated according to paper[10], on the basis of the thermogravimetric curves. The heats of the reactions were followed using the DSC-1B differential calorimeter (Perkin Elmer), in aluminium pans with pressed-on lids. The sample weight used was 5 mg, the heating rate, 8 K min^{-1}. The infrared absorption spectra were measured with the Perkin Elmer 137 spectrophotometer, in Nujol suspension, within the range, of 700 to 3400 cm^{-1}. The electron spectra were measured with the Perkin Elmer 450 spectrophotometer, within the range, of 20000 to 8000 cm^{-1}. The transparence of the sample-nujol suspension, deposited on a chromatographic paper, was measured. The EPR spectra were measured at laboratory temperature using a polycrystalline sample and the ER-9 spectrophotometer (Zeiss, Jena). The values of the g-factors were obtained by the Kneubühl approximation[11]. DPPH was used as the calibration standard, and the procedure and the precision of the results were tested using copper(II) sulphate pentahydrate.

DISCUSSION

The crystal structure of the $Cu(COO)_2(NH_3)_2.2 H_2O$ complex consists of infinite linear chains, arranged along the y-axis. The chains are bonded to each other by
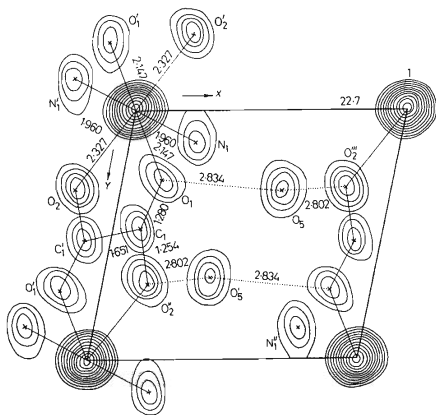

Fig. 1

The Projection of the Crystal Structure of $Cu(C_2O_4)(NH_3)_2.2 H_2O$

hydrogen bonds. Each water molecule forms two hydrogen bonds with the lengths 2·802 and 2·834 Å (Fig. 1, Table III); the O_1—O_5—O_2 bond angle is 121° (Table IV).

TABLE I

The Observed (D_{obs}) and Calculated (D_{cal}) Interplanar Distances with the Relative Intensities for $Cu(C_2O_4)(NH_3)_2 \cdot 2 H_2O$

The data were obtained using the Guinier powder patterns.

No	h	k	l	D_{obs}	D_{cal}	I_{rel}[a]
1	1	0	0	5·996	6·044	100
2	0	—1	0	5·435	5·516	10
3	0	0	—1	5·334	5·356	90
4	1	—1	0	4·578	4·589	14
5	1	0	—1	4·309	4·317	100
6	1	—1	—1	3·995	4·028	80
7	1	0	1	3·727	3·759	62
8	1	1	0	3·683	3·700	10
9	0	—1	1	3·532	3·538	59
10	1	—1	1	3·115	3·115	82
11	1	—1	1	3·091	3·097	13
12	2	0	0	3·035	3·022	20
13	1	1	—1	3·003	2·995	5
14	2	—1	0	2·925	2·926	40
15	2	—1	—1	2·854	2·858	3
16	2	0	—1	2·797	2·804	83
17	1	—2	—1	2·718	2·718	73
18	0	0	—2	2·667	2·678	13
19	0	—1	—2	2·597	2·599	23
20	1	0	—2	2·579	2·585	34
21	2	—2	0	2·295	2·295	28
22	1	—2	1	2·226	2·230	36
23	2	0	—2	2·157	2·158	37
24	1	—1	2	2·090	2·093	30
25	3	—1	—1	2·048	2·050	22
26	2	—2	1	1·938	1·938	30
27	2	0	2	1·879	1·879	18
28	3	—2	—1	1·866	1·869	10
29	1	—1	—3	1·828	1·829	6
30	3	—2	0	1·821	1·822	8
31	3	—1	—2	1·810	1·812	14
32	3	0	1	1·803	1·805	16
33	1	0	—3	1·780	1·781	7
34	2	2	1	1·767	1·769	10

[a] Relative intensities were estimated photometrically.

The central copper atom lies at the centre of symmetry. It is co-ordinated by two nitrogen atoms, at the shortest distance (Figs 1, 2). Four oxygen atoms from the oxalate groups are located further from the Cu(II)atom. The chemical bonds between the central atom and the four oxygen atoms are obviously longer than the corresponding sum of the co-valent radii (1·17 + 0·74 Å) or than the values found in other oxalate complexes[4,12]. From this point of view, in the crystals of the copper(II) oxalate diammine complex, there is no common type of the octahedron distortion with two weak Cu—L bonds. In the present compound, the Cu—O chemical bonds are not identical as far as their length is concerned. They are changed, compared to the normally distorted octahedron usually found in complexes of the CuA_2X_4 type, they are changed as shown in Fig. 2, in the direction of a compressed octahedral bipyramide. The oxalate group has the function of a chelate and is bonded

TABLE II

The Atom Positions in Fractional Co-Ordinates with the Standard Deviations ($\times 10^4$) in Å, and the Temperature Factors, B

Atom	X/a	X/b	Z/c	B
Cu	0·0 (0)[a]	0·0 (0)[a]	0·0 (0)[a]	0·81 (1)[a]
O 1	0·1398 (26)	0·2883 (36)	0·2071 (29)	3·08 (4)
O 2	0·1634 (25)	0·6822 (36)	0·2204 (28)	2·88 (4)
O 5	0·6019 (29)	0·3113 (39)	0·2986 (32)	3·76 (5)
N 1	0·7549 (32)	0·8901 (45)	0·1991 (36)	2·82 (4)
C 1	0·0996 (30)	0·4994 (44)	0·1200 (32)	1·50 (2)

[a] The standard deviations ($\times 10^4$) are given in brackets.

TABLE III

The Interatomic Distances in $Cu(C_2O_4)(NH_3)_2.2 H_2O$, with their Standard Deviations (in Å)

Atom	Distances	Atom	Distances
Cu—2 N	1·960 (19)[a]	O 2—C 1	1·245 (29)
Cu—2 O 1	2·147 (19)	C 1—C 2	1·651 (35)
Cu—2 O 2	2·327 (18)	O 1—O 5	2·834 (23)
O 1—C 1	1·280 (31)	O 2—O 5	2·802 (23)

[a] The standard deviations ($\times 10^4$) are given in brackets.

to two copper atoms in the manner shown in Figs 1 and 2. Similarly to the structure of α-$Cu(C_2O_4)(NH_3)_2$, the oxalate group is also planar in this structure. The $Cu(C_2O_4)(NH_3)_2.2\ H_2O$ complex easily liberates water, and the X-ray powder patterns have shown that the so-called β-form appears on the decomposition of the dihydrate. It was observed that the dihydrate decomposition is often irreproducible and that even small changes in the decomposition conditions have a considerable influence on the resulting product with the formula $Cu(C_2O_4)(NH_3)_2$. It is probable that the decomposition irreproducibility is due to the moistening of the sample during the decomposition which can cause substantial structural changes.

It can be seen from the thermogravimetric curve that rapid decomposition of the hydrate takes place at 75°C. The first part of the thermogravimetric curve (Fig. 3), corresponding to the liberation of two water molecules, was subjected to kinetic analysis. It was found that the apparently order, $n = 2/3$, conforms best with the reaction. The E_A value for the reaction
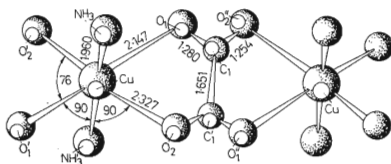

FIG. 2

The Co-ordination of the Central Atom and the Function of the Oxalate Groups in $Cu(C_2O_4)$. $.(NH_3)_2\ 2\ H_2O$
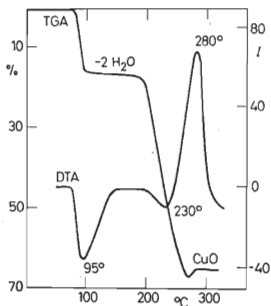
FIG. 3

The Derivatographic Record of the Thermal Decomposition of $Cu(C_2O_4)(NH_3)_2.2\ H_2O$

$$Cu(C_2O_4)(NH_3)_2 . 2 H_2O_{(S)} \rightarrow \beta\text{-}Cu(C_2O_4)(NH_3)_{2(S)} + 2 H_2O_{(G)} \qquad (A)$$
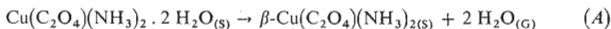
was obtained from the slope of the straight line, computed according to the literature[10]. The E_A value obtained from repeated measurement is 19 ± 0.3 kcal mol^{-1}. The reaction proceeds in one step under the given experimental conditions. From the calorimetric measurements, it follows that the reaction is endothermic, and the consumed heat, $\Delta H = 9 \pm 0.5$ kcal mol^{-1}. The relatively low values of E_A and ΔH indicate no rearrangement of the Cu—O bonds, during the conversion of Cu.$(C_2O_4)(NH_3)_2.2 H_2O$ into $\beta\text{-}Cu(C_2O_4)(NH_3)_2$, which would lead to a change in the oxalate group function. The X-ray powder patterns of both the complexes are similar, although there are certain shifts in the angles at which some intense diffraction maxima are located ($16.8°$ and $24°$) and also changes in the relative intensities of the diffraction bands.

The dehydratation reaction may also lead to the formation of another $Cu(C_2O_4)$.$(NH_3)_2$ modification and/or that of $Cu(C_2O_4)(NH_3)$. The copper (II) ammine oxalate complex that is formed by the reaction discussed is, as to the X-ray bands, identical with the crystalline $Cu(C_2O_4)(NH_3)$, the preparation of which has been described[1]. It was assumed in the extrapolation of the bond changes which occur during the dihydrate decomposition that, on liberation of the two water molecules, there are no substantial changes in the function of the oxalate groups and in the inner sphere of the copper(II) complex. Thus the co-ordination of Cu(II) in $\beta\text{-}Cu(COO)_2$.$(NH_3)_2$ would be as shown in Fig. 4. The validity of this assumption was verified by measuring and interpreting the spectra.

TABLE IV

The Bond Angles (in degrees) and their Standard Deviations for $\beta\text{-}Cu(C_2O_4)(NH_3)_2.2 H_2O$

Atoms	Bond angles	Atoms	Bond angles
O 1—Cu—O′ 1	180·0 (0·0)[a]	Cu—O 1—O 5	105·9 (0·8)[a]
O 1—Cu—O 2	104·0 (0·6)	O 2—O 1—O′ 2	90·8 (0·8)
O 1—Cu—O 2	76·0 (0·6)	N 1—O 1—N′ 1	84·8 (0·7)
O 1—Cu—O 1	90·0 (0·8)	Cu—O 2—O 5	122·2 (0·8)
O 1—Cu—N′ 1	90·0 (0·8)	Cu—O 2—C′ 1	111·7 (1·3)
N 1—Cu—N′ 1	180·0 (0·0)	O′ 5—O 2—C 1	124·9 (1·5)
O 2—Cu—O′ 2	180·0 (0·0)	O 1—O 5—O 2	121·0 (0·8)
O 2—Cu—N 1	90·9 (0·8)	O 1—C 1—O 2	127·2 (1·8)
O 2—Cu—N′ 1	89·1 (0·8)	O 2—C 1—C′ 1	118·8 (2·4)
Cu—O 1—C 1	119·6 (1·3)	O 1—C 1—C′ 1	112·7 (2·3)

[a] Standard deviations.

The infrared spectra of complexes with ammonia or with an oxalate group as a ligand are relatively well known[13] and some generalizations have been made on the basis of the extensive experimental material. According to the literature[14], if the vibration frequency of Cu—O is not directly measured, the shifts of the valence vibrations of Cu—O can be used for judging the stability of this bond. As follows from Table V, in which are given the values of the frequencies of various vibrations, it can be assumed that the stability of the Cu—O bonds in β-Cu(C$_2$O$_4$)(NH$_3$)$_2$ will be close to that in Cu(C$_2$O$_4$)(NH$_3$)$_2$.2 H$_2$O. On the basis of the value ν_{as} O—C—O, the degree of covalent character of the oxalate bond can be presumed[15]. According to the data in Table V, a low degree of covalent character of the Cu—O bond must be assumed for Cu(C$_2$O$_4$)(NH$_3$)$_2$.2 H$_2$O, in agreement with the results of the X-ray structure analysis (the Cu—O distances are larger than the sum of the covalent radii of Cu and O). The same assumption also holds for β-Cu(C$_2$O$_4$)(NH$_3$)$_2$, even if the overall character of both spectra is similar to that of the spectrum of K$_2$Cu(C$_2$O$_4$)$_2$. .2 H$_2$O, in which the oxalate groups are bonded to the copper as chelates. The Cu(C$_2$O$_4$)(NH$_3$) spectrum indicates $(\nu_7$ and $\nu_1)$ that the oxalate group is relatively firmly bonded to the central atom, more firmly than in both the previous complexes; this is also indicated by the data of the X-ray structure analysis[12], according to which the Cu—O bonds in this complex are substantially shorter than in Cu(C$_2$O$_4$)(NH$_3$)$_2$. .2 H$_2$O.

The diffusion reflection spectra of Cu(C$_2$O$_4$)(NH$_3$)$_2$.2 H$_2$O and of the complex denoted by us as β-Cu(C$_2$O$_4$)(NH$_3$)$_2$ were measured by Hathaway and coworkers[3,16].

α-Cu(C$_2$O$_4$)(NH$_3$)$_2$ β-Cu(C$_2$O$_4$)(NH$_3$)$_2$
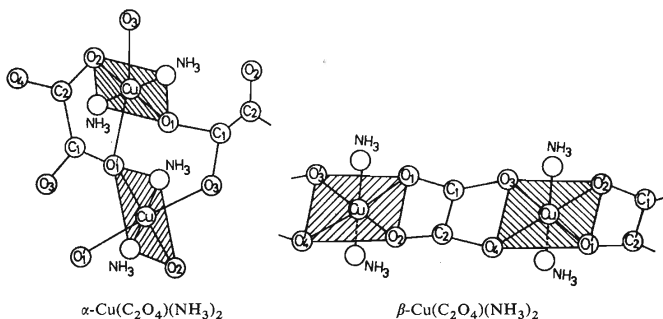
FIG. 4

The Co-Ordination of the Central Atom and the Function of the Oxalate Groups as Ligands in α- and β-Cu(C$_2$O$_4$)(NH$_3$)$_2$

The first of the complexes mentioned exhibits a band with a maximum at 14 700 cm^{-1} and a shoulder at 10 000 cm^{-1}, while the latter[3] exhibits two bands with practically equal intensities and with maxima at 13 500 and 9 500 cm^{-1}, so that *cis*-octahedral arrangement of the ligands[3] can be assumed. According to our results, the electron spectrum of β-Cu(C$_2$O$_4$)(NH$_3$)$_2$ is close to that of the dihydrate, with one maximum

TABLE V

The Wave Number Values and Attribution of the Bands in the Complexes Studied

Attribution of the band[a]	The wave number values, cm^{-1}			
	A^b	B	C	D^c
(ν_7)	1 683	1 665	1 694	1 672
ν_{as}(O—C—O)				(1 720)
(ν_1)	1 610	1 624	1 669	1 645
ν_s(O—C—O)			1 366	
(ν_2)	1 397	1 409	1 316	1 411
ν_s(O—C—O)				
(ν_8)	1 277	1 283	1 250	1 277
δ(O—C—O)	792	781	813	
	775	777	783	795

[a] The bands were attributed according to the literature[15,16]. [b] A = Cu(C$_2$O$_4$)(NH$_3$)$_2$.2 H$_2$O, B = β-Cu(C$_2$O$_4$)(NH$_3$)$_2$, C = Cu(C$_2$O$_4$)(NH$_3$), D = K$_2$Cu(C$_2$O$_4$)$_2$.2 H$_2$O. [c] According to the literature[14].

TABLE VI

The g-Factor Values of the Complexes Studied

Complex	$g_\perp$ or g_1	$g_\parallel$ or g_2	G
CuSO$_4$.5 H$_2$O^a	2·27 (2·27)	2·08 (2·08)	—
Cu(C$_2$O$_4$)(NH$_3$)$_2$.2 H$_2$O^b	2·04	2·279	6·96
Cu(C$_2$O$_4$)(NH$_3$)$_2$^{b}	2·053	2·257	4·85
β-Cu(C$_2$O$_4$)(NH$_3$)$_2$	2·040	2·250	6·25
Cu(C$_2$O$_4$)(NH$_3$)	2·165	—	—

[a] The values in brackets correspond to the values obtained for a single crystal[11]; [b] quoted according to the literature[16].

at $15\,600\,cm^{-1}$, which has a shoulder at $11\,500\,cm^{-1}$. The spectrum assigned to this modification corresponds to the electronic spectrum of $Cu(C_2O_4)(NH_3)$. The values for the maxima of the two approximately equally intense bands, obtained in the present paper, are $13\,300$ and $9\,500\,cm^{-1}$. On the basis of our spectra, and, in agreement with other experimental results, the *cis*-octahedral arrangement of the ligands in β-$Cu(C_2O_4)(NH_3)_2$ can practically be excluded.

The EPR spectra of $Cu(C_2O_4)(NH_3)_2.2\,H_2O$ and of an unspecified modification of $Cu(C_2O_4)(NH_3)_2$ have already been measured[16]. These results, together with ours are given in Table VI. Two values of the g-factor were found for β-$Cu(C_2O_4)(NH_3)_2$ and an isotropic spectrum with one value of the g-factor was obtained for $Cu(C_2O_4)$. .(NH_3). The β-$Cu(C_2O_4)(NH_3)_2$ spectrum corresponds to the axial symmetry of the complex. However, it is known from the literature[16] that such spectra are rather frequently observed with complexes of the type CuX_2A_2, even if they exhibit a lower complex symmetry. If it is assumed that the tetragonal axes of the complex units are arranged in β-$Cu(C_2O_4)(NH_3)_2$ in parallel, similar to those in the dihydrate, the g-factor values observed correspond to the symmetry of the local surroundings of the central atom. The EPR spectrum of β-$Cu(C_2O_4)(NH_3)_2$ is similar to that of $Cu(C_2O_4)$. .$(NH_3)_2.2\,H_2O$. Taking into account the precision of the approximation used for evaluating the EPR spectra both in the paper[16] and in the present work, we assume that the G values are approximately equivalent for the two complexes and, on the basis of these facts, we also assume that the character of the co-ordination of the oxalate group and of the ammonia molecules did not change during the dehydration. We assume that the isotropic EPR spectrum observed with $Cu(C_2O_4)(NH_3)$ is connected with a large exchange interaction in this complex. The data on the structure[12] of this compound support our assumption.

Hathaway and Tomlinson assume, on the basis of the electron reflection spectra, that the decomposition product, denoted by them as γ-$Cu(COO)_2(NH_3)_2$, has a *cis*-configuration with distorted octahedral arrangement of the ligands around the Cu(II) (Fig. 4). This assumption is unexpected from the structural point of view, since it requires considerable structure changes during the decomposition of $Cu(COO)_2(NH_3)_2.2\,H_2O$. Such a change is possible, if the dihydrate decomposition took place under conditions where extensive moistening of the substance occurred.

The results given above indicate a close connection between the structures of $Cu(C_2O_4)(NH_3)_2.2\,H_2O$ and β-$Cu(C_2O_4)(NH_3)_2$ and, for this reason, we assume that the structure of the β-modification is identical with that in Fig. 4. For the sake of comparison, the schematic structure of the crystalline, so-called α-modification of $Cu(C_2O_4)(NH_3)_2$ is also given in Fig. 4.

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