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Spectral and Magnetic Properties of Some Oxalate-ammine-copper(II) Complexes

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The paper deals with preparation, spectral and magnetic properties of α*–,* β*–, and* γ*–*$Cu(C_2O_4)(NH_3)_2$*,* $Cu(C_2O_4)(NH_3)$*,* $Cu(C_2O_4)(NH_3)_2\ 2H_2O$*, and* $(NH_4)_2Cu(C_2O_4)_2\ 2H_2O$*. Spectral and magnetic properties of* α*–*$Cu(C_2O_4)(NH_3)_2$*,* $Cu(C_2O_4)(NH_3)$ *and both dihydrates are compared with their known structures. and possible structure of* β*– and* γ*–*$Cu(C_2O_4)(NH_3)_2$ *is discussed on the basis of the results obtained. According to the experimental data the structure of* γ*–*$Cu(C_2O_4)(NH_3)_2$ *is near to the structure of the* α*–modification with its basic state* $d_{x^2-y^2}$*. On the other hand, similar stereochemical arrangement alike in* $Cu(C_2O_4)(NH_3)_2\ 2H_2O$ *is proposed for the* β*–modification with its basic state* d_{z^2}*.*

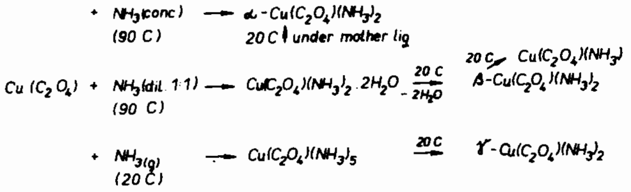
Introduction

Attention is paid in our working place to the questions of study of the unclassical type of isomerism in the copper(II) complexes of the general formula CuX_2A_2 in solid state. Modifications in $CuX_2(NH_3)_2$ have been prepared, where X = Cl^-, Br^-, SCN^- [1,2,3] and $Cu(CHA)_2Cl_2$[4]. X-Ray structural analysis as well as indirect methods of study of their structures[5-9] point to the fact that some of them differ in various degrees of deformation of the coordinate polyeder.

Already in older papers hints are made that $Cu(C_2O_4)(NH_3)_2$ exists in two modifications[10]. The oxalate ion itself is marked by its great variability of possibilities to be linked in complexes, which has been confirmed in solving the structure of some oxalate copper(II) complexes[11-13]. Although the properties of modification of oxalate–ammine–copper(II) complexes are mentioned in a summary paper[14] and some original works[13,15,16,17], a more detailed view of preparation, spectral and magnetic properties has not yet been presented. This is aim of this paper.

Experimental Section

Preparation of Complexes. The complexes have been prepared according to the followin scheme:



α– and γ–$Cu(C_2O_4)(NH_3)_2$, $Cu(C_2O_4)(NH_3)_2 \cdot 2H_2O$ have been prepared according to[10]. More detailed conditions of preparation of β–$Cu(C_2O_4)(NH_3)_2$ as well as of $Cu(C_2O_4)(NH_3)$ in powder are given in paper[13]. The $(NH_4)_2Cu(C_2O_4)_2 \cdot 2H_2O$ not quoted in the scheme has been prepared according to Viswamitra[11].

IR-spectra of the complexes investigated in the region from 3300 to 200 cm^{-1} have been measured with the spectrophotometer Perkin-Elmer 225 by means of the Nujol suspension technique.

Electronic spectra in the region of 12-20 kK have been measured with the spectrophotometer Perkin-Elmer 450 using the Nujol suspension technique. Temperature dependence of magnetic susceptibility has been measured from 86 to 300 K with Guy's method utilizing an instrument of "Newport Instruments Ltd". $CuSO_4 \cdot 5H_2O$ has been taken as a standard[18]. Diamagnetic corrections have been computed by means of Pascal's constants[19]. The values of effective magnetic moment have been computed according to the relation:

$$\mu_{eff} = 2.83\ \sqrt{\chi_M' . T}$$

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(1) J. Gažo, K. Serátorová, and M. Serator *Chem. zvesti*, *13*, 5 (1959).
(2) J. Garaj and J. Gažo, *Chem. zvesti*, *19*, 593 (1965).
(3) J. Gažo, *Chem. zvesti*, *20*, 212 (1966).
(4) L. Macášková, M. Melník, M. Kabešova, and J. Gažo, *Suomen Kemistilehti* B46, 106 (1973).
(5) F. Hanic, *Acta Cryst.*, *11*, 610 (1958).
(6) F. Hanic, *Acta Cryst.*, *12*, 739 (1959).
(7) L. Zsoldos, *Magy. Fiz. Folyóirat*, *10*, 189 (1962).
(8) J. Garaj, *Z. Struk. Chim.*, *7*, 727 (1966).
(9) M. Kabešová, J. Garaj, and J. Gažo, *Coll. Czechoslov. Chem. Commun.*, *37*, 942 (1972).
(10) Gmelis Handbuch der Anorganischen Chemie, Kupfer, Syst. No. 60, Teil B, Lief. 2, Weinheim, 1961.
(11) M.A. Viswamitra, *J. Chem. Phys.*, *37*, 1408 (1962).
(12) J. Garaj, *Chem. Commun.*, 904 (1968).
(13) J. Garaj, H. Langfelderová, G. Lundgren, and J. Gažo, *Coll. Czechoslov. Chem. Commun.*, *Suomen Kemistilehti* 37, 3181 (1972).
(14) B.J. Hathaway and A.A.G. Tomlinson, *Coord. Chem. Rev.*, 5, 1 (1970).
(15) H. Langfelderová, J. Mikovič, and J. Gažo, *Thermochimica Acta* 5, 303 (1973).
(16) A.A.G. Tomlinson, B.J. Hathaway, and P. Nicholls, *J. Chem. Soc.*, *A*, 1678 (1968).
(17) L. Cavalca, A. Ch. Villa, A.G. Manfredotti, A. Mangia, and A.A.G. Tomlinson, *J. Chem. Soc.*, *Dalton Trans.*, 391 (1972).
(18) B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 331 (1959).
(19) A. Earnshow, Introduction to Magnetochemistry, Academic Press, London, 1968.

Table I. The infrared spectra (200-3300 cm^{-1}) of α– (I), β– (II), γ–$Cu(C_2O_4)(NH_3)_2$ (III), $Cu(C_2O_4)(NH_3$ (IV), $Cu(C_2O_4)(NH_3)_2 . 2H_2O$ (V), and $(NH_4)_2Cu(C_2O_4)_2 . 2H_2O$ (VI) complexes. Vibrational frequencies (cm^{-1}) with assignments for complexes.

	I	II	III	IV	V	VI
	3180	3218	3179	3190	3220	
ν_{NH}						3077
	3125	3124	3125	3150	3083	
	1715	(1710) sh				1680
ν_{as}(O-C-O)			1665	1694	1683	
	1685	1665				1654
	1615					
ν_{as}(O-C-O)		1624	1624	1669	1610	1625
	1630					
$\delta_d NH_3$	1595	1587	1601	1574	1601	1560
				1366		
ν_s(O-C-O)	1340	1409	1417		1397	1397
				1316		
		1300	1296			
$\delta_s NH_3$	1290			1296	1330	1280
		1283	1290			
ν_s(O-C-O)	1270	1263	1263	1250	1277	1263
ν_s(O-C-O)			893			
	890	888				897
+δ(O-C-O)			884			
		781	790	813	792	
δ(O-CO)	778					803
		777	781	783	775	
	680					
ρNH_3		685	680	670		670
	665					
δ(O-C-O)	505 sh	509				542
						500
	498					
ν(Cu-O)		480	488	460		484
	488					
						442
νCu-N	444	440	450	412		434
						426
	381					
δO-C-$O^{\nu 12}$		368	380			372
	379					
$\pi C_2O_4^{2-}$				315		332
δO-Cu-N^+	300	300		310		
δ(O-Cu-O)	309		300			292
	290	290		290		
lattice vibrations	221	225		268		
	211	215	225			240
	205	205		218		

EPR spectra have been measured with Varian spectrometer 3 in the X-region on polycrystalline samples.

Results and Discussion

Studying the dependences of properties of the chemical compounds $Cu(C_2O_4)(NH_3)_2$ on the method of their preparation, it has been found that they exist in three different modifications[10,12-14], marked as α–, β–, and γ–$Cu(C_2O_4)(NH_3)_2$.

Infrared spectra of oxalate–ammine–copper(II) complexes have been studied from the viewpoint of bond of ammine and oxalate group to the central atom as well as from the viewpoint of the relative strength of these bonds. Valence vibrations (ν_{N-H}) of the coordinated molecules of ammine have mutually near values of frequencies in α– and γ–$Cu(C_2O_4)(NH_3)_2$, and $Cu(C_2O_4)(NH_3)$. This agree well with crystal structure of α–$Cu(C_2O_4)(NH_3)_2$[12,20] as well as $Cu(C_2O_4)(NH_3)$[17], according to which the distances Cu-NH_3 in those complexes are almost equal. To a higher frequency shifted valence vibration ν_{N-H} in β–$Cu(C_2O_4)(NH_3)_2$ suggests a relatively lower strength of the bond Cu–NH_3, or weaker hydrogen bonds in this complex. The difference of 32 cm^{-1} between the values of valence vibration of ν_{Cu-N} bonds in α–$Cu(C_2O_4)(NH_3)_2$ and $Cu(C_2O_4)(NH_3)$ seems to be caused by higher degree of hydrogen bonds formation. The highest value of ν_{Cu-N} vibration in γ–$Cu(C_2O_4)(NH_3)_2$ suggests that there must be the weakest Cu-NH_3 bonds. The oxalate group in α–$Cu(C_2O_4)(NH_3)_2$ has a relatively wide, richly articulated absorption band in the region of 1700-1600 cm^{-1} belonging to antisymmetric valence vibrations ($\nu_{as\ O-C-O}$), which is similar to the corresponding band in $Cu(C_2O_4)(NH_3)$ shifted to the regions which are characteristic for the expressively covalent way of oxalate group bonding. β– and γ–$Cu(C_2O_4)(NH_3)_2$ have their most intense maxima of the corresponding absorption band shifted

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(20) J. Garaj and G. Lundgren, in press.

Table II. Magnetic Data of α—, β—, and γ—$Cu(C_2O_4)(NH_3)_2$ ($-\Delta\times10^6 = 84$).

T/K	$\chi_s\times10^6$ α—	β—	γ—	μ_{eff} B.M. α—	β—	γ—
88	21.45	21.22	21.04	1.695	1.685	1.68
103	18.76	18.61	18.46	1.716	1.71	1.70
123	15.99	16.09	15.90	1.735	1.74	1.73
143	14.09	14.09	13.76	1.76	1.76	1.74
163	12.45	12·47	12.29	1.77	1·77	1.76
183	11.21	11.20	10.90	1.78	1.78	1.76
203	10.23	10.14	10.04	1.796	1.79	1.78
223	9.22	9.33	8.99	1.79	1.80	1.77
243	8.54	8.53	8.37	1.80	1.80	1.785
263	7.86	·7.92	7.79	1.80	1.81	1.795
293	7.12	7·17	6.92	1.816	1·82	1.794

Table III. The Parameters Obtained from Curie-Weiss Law and Ising Model.

Compound	C	Curie-Weiss Law Θ[K]	g	$-2J$, cm^{-1}	Ising Model T_N[K]	g	$-2J$, cm^{-1}
α—$Cu(C_2O_4)(NH_3)_2$	0.437	—18.9	2.161	13.1	17.7	2.158	12.3
β—$Cu(C_2O_4)(NH_3)_2$	0·440	—20.2	2.168	13.9	19.1	2.168	13.3
γ—$Cu(C_2O_4)(NH_3)_2$	0.425	—17.1	2.131	11.9	17.5	2;134	12·2
$Cu(C_2O_4(NH_3)_2 . 2H_2O$	0.489	—17.3	2.286	12	17	2.290	11.9
$(NH_4)_2Cu(C_2O_4)_2 . 2H_2O$	0·423	—	2.125	—	—	—	—

to lower values; this band by its form and number of arms conforms to a more symmetric bonding of the oxalate group as it is in α–$Cu(C_2O_4)(NH_3)_2$, in $Cu(C_2O_4)(NH_3)_2 \cdot 2H_2O$ or $(NH_4)_2Cu(C_2O_4)_2 \cdot 2H_2O$. IR spectra data are given in Table I.

Investigating the magnetic properties of α–, β–, and γ–$Cu(C_2O_4)(NH_3)_2$ it has been shown that at room temperature their magnetic moments are higher than the spin value only (1.73 B. M.); however, with decreasing temperature they decrease below this value (Tab. II).

The reserved values of their corrected molar susceptibilities show a linear dependence on absolute temperature but the corresponding straight lines cut out sections in the region of negative values on temperature axis (Fig. 1 and 2). It means that the magnetic behaviour of those complexes agrees to Curie-Weiss' law, $\chi_M' \propto C/(T-\theta)$, whose parameters are quoted in Tab. III together with the values of g-factors computed from the relationship

$$\frac{C}{T} = \frac{g^2N\beta^2\ S(S+1)}{3kT}$$

where $S = 1/2$ and the other symbols are evident. The values of exchange interaction between singlet and triplet levels of 2J, which have been obtained from the relation $2J = \theta . k$, are also quoted in Tab. III. Those experimental results indicate antiferromagnetic behaviour of the complexes discussed.

Two nitrogen atoms in trans-position together with two oxygen atoms of two oxalate groups form a planar coordination of Cu(II) in the crystal structure of α–$Cu(C_2O_4)(NH_3)_2$ with orthorombic symmetry. The fifth and sixth crystallographic coordination places are completed with oxygen atoms of oxalate groups under formation of a deformed tetragonal bipyramid. Oxalate groups function as bonds linking copper atoms in chains[12,20]. In these chains, the distance Cu-Cu is 3.813 Å. This is relatively large for overlapping of d-d orbitals, bridge oxygen atoms provide a sufficient possibility of interaction of a super-exchange type. Owing to the above said, it has appeared useful to test Ising's anisotropic model[21,22] for temperature dependence of susceptibility. According to this model, temperature dependence of susceptibility of linear antiferromagnetism applies in the region above Néel's temperature to the equation

$$\chi_M' = \frac{g^2N\beta^2}{4kT} \exp\left(\frac{2J}{kT}\right)$$

where J means energy of exchange interaction, and the meaning of the other symbols is evident. As it can be seen in Fig. 1 and 2, the dependence of log $[4kT\chi_M'/N\beta^2]$ on T^{-1} is linear, which proves the validity of this model. The value of $-2J = 12.3$

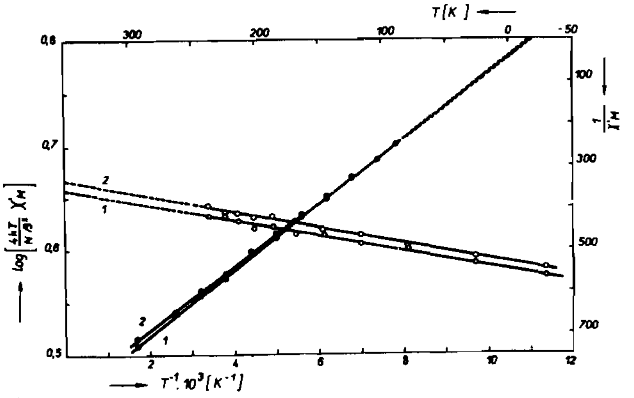

Figure 1. Magnetic behaviour with temperature of γ–$Cu(C_2O_4)(NH_3)_2$ (1) and α–$Cu(C_2O_4)(NH_3)_2$ (2); closed circles, plots of $1/\chi_M'$ vs. T; open circles, plots of log $[4kT/N\beta^2\ \chi_M']$ vs. T^{-1}.

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(21) G.F. Nervell and E.W. Montroll, *Rev. Mod. Phys.*, 25, 353 (1953).

cm^{-1} comes out from the line slope for energetic separation between singlet and triplet levels, and it is very near to the value obtained in utilizing Weiss' constant (Tab. III). Also the value of spectroscopic factor of fission $g = 2.158$ is practically the same as the value obtained by means of Curie's constant, $g = 2.161$.

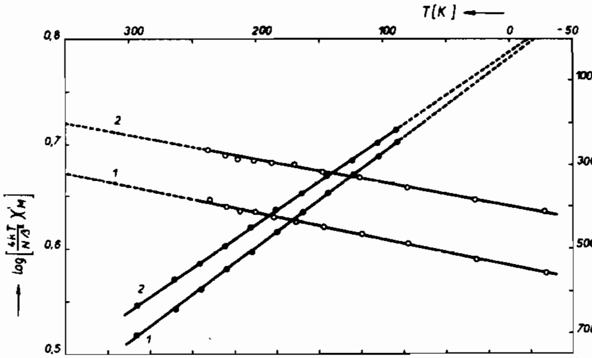

Figure 2. Magnetic behaviour with temperature of β—$Cu(C_2O_4)(NH_3)_2$ (1) and $Cu(C_2O_4)(NH_3)_2 . 2H_2O$ (2); closed circles, plots of $1/\chi_M'$ vs. T; open circles, plots of log $[4kT/N\beta^2\ \chi_M']$ vs. T^{-1}.

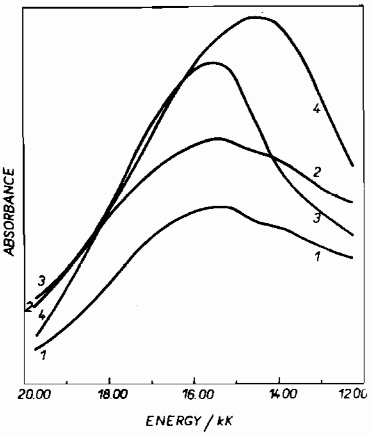

Figure 3. Electronic spectra of α— (1), β— (2), γ—$Cu(C_2O_4)(NH_3)_2$ (3), and $(NH_4)_2Cu(C_2O_4)_2 . 2H_2O$ (4).

Electronic spectrum (Fig. 3) of this complex shows a band in the region about 15.40 kK with an arm about 14.50 kK which can be assigned to d-d transitions of the Cu^{II} ion

$$^2E_g,\ ^2B_{2g} \leftarrow\ ^2B_{1g}, \text{ and } ^2A_{1g} \leftarrow ^2B_{1g}$$

Two values of g-factor (Tab. IV) have been obtained from anisotropic EPR spectrum of polycrystallic α—$Cu(C_2O_4)(NH_3)_2$ in utilizing Kneubühl's method[23], and $g_\perp < g_\parallel$. This allows to point to the presence of a structure with the value of effective spin $S = 1/2$ and basic state $^2B_{1g}$ $(d_{x^2-y^2})$. In this case the following relations apply for $g_\perp$ and $g_\parallel$[24]

$$g_\perp = 2-2k_\perp^2\lambda \;/\; E(^2E_g \leftarrow\ ^2B_{1g}) \text{ and}$$

$$g_\parallel = 2-8k_\parallel^2\lambda \;/\; E(^2B_{2g} \leftarrow ^2B_{1g})$$

where k is an orbital reduction factor, and λ is a constant of spin-orbital connection, having the value $-829\ cm^{-1}$ for the free Cu^{II} ion[25]. The values of $k_\perp = 0.63$ and $k_\parallel = 0.76$ computed from the above relations show a marked covalency of bonds at an important participation of out-of-plane π–bonds. This is in good agreement with exchange interaction which can be performed just by means of π–pathway.

The degree of tetragonal distortion $T = 0.83$ ($T = R_S/R_L$, where R_S is average value of short bonds, and R_L – average value of long bonds of copper – ligands), is lower than that usually occurring in tetragonal octaedric complexes which suggests a transition to orthorombic distortion.

The results obtained for spin-orbital connection $\lambda_\parallel' = -479\ cm^{-1}$ and $\lambda_\perp' = -325\ cm^{1-}$ from the relations $\lambda_\parallel' = k_\parallel^2 \cdot \lambda$ or $\lambda_\perp' = k_\perp^2\ \lambda$, are markedly lower than the value for the free Cu^{II} ion $-829\ cm^{-1}$.

The ratio $\lambda'/\lambda \approx 0.5$ indicates a relatively marked delocalization of the unpaired Cu^{II} electron which remains about 50% of time in the $d_{x^2-y^2}$ orbitals and the rest on ligand orbitals.

The spectral and magnetic data of three modifications of $Cu(C_2O_4)(NH_3)_2$ indicate unambiguously the highest relationship between α– and γ–$Cu(C_2O_4)(NH_3)_2$. Based on the above it is possible to ascribe to the γ–modification a stereochemical arrangement similar to the α–modification.

In the previous papers[12,13] it has been shown that by dehydration of $Cu(C_2O_4)(NH_3)_2 \cdot 2H_2O$, already at room temperature the latter shifts to β-$Cu(C_2O_4)(NH_3)_2$ and then it is possible to expect in both cases similar stereochemical arrangement in the environment of copper(II). This assumption was stated on the basis of properties observed as well as on the basis of a marked similarity of X-ray powder photos of both compounds[13].

Magnetic behaviour of β–modification (Tab. II, Fig. 2) does not negate the assumption of the proposed structure in which, in contradiction to α–modification, there is another number of coordinated oxygen atoms and then it differs in the symmetry of oxalate groups. In α–$Cu(C_2O_4)(NH_3)_2$ three oxygen atoms of oxalate group are bonded with the central atom so as they form a chelate with expressively inequivalent lengths o fCu–O bonds and at the same time they form bridges among copper atoms[12]. While in the α–modification the co-ordinate polyhedron is an elongated tetragonal bipyramid, for the β–modification a compressed tetragonal bipyramid is assumed[13], in which all the four oxygen atoms of oxalate group are bonded with copper(II). It is evident from Fig. 4 that even in the case of the β–modification, antiferromagnetic interaction is possible only through oxygen atoms, i.e. of a super-exchange type.

EPR spectrum of β–$Cu(C_2O_4)(NH_3)_2$ is clearly anisotropic with two values of g-factor (Tab. 4), and $g_\perp < g_\parallel$, which indicates rather the basic state of

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(22) C.G. Barraclough and C.F. Ng, *Trans. Faraday Soc.*, *60*, 836 (1964).
(23) F.K. Kneubühl, *J. Chem. Phys.*, 33, 1074 (1960).
(24) C.J. Ballhausen, «Introduction to Ligand Field Theory», Mc Graw-Hill, New York, 1962.
(25) B.N. Figgis and Lewis J., *Proc. Inorg. Chem.*, 6, 37 (1964).

Table IV. Spectral data of α—, β—, and γ—$Cu(C_2O_4)(NH_3)_2$.

	$g_\perp$	$g_\parallel$	g_{av}	G	$K_\perp$	$K_\parallel$	$\lambda'_\perp(cm^{-1})$	$\lambda_\parallel'(cm^{-1}$
α—$Cu(C_2O_4)(NH_3)_2$	2.057	2.249	2.123	4.40	0.63	0.76	−325	—479
β—$Cu(C_2O_4)(NH_3)_2$	2.041	2.236	2.100	5.75	0·54	074	−236	—460
γ—$Cu(C_2O_4)(NH_3)_2$	2.062	2.256	2.129	4.13	0.65	0.78	−344	—503

Table V. Magnetic Data of $(NH_4)_2Cu(C_2O_4)_2 . 2H_2O$ and $Cu(C_2O_4)(NH_3)_2 . 2H_2O$ $(-\Delta \times 10^6 = 115.6)$ $(-\Delta \times 10^6 = 110)$.

T/K	$\chi_g \times 10^6$	μ_{eff}	$\chi_g \times 10^6$	μ_{eff}
88.2	14.86	1.83	20.23	1.80
103.2	12.60	1.83	17·66	1.82
123.2	10.65	1.84	15.15	1.85
143.2	9.09	1.84	13.27	1.87
163.2	7.89	1.835	11·74	1.88
183.2	6.98	1.83	10.61	1.90
203.2	6.34	1.84	9.54	1.903
223.2	5.70	1.84	8·68	1.906
243.2	5.22	1.84	7.95	1.91
263.2	4.85	1.85	7.37	1.92
293.8	4.24	1.84	6·64	1.93

$d_{x^2-y^2}$ than the expected d_z^2. The fact that the value G = 5.75, computed from the relation $G = (g_\parallel - 2)/(g_\perp - 2)$ is much higher than 4, indicates a lower symmetry with hardly discernable values of g_x and g_y. On the other hand, however, $g_\perp$ and $g_\parallel$ are at a significant distance, which is a case frequent enough in measuring polycrystallic samples[26].

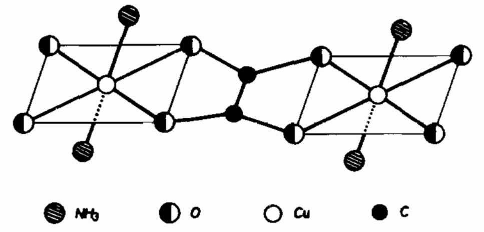

Figure 4. The assumed co-ordination of the copper atom and function of the oxalate group in β—$Cu(C_2O_4)(NH_3)_2$.

The crystal structure of the complex $Cu(C_2O_4)(NH_3)_2 \cdot 2H_2O$ consists of infinite linear chains where each Cu^{II} atom is bonded with two nitrogen atoms on the z-axis at a distance of Cu—N = 1.96 Å, and four oxygen atoms from two oxalate groups on the x— and y—axes, their Cu—O distances being 2.147 Å and 2.327 Å. The Cu^{II} atom lie in the centre of symmetry of the so formed compressed tetragonal bipyramid[13]. Its antiferromagnetic behaviour has been found in studying the magnetic properties of this complex (Tab. V, Fig. 2). This can be ascribed only to the interaction of a super-exchange type through oxygen atoms of planar oxalate groups, owing to the fact that the distance Cu-Cu = 5.539 Å is very great for overlapping of d-d orbitals.

Hathaway and Tomlinson[14] have measured electronic spectrum of the single crystallic $Cu(C_2O_4)(NH_3)_2 \cdot 2H_2O$ and the bands about 10.0 kK, 12.5 kK, and 14.5 kK have been ascribed to d-d- transitions, i.e.: $d_{x^2-y^2} \rightarrow d_{z^2}$, $d_{xy} \rightarrow d_{z^2}$ and d_{xz}, $d_{yz} \rightarrow d_{z^2}$. On the other hand, analyzing EPR spectra of this complex (polycrystallic sample), the authors[27] found that $g_\perp < g_\parallel$ with values $g_\perp = 2.04$ and $g_\parallel = 2.279$, which is in some contradiction with the structure as well as electronic spectrum of this complex. Analyzing EPR spectrum of this complex measured by us, three values of g-factor have been obtained (Tab. VI), the lowest value of g being < 2.04, and $(g_2-g_1) > (g_3-g_2)$ indicates the presence of the basic state d_{z^2} [28-30], which agrees with x-ray analysis of this complex. Owing to the fact that the investigated dihydrate is relatively unstable, it seems that disagreement of the results presented with the results quoted in[27] is caused by the fact that the sample measured by them could be already partly dehydrated.

Comparing the values of g-factors in β—$Cu(C_2O_4)(NH_3)_2$ and dihydrate, it may be stated that by reducing two water molecules from the dihydrate, Cu—O bonds are shortened in the β—$Cu(C_2O_4)(NH_3)_2$.

The complex compound $(NH_4)_2Cu(C_2O_4)_2 \cdot 2H_2O$ pertains to magnetically diluted copper(II) complexes, its value of effective magnetic moment being 1.84 B.M. which is not practically changed with temperature (Tab. V). Dependence of the reversed value of the corrected molar magnetic susceptibility on temperature complies with Curie's law in the form $\chi_M' \propto C/T$. Its EPR spectrum is anisotropic with three g-factors (Tab. VI). The lowest value of the factor g > 2.04 as well as the fact that $(g_2-g_1) < (g_3-g_2)$ indicate the presence of the basic state $d_{x^2-y^2}$.

Electronic spectrum of this complex presents a relatively wide band of d-d transitions of Cu^{II} in the region of 14.50 kK. The results presented for $(NH_4)_2Cu(C_2O_4)_2 \cdot 2H_2O$ agree well with the structure solved[11]. Co-ordinated water molecules are in the direction of z-axis in an elongated octaeder, and in the x— and y—plane there are co-ordinated oxygen atoms of oxalate groups.

The results of J magnitude seem to be surprising enough when compared with the Cu-Cu distance (Tab. VII). As it is seen, even with the same type of bridge-bonded atoms, J. magnitude is higher at greater separation of copper-copper. This indicates the reality that in the case of exchange interaction of super-exchange type an important role is played not

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(26) B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, 5, 143 (1970).

(27) A.A.G. Tomlinson and B.J. Hathaway, *J. Chem. Soc.*, *A*, 2578 (1968).

(28) R.C. Slade, A.A.G. Tomlinson, B.J. Hathaway, and D.E. Billing, *J. Chem. Soc.*, *A*, 61 (1968).

(29) B.J. Hathaway, D.E. Billing, R.J. Dudley, R.J. Fereday, and A.A.G. Tomlinson, *J. Chem. Soc.*, *A*, 806 (1970).

(30) R.J. Dudley and B.J. Hathaway, *J. Chem. Soc.*, *A*, 2799 (1970).

Table VI. Spectral data of $Cu(C_2O_4)(NH_3)_2 . 2H_2O$ and $(NH_4)_2Cu(C_2O_4)_2 . 2H_2O$.

Complex	g_1	g_2	g_3	g_{av}	R*
$Cu(C_2O_4)(NH_3)_2 . 2H_2O$	2.009	2.145	2.253	2.253	1·26
$(NH_4)_2Cu(C_2O_4)_2 . 2H_2O$	2.056	2.079	2.301	2.149	0.104

* $R = (g_2-g_1)/(g_3-g_2)$.

Table VII. Values of J required by the Ising model of some linear antiferromagnetics.

Complex	$-J/cm^{-1}$	Cu . . . Cu/Å
$Cu(PhCOO)_2 . 3H_2O$ [a]	8.8	3.15
$Cu(C_2O_4)(NH_3)_2 . 2H_2O$	11.9	3·539
$\alpha-Cu(C_2O_4)(NH_3)_2$	12.3	3.813
$Cu(CH_3COO)_2$(*p*-toluidine)$_2 . 3H_2O$ [a]	cca 23	4.73

[a] Komson, R.C.; McPhail, A.T.; Mabbs, F.E., and Porter, J. K., *J. Chem. Soc. A*, 3447 (1971).

Table VIII. Magnetic Data and Values of Equilibrium Constants of $Cu(C_2O_4)(NH_3)$ at various temperatures.
$(-\Delta \times 10^6 = 56)$

T/K	$\chi_g \times 10^6$	μ_{eff} B.M.	Keq
88.2	1.85	0.52	0.055
103.2	2.74	0.67	0.094
123.2	3.81	0.83	0.153
143.2	4.66	0.98	0·226
163.2	5.27	1.11	0.310
183.2	5.67	1.21	0.400
203.2	5.91	1.31	0.491
223.2	5·99	1.38	0.576
243.2	6.02	1.44	0.661
263.2	6.00	1.50	0.761
296.2	5.86	1.57	0.851

only by bridge groups but also by their geometric arrangement.

In the series of oxalate-copper(II) complexes we have also studied the powder oxalate monoammine copper(II) complex obtained by decomposition of $\beta-Cu(C_2O_4)(NH_3)_2$.

Magnetic data of $Cu(C_2O_4)(NH_3)$ are given in Tab. VIII and Fig. 5. As it is seen from Fig. 5, with increasing temperature above the value of absolute zero, the paramagnetic triplet level enriches to the detriment of diamagnetic singlet level, which appears in increasing values of magnetic susceptibility with the maximum in the range of Néel temperature i.e. at 243°K. At further increasing the values of susceptibility decrease.

The value of singlet – triplet separation, $-2J = 270\ cm^{-1}$, obtained in computing from the relation[31]: $2J = 1.6\ kT_N$ indicates a very strong antiferromagnetic interaction.

Bleaney-Bowers' relation[32] has been utilized to compute theoretical values of molar susceptibility

$$\chi_M' = \frac{g^2N\beta^2}{3kT}\ \frac{1}{1+1/3\ \exp\ (2J/kT)} + N\alpha$$

in which g is Lande's factor with the value g = 2.282 computed by means of the above relation utilizing the χ_M' value at Néel's temperature; the meaning of the other symbols is evident. As it seen in Fig. 5 and Tab. VIII, the experimental values of molar susceptibility agree well with theoretical values.

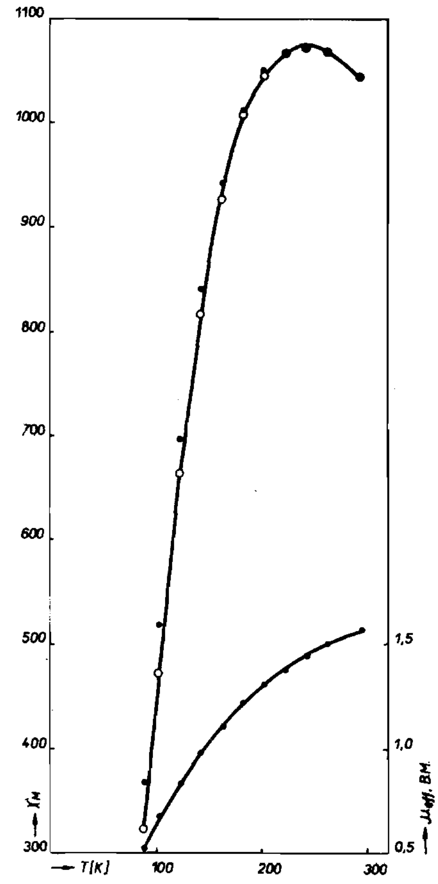

Figure 5. The temperature variation of the magnetic susceptibility (experimental ● and calculated ○); and plots of μ_{eff} vs.T of $Cu(C_2O_4)(NH_3)$ in the temperature range 90-300 K.

Equilibrium constants of singlet-triplet separation have been computed from magnetic data in temperature dependence according to Hatfield et al[33]. The K_{eq} values are quoted in Tab. VIII. Enthalpy value, $\Delta H^\circ = 243\ cm^{-1}$, and entropy value, $\Delta S^\circ = 2.1$ e.u., have been computed from graphic dependences $-\ln K_{eq}/T^{-1}$ and $RT\ln K_{eq}/T$.

EPR spectrum of this complex at 296 K is isotropic with g = 2.150, while at 123 K it is anisotropic where $g_\perp = 2.072$ and $g_\parallel = 2.305$.

Recently Cavalca et al.[17] solved the structure of

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(31) B.N. Figgis and R.L. Martin, *J. Chem. Soc.*, *A*, 3837 (1956).

(32) B. Bleaney and K.D. Bowers, *Proc. Roy. Soc.*, *A*, *214*, 451 (1952).

(33) W.E. Hatfield, T.S. Piper, and Klabunde, *Inorg. Chem.*, 2, 629 (1963).

$Cu(C_2O_4)(NH_3)$ obtained by crystallization from solution, by means of the single crystal method and they studied its spectral and magnetic properties. The results presented agree well with the results obtained by the above mentioned authors. Based on the above, it is possible to ascribe to the powdery complex compound $Cu(C_2O_4)(NH_3)$, obtained by decomposition of β–$Cu(C_2O_4)(NH_3)_2$, a structure similar to the crystallic one[17]. In this polymeric structure there is clearly an interaction of a super-exchange type as the distance Cu-Cu = 4.180 Å is great to overlap d-d orbitals. A primary role in the super-exchange interaction of this complex is played clearly by the "axial" oxygen atom, and the contribution of planary co-ordinated oxalate groups is essentially lower.

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