

PARENT AND MIXED LIGAND COMPLEXES IN THE COPPER(II)-ETHYLENE GLYCOL-SULPHATE SYSTEM

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Eleven copper(II)-ethylene glycol-sulphate complexes of different compositions were prepared, one of them— $\text{CuGl}_2(\text{H}_2\text{O})_2\text{SO}_4$ —in single-crystal form. A thermoanalytical study of these complexes revealed three types of thermal decomposition pattern. The X-ray structure of the single-crystal demonstrated the presence of ethylene glycol bridges resulting in endless chains in the crystal.

Investigation of the metal complexes of simple model ligands may help in the structural study of analogous compounds of macromolecular or polyfunctional ligands. Thus, a coordination chemical study of diols can serve as the basis of metal complexation studies of carbohydrates and other sugar-type ligands. We have therefore started the preparation and structural study of complexes of the simplest diol, ethylene glycol. Copper(II) ions served as the metal in the first series of measurements.

Several papers on copper-chloro-diol complexes have been published in the past few years [1-8]. X-ray structural studies [1-6] have given direct information on their structures. They have shown that complexes of the general formula $\text{CuCl}_2(\text{diol})_x(\text{SH})_y$ can be synthesized (where SH denotes the solvent, $x = 0.5, 1, 1.5$ or 2, and $y = 0, 0.5$ or 1). In these complexes, only one diol molecule (as chelating ligand) is coordinated to the copper(II) ion; the remaining diol and solvent molecules are linked to these $\text{CuCl}_2(\text{diol})$ units through H-bonds. Much less is known on the compositions and structures of the sulphate-containing copper-ethylene glycol complexes. Since the sulphate ion has a lower affinity than chloride towards copper(II), the complexes containing sulphate better reflect the coordi-

nating ability of an organic ligand. To our knowledge, only one such complex, CuGl_3SO_4 , has so far been studied by single-crystal X-ray techniques [9].

For X-ray structural studies, monocrystals have to be prepared; however, this is usually not feasible for every member of a series of complexes built up from the same parent units, and other methods too have to be used for the characterization of the systems. We have therefore chosen thermoanalytical methods for a preliminary study of the copper-glycol-sulphate system, with a view to drawing conclusions from the mode of the thermal decomposition of compounds with different compositions on the order of the bonding strengths of the ligands in the different complexes. For these measurements the series of copper-glycol-sulphate complexes shown in Table 1 were prepared. Only two of the compounds (I and VIII) were previously known in the literature [10]. However, the composition of compound I, prepared by the procedure described in [10], proved to have a composition different from that reported in [10].

Table 1 The composition of the complexes and the weight losses measured (m) and calculated (c) according to the suggested general scheme in different temperature intervals

Composition suggested by analysis	Melting interval, °C	Weight loss, %						Type of thermal behaviour
		80–160 °C		160–210 °C		210–270 °C		
		m	c	m	c	m	c	
I $\text{Cu}(\text{Gl})_{0.15}(\text{H}_2\text{O})_{2.5}\text{SO}_4$	> 250	16.8	16.8			8.5	8.6	A
II $\text{Cu}(\text{Gl})_{0.25}(\text{H}_2\text{O})_{4.5}\text{SO}_4$	> 250	30.0	28.1			8.0	9.6	A
III $\text{Cu}(\text{Gl})(\text{H}_2\text{O})_2\text{SO}_4$	78–80	26.0	26.0	13.5	12.0			B
IV $\text{Cu}(\text{Gl})_{1.25}(\text{H}_2\text{O})\text{SO}_4$	77–80	21.0	22.3	15.5	15.2			B
V $\text{Cu}(\text{Gl})_2(\text{H}_2\text{O})_2\text{SO}_4$	78–80	34.2	35.5	14.1	14.6			B
VI $\text{Cu}(\text{Gl})_{2.25}(\text{H}_2\text{O})_2\text{SO}_4$	80–85	37.2	38.5	12.8	13.9			B
VII $\text{Cu}(\text{Gl})_3(\text{H}_2\text{O})_2\text{SO}_4$	70–75	24.0	25.7	30.8	32.5			C
VIII $\text{Cu}(\text{Gl})_3\text{SO}_4$	60–70	32.2	35.9	17.5	17.9			B
IX $\text{Cu}(\text{Gl})_4(\text{H}_2\text{O})_2\text{SO}_4$	90–100	49.6	50.1	13.6	14.0			B
X $\text{Cu}(\text{Gl})_{3.5}(\text{H}_2\text{O})_2\text{SO}_4$	60–70	22.0	23.8	41.0	37.6			C
XI $\text{Cu}(\text{Gl})_{4.5}(\text{H}_2\text{O})_2\text{SO}_4$	60–65	32.0	33.7	34.0	32.7			C

We succeeded in the preparation of a single-crystal in one of the systems: $\text{CuGl}_2(\text{H}_2\text{O})_2\text{SO}_4$. The results of thermoanalytical and X-ray investigations are presented below.

Experimental

Preparation mode

Complexes II, V, VI, VII, IX, X and XI were prepared by leaving them to crystallize at different temperatures from saturated solutions of copper sulphate pentahydrate in a series of glycol-water mixtures of different compositions; compound I by precipitation with ethanol from the corresponding solution; and complexes III and IV by precipitation caused by heat treatment of the solution. The crystallized or precipitated compounds were collected on a glass filter, washed with ether or dimethoxyethane and stored over CaCl_2 (III–VII), over P_2O_5 (IX, X, XI), over P_2O_5 in vacuum (VIII), or under normal laboratory conditions (I, II).

The compositions of the solid complexes shown in the second column of Table 1 were established by standard analytical procedures used for the determination of copper, glycol and water contents.

Thermoanalytical studies

The thermal decompositions of the complexes were investigated with a MOM OD-2 derivatograph at a heating rate of 2 deg/min. The weight of the investigated samples was 200 mg. The measurements were carried out in a platinum crucible in air atmosphere. $\alpha\text{-Al}_2\text{O}_3$ served as reference substance.

The melting temperatures were measured on a Kofler-Block. The melting intervals of the complexes, together with the experimental and calculated weight losses in the thermoanalytical studies, are listed in Table 1.

X-ray studies

Data collection

A blue needle crystal of composition $\text{CuSO}_4 \cdot 2\text{G}1 \cdot 2\text{H}_2\text{O}$, having approximate dimensions of $0.20 \times 0.20 \times 0.50$ mm, was mounted in a glass capillary with its long axis roughly parallel to the φ axis of the goniometer.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $48^\circ < \theta < 50^\circ$, measured with Cu-K_α radiation ($\lambda = 1.54184 \text{ \AA}^*$, on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromator, by the computer-controlled diagonal slit method of centring. The

* In accordance with the convention accepted at the 11th International Congress of the International Union of Crystallography (IUCr) in Warsaw in 1978 for measuring atomic distances, etc., \AA is still commonly used.

monoclinic cell parameters and calculated volume are: $a = 7.249(1)$, $b = 15.539(2)$, $c = 10.027(1)$ Å, $\beta = 103.42(1)^\circ$, $V = 1098.6$ Å³. For $Z = 4$ and $F.W. = 319.77$, the calculated density is 1.93 M g/m³. Omega scans of several intense reflections were measured, and indicated good crystal quality. From the systematic absences of:

$$\begin{array}{l} hkl \quad h = k = 2n \\ hkl \quad l = 2n \end{array}$$

and from the least-squares refinement, the space group was determined to be $C2/c$ (No. 15).

The data were collected at a temperature of 320 ± 3 K using the $\omega - 2\theta$ scan technique in the range $3.0^\circ < 2\theta < 150^\circ$. The scan width was calculated as follows:

$$\text{scan width} = 0.5 + 0.3 \tan \theta$$

Data reduction

A total of 1217 reflections were collected, of which 1139 were unique and not systematically absent. As a check on crystal and electronic stability, 3 representative reflections were measured every hour. The intensities of these standards remained constant within experimental error throughout the data collection. No decay correction was applied.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 50.7 cm^{-1} for Cu-K α radiation. Absorption correction was made by use of the program DIFABS [11] at the end of isotropic refinement.

Structure solution and refinement

The structure was solved by direct methods using 185 $E \geq 1.43$ normalized structure factors and 2744 relationships; a total of 17 phase sets were produced in the non-centric space group Cc. A total of 15 atoms were located from an E -map prepared from a phase set with probability statistics: ABSFOM = 1.05, RESID = 9.40, and PSIZERO = 3.620. A remaining atom was located in succeeding difference Fourier synthesis. Hydrogen atoms were located and their positions and isotropic thermal parameters were refined. At this stage the internal C_2 symmetry of the molecule was revealed and the space group was converted to $C2/c$, in which the refinement was continued.

Scattering factors were taken from Cromer and Waber [12]. Anomalous dispersion effects were included in $F \delta$ [13]; the values of $\delta F'$ and $\delta F''$ were those of Cromer [14]. Only 1099 reflections with $I > 3.0 \sigma(I)$ were used in the refinements. The final cycle of refinement for 75 variable parameters converged (the largest

parameter shift was 0.68 times its e.s.d) to

$$R = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|} = 0.057$$

$$R_w = \left[\frac{\sum \omega (|F_0| - |F_c|)^2}{\sum \omega F_0^2} \right]^{1/2} = 0.108$$

The standard deviation of an observation of unit weight was 3.15. The highest peak in the final difference Fourier had a height of $0.60 e/\text{\AA}^3$ with an e.s.d. of 0.15.

All calculations were performed on a PDP-11/34 computer using program package SDP-PLUS.

Results and discussion

Thermoanalytical measurements

Three types of thermal decomposition behaviour could be observed:

A. The differential thermogravimetric (DTG) curves show a broad peak reflecting two overlapping processes between 80° and 130° . The thermogravimetric (TG) curves do not show weight changes between 130° and 210° . In the DTG curves, a double, more or less separated peak appears between 210° and 270° , with maxima at 230° and 265° (Fig. 1).

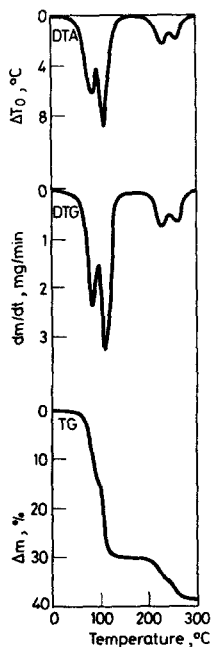


Fig. 1 Thermoanalytical curves of $\text{CuGl}_{0.25}(\text{H}_2\text{O})_{4.5}\text{SO}_4$

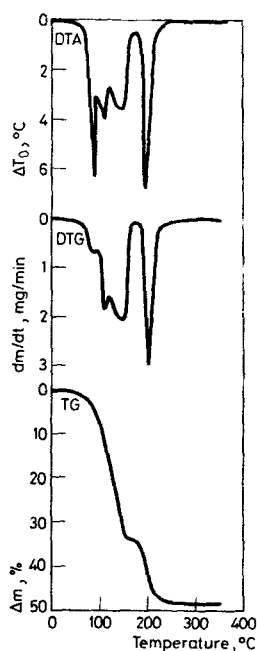


Fig. 2 Thermoanalytical curves of $\text{CuGl}_2(\text{H}_2\text{O})_2\text{SO}_4$

B. The DTG curves start with one peak between 80° and 160° (except for complexes containing less than three glycol molecules, which show two peaks in this region), followed by a horizontal part between 160° and 190°. At higher temperatures only a single peak appears, with maximum at about 200° (Fig. 2).

C. The DTG and DTA curves are analogous with pattern *B* below 160° and above 190°. They differ, however, between 160° and 190°, where the DTG curves show a peak (Fig. 3).

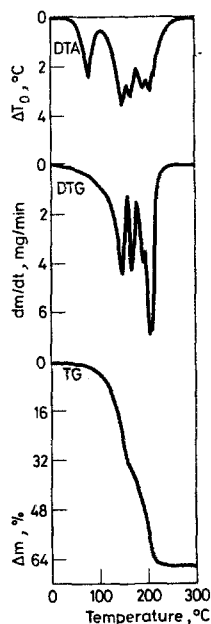


Fig. 3 Thermoanalytical curves of $\text{CuGl}_{4.5}(\text{H}_2\text{O})_2\text{SO}_4$

For complexes exhibiting *B* and *C* type behaviour, the DTA curves contain one peak at 80°, which is not accompanied by weight loss. In accordance with the melting temperature measurements, these DTA peaks can be assigned to the melting of the compound.

For the assignment of the different DTG peaks to the corresponding thermal decomposition processes, the decomposition products were prepared by stopping the heating process with the derivatograph at 170° and, for independent control measurements, by heating the initial substance for 2 hours at a constant temperature of 110° and 150°, respectively. The corresponding decomposition products were separated and analysed. On the basis of the analytical results, the individual DTG peaks could be assigned to the thermal decomposition processes for the three groups of compounds as follows:

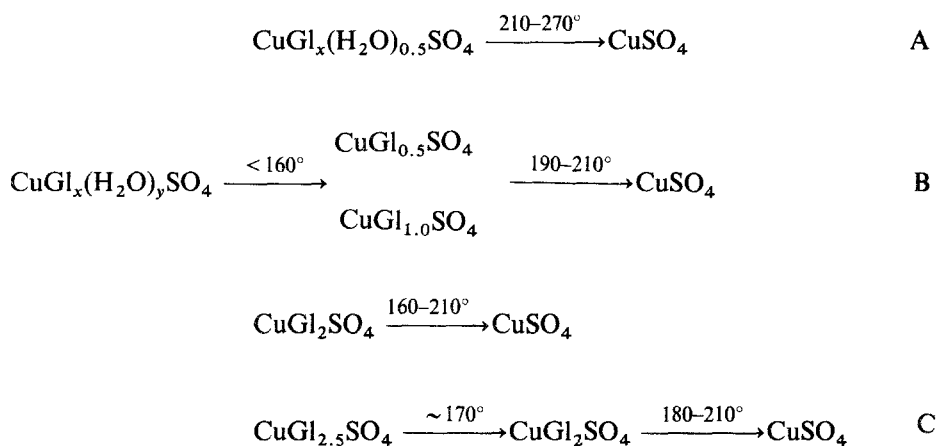
A: Since $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals lose their water content in several steps, the first at around 100° , the last at above 250° [15], it is concluded that the double peak at about 100° in the DTG curve and the last peak at 265° in the same curve can be attributed to the removal of water molecules bound in the complex. Since glycol was present in the thermal decomposition products prepared by stopping the heating of the parent compounds at 170° , the DTG peak at 230° is assigned to the release of glycol.

B: Thermal decomposition products prepared in a similar way at 170° contained only glycol besides copper sulphate, indicating that the peak at 200° can be attributed to the removal of glycol in the thermal process. At temperatures lower than 160° , water and glycol molecules are released together. This is remarkable since the boiling point of glycol is 197° . Thus, the glycol molecules are bound more strongly to the neighbouring glycols by H-bonds in the liquid state than by coordinate bonds in the copper complex.

C: Since water was not present in the thermal decomposition products of the complexes heated at 110° and 150° , respectively, the weight decrease at $160\text{--}190^\circ$ is assigned to the release of glycol.

The end-product of the thermal decomposition (at 300°) was in all cases CuSO_4 . This allowed an independent control of the chemical analytical data by stoichiometric calculations.

On the basis of the analytical data and the thermoanalytical curves, the following general scheme is suggested for the thermal decomposition of this class of complexes:



Weight loss data calculated on the basis of the above scheme for each of the complexes are compared with the experimental data in Table 1. The good

agreement between the measured and calculated values indicates the analogous behaviour of the complexes belonging to the same group in this scheme.

The thermoanalytical studies show that both water and glycol molecules can be bound with different strengths in the complexes.

Discussion of the crystal structure

General description

The crystal structure of $\text{CuGl}_2(\text{H}_2\text{O})_2\text{SO}_4$ was determined by means of X-ray diffraction. Two characteristic features of this complex are the distinct separation of differently charged ionic species in the crystal, and the preservation of an exact twofold (C_2) symmetry in the 'molecule' of $(\text{CuSO}_4 \cdot 2\text{H}_2\text{O} \cdot 2\text{C}_2\text{H}_6\text{O}_2)$ formal stoichiometry (Fig. 4). All four chemical entities comprising the crystal (copper cation, water, ethylene glycol and sulphate anion) are fused into endless chains in the crystal, where cations and anions are fully shielded from one another *via* water and glycol molecules (Fig. 5). As a consequence of the exact C_2 symmetry

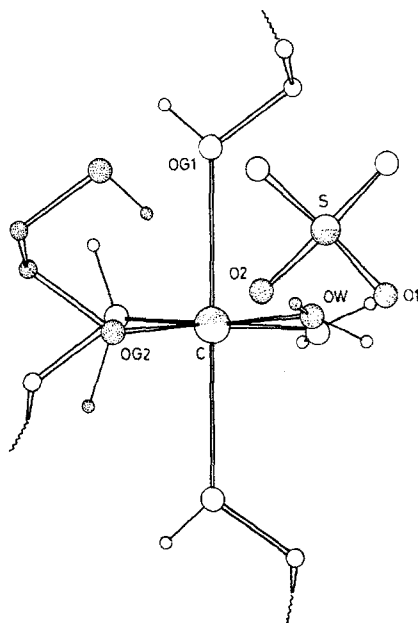


Fig. 4 Excerpt from the crystal structure of the complex $\text{CuGl}_2(\text{H}_2\text{O})_2\text{SO}_4$, showing the content of the asymmetric unit (dotted atoms) and the coordination around the cation. C—H hydrogen atoms are omitted for clarity

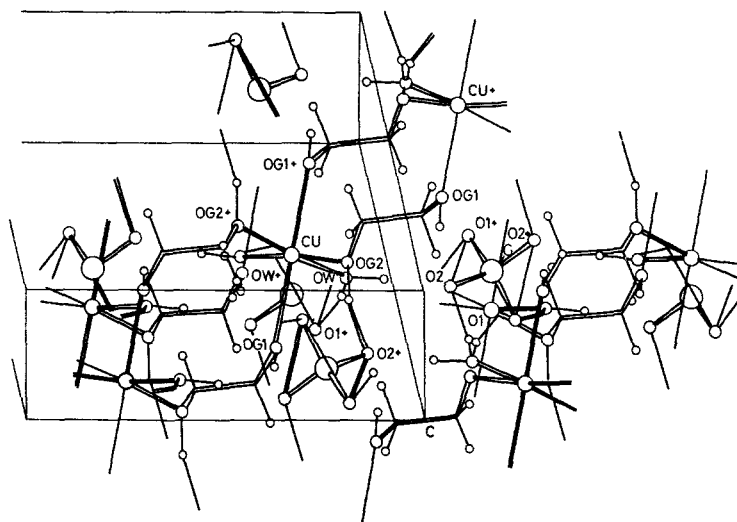


Fig. 5 Crystal structure of the complex $\text{CuGl}_2(\text{H}_2\text{O})_2\text{SO}_4$ reflecting intermolecular interactions and the outer sphere situation of the sulphate ion

(coinciding with a two-fold rotor of the space group parallel to crystal axis b), the asymmetric unit comprises only one water and one ethylene glycol molecule, with the cation and the S atom of the anion in special positions. The coordination polyhedron may be termed an almost regular tetragonal bipyramid (Table 2).

Table 2 Coordination sphere around copper ion. Only symmetry independent angles are shown

Distances	
OW_i	1.952(2)
OW_{ii}	1.952(2)
OG1_{iii}	2.378(2)
OG1_{iv}	2.378(2)
OG2_i	1.979 (2)
OG2_{ii}	1.979(2)
Angles	
$\text{OW}-\text{Cu}-\text{OG1}$	89.8(1)
$\text{OW}-\text{Cu}-\text{OG2}$	88.6(1)
$\text{OW}-\text{Cu}-\text{OG2}$	174.0(1)
$\text{OG1}-\text{Cu}-\text{OG2}$	84.2(1)
$\text{OG2}-\text{Cu}-\text{OG2}$	94.6(1)

Chiffre:

$$i: x, y, z; ii: 1-x, y, 1-\frac{1}{2}-z; iii: x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}; iv: 1-\frac{1}{2}-x, \frac{1}{2}-y, 2-z,$$

Special features

There are some differences in the bonding of the same moieties (e.g. C—O and S—O distances) in the crystal; these originate from the different roles of the chemically identical entities in the building-up of the crystal lattice. The Cu ion is almost equally strongly coordinated to the axially positioned water and an oxygen atom (OG2) of the ethylene glycol (Table 3). The apically situated second hydroxy

Table 3 Bond lengths (Å) and bond angles with e.s.d.'s for non-H atoms

S—O1	1.470(2)
S—O2	1.501(2)
OG1—C1	1.423(4)
OG2—C2	1.448(3)
C1—C2	1.506(4)
O1—S—O2	109.8(2)
OG1—C1—C2	111.1(4)
OG2—C2—C1	110.3(4)
Torsion angle describing ethyleneglycol conformation	
OG2—C2—C1—OG1	62.4(4)

group of the latter moiety binds weakly, as is usually observed for such a geometric arrangement. Thus, the unequal participation of these two —OH groups is also manifested in the markedly different C—O bond lengths: 1.448(3) Å for OG2 and 1.423(4) Å for OG1. Further, as demonstrated by analysis of the H-bonds (Table 4), the oxygen atoms of the anion also play unequal roles. Atom O2 has virtually no lone pairs free, being a three-fold acceptor of H-bonds from the two hydroxy groups and a H-atom of a water molecule, while O1 has only one such acceptor contact. Consequently, the S—O bonding changes accordingly: the distance is longer for S—O2 (1.501(2) Å) than for S—O1 (1.470(2) Å). There are no significant differences in the thermal parameters of these oxygen atoms which would give rise to disordering, so the observed differences are most probably genuine. The conformation of the ethylene glycol molecule is the expected gauche one.

Table 4 Hydrogen bonding distances (Å) and angles (°) with e.s.d.'s (in parentheses) at relevant H atoms

	Donor-H	Acceptor...H	A	D-H...A angle	D...A
OW—H1W...	0.82(8)	1.85(8)	01	165(6)	2.66
OW—H2W...	0.99(10)	1.74(11)	02	174(7)	2.72
OG1—HO1...	0.87(7)	1.99(7)	02	168(6)	2.84
OG2—HO2...	1.08(8)	1.64(8)	02	164(5)	2.69

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Zusammenfassung — Elf Kupfer(II)-äthylenglykol-sulfat-Komplexe unterschiedlicher Zusammensetzung wurden dargestellt, einer davon — $\text{CuGl}_2(\text{H}_2\text{O})_2\text{SO}_4$ — in Form von Einkristallen. Die thermoanalytische Untersuchung dieser Komplexe ergab drei Typen der thermischen Zersetzung. Die röntgendiffraktometrische Bestimmung der Struktur des in Form von Einkristallen erhaltenen Komplexes zeigte, daß den Kristall endlose Ketten von Äthylenglykolbrücken durchziehen.

Резюме — Получено одинадцать комплексов различного состава медь(II) — этиленгликоль — сульфат, один из которых — $\text{CuGl}_2(\text{H}_2\text{O})_2\text{SO}_4$ — в монокристаллической форме. Термоаналитическое исследование этих комплексов обнаружило три типа их разложения. Рентгеноструктурное исследование монокристаллического комплекса показало, что молекулы этиленгликоля связаны мостиковыми связями, образуя бесконечные цепи в кристалле.