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# ON THE RELATIONSHIP BETWEEN THE STRUCTURES OF Cu(II) COMPLEXES AND THEIR CHEMICAL TRANSFORMATIONS

## V. Kinetics of thermal decomposition of Cu(II) aquacomplexes with heterogeneous coordination sphere

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The experimental activation energies ($E^*$) of dehydration of $Cu(NH_3)_4(H_2O)SO_4$, $Cu(en)_2(H_2O)X_2$ ($X = Cl^-, Br^-$), $Cu(en)(H_2O)_2SO_4$, $Cu(py)_2(H_2O)_2SO_4$, $CuCl_2 \cdot 2\,H_2O$ and $M^I_2CuCl_4 \cdot 2\,H_2O$ ($M^I = NH_4$, K, Rb) were obtained from their non-isothermal thermogravimetric curves using the Coats–Redfern method. These $E^*$ values were compared with known data on the structures of the Cu(II) coordination polyhedra in the above complexes. No dependence of the $E^*$ values was found on either the central atom – released ligand bond length, or the number and lengths of the hydrogen bonds formed by the released water molecules. However, it was found that it is justified to seek some relationship between the $E^*$ values and the anisotropic temperature factors of the donor atoms of the ligands split off.

In earlier papers we pointed to the fact that some parameters of the thermal decomposition of Cu(II) complexes, e.g. the decomposition temperature, the experimental activation energy and the reaction enthalpy [1–4] in series of isostructural complexes or of complexes with analogous compositions, may be correlated with the structures of the coordination polyhedra of the complexes undergoing decomposition, or with the degree of their tetragonal distortion.

The aim of the present study was to investigate the dependence of the experimental activation energies of dehydration of $Cu(NH_3)_4(H_2O)SO_4$, $Cu(en)_2(H_2O)X_2$ ($X = Cl^-$, $Br^-$), $Cu(en)(H_2O)_2SO_4$ (*en* = ethylenediamine), $Cu(py)_2(H_2O)_2SO_4$ (*py* = pyridine), $CuCl_2 \cdot 2\,H_2O$ and $M^I_2CuCl_4 \cdot 2\,H_2O$ ($M^I = NH_4$, K, Rb) on their structures.

In an attempt to determine some relationship between the structures of complexes and the course of their thermal decomposition, the question arises as to which of the structural data reflect the energetic conditions in compounds with a heterogeneous coordination sphere to such an extent that they should be the most significant for this relation. Since the present study deals with complexes, all of which are not mutually isostructural and which contain ligands with considerably different properties, the $E^*$ values obtained could not be compared with the degree of tetragonal distortion of the Cu(II) coordination polyhedra, as was done earlier [1, 3, 4]. In an effort to establish some relationship for the found activation energies, we therefore considered the central atom-released ligand interatomic distances, and the number and lengths of the hydrogen bonds formed by the split-off ligand. In cases when the bond between Cu(II) and the donor oxygen atom of the water molecules lies in the direction of some crytallographic axis, we compared the $E^*$ values with the anisotropic temperature factors of the oxygen atoms $U_{ii}$(O) of the released water molecules in the direction of the respective crystallographic axis, corrected for thermal movement of the central atom $U_{ii}$(Cu), also in the direction of the respective axis, i.e. $\Delta U_{ii}^{1/2} = (U_{ii}(\mathrm{O}) - U_{ii}(\mathrm{Cu}))^{1/2}$ [5]. For compounds in which the Cu–O bonds do not lie in the direction of one of the crystallographic axes, the $E^*$ values were compared with the mean anisotropic temperature factors of the donor oxygen atoms ($U_{\mathrm{mean}}$). A comparison of the values of $\Delta U_{ii}^{1/2}$ or $U_{\mathrm{mean}}$, respectively, with those of $E^*$ is interesting mainly because the temperature factors of the atoms in crystal structures reflect to some extent the "freedom" of the atom and/or of the whole Cu–OH$_2$ bond movement. It is a disadvantage, however, that not all temperature factors were determined with sufficient precision [6].

## Experimental

### *Chemicals*

$CuSO_4 \cdot 5\,H_2O$, $NH_4Cl$, KCl, RbCl, all p.a. Ethylenediamine p.a. and pyridine p.a. were freshly distilled before use.

### *Syntheses*

The complexes under study were prepared according to known methods, viz. $Cu(NH_3)_4(H_2O)SO_4$ [7], $Cu(en)_2(H_2O)X_2$ [8] $Cu(en)(H_2O)_2SO_4$ [8], $Cu(py)_2(H_2O)_2SO_4$ [9] and $M^{I}_2CuCl_4 \cdot 2\,H_2O$ crystallized from aqueous solutions containing $CuCl_2$ and MCl in a molar ratio of 1:2.

### *Analytical methods*

The Cu(II) contents were determined by complexometric titration with murexide as indicator, while those of the halides were found argentometrically and the $NH_3$ contents by distillation. In complexes with ethylenediamine or pyridine the C, N and H contents were determined by elemental analysis. The analytical compositions of the prepared complexes corresponded to the stoichiometric compositions.

### *Apparatus and measuring processes*

The thermal decomposition was performed on an OD 102 derivatograph (MOM, Budapest). Ceramic crucibles with an upper diameter of 14 mm, supplied for the apparatus, were used. The temperature was measured with Pt, Pt–Rh thermocouples. The sample weight was 100 mg; the temperature increase was 3 degree min$^{-1}$. Before measurements, all samples were finely powdered and sieved to a mesh size of 0.05. Because of the strong adhesivity between $Cu(py)_2(H_2O)_2SO_4$ crystals, this sample could not be sieved before measurement, and was only powdered. The thermogravimetric curves of decomposition of $Cu(en)(H_2O)_2SO_4$ and $K_2CuCl_4 \cdot 2\,H_2O$ were obtained using a Mettler thermobalance. The sample weight was 7 mg, and the heating rate 6 degree $min^{-1}$, in an air flow at 7 $dm^3$/hour. Under the above conditions, a linear temperature increase was obtained in the region of complex dehydration.

The thermogravimetric curves were evaluated by the Coats–Redfern method [10], using the least squares procedure. A reaction order of one appeared to be the most convenient for all reactions studied. The experimental activation energies of the decomposition reactions as presented below were the averages of 6–8 measurements.

The reversibility of the reactions was studied by exposing the samples to water vapour after the completed decomposition. The compositions and structures of the complexes were checked analytically and via powder diffractograms before the reaction and after the completed rehydration. Except for $Cu(NH_3)_4(H_2O)SO_4$, the dehydrations of the studied compounds proved to be reversible.

## Results and discussion

The experimental activation energies of the decomposition reactions are listed in Table 1. Known data on the structures of the complexes are presented in Table 2. For comparison purposes, the data on $CuSO_4 \cdot 3\,H_2O$ are also given; for the dehydration of this the $E^*$ value is 199±5 kJ $mol^{-1}$. Unfortunately, the structural data on some of the studied complexes are either incomplete (e.g. for $Rb_2CuCl_4 \cdot 2\,H_2O$ only the lattice parameters are known [19]), or are totally missing.

A comparison of the activation energies with the Cu(II) – released ligand interatomic distances shows that the lowest $E^*$ value was not found for $Cu(en)_2(H_2O)Br_2$ (with the longest split bond). From a comparison of the data in Tables 1 and 2 it may be seen that for the removal of the water molecules from $CuSO_4 \cdot 3\,H_2O$ ($W_1$ and

**Table 1** The values of activation energies of the studied decomposition reactions

| Complex | Reaction | $E^*$, kJ $mol^{-1}$ |
|---|---|---|
| $Cu(NH_3)_4(H_2O)SO_4$ | $-H_2O - 0.5\,NH_3$ | 108±5 |
| $Cu(en)_2(H_2O)Cl_2$ | $-H_2O$ | 132±6 |
| $Cu(en)_2(H_2O)Br_2$ | $-H_2O$ | 156±6 |
| $Cu(en)(H_2O)_2SO_4$ | $-2\,H_2O$ | 108±5 |
| $Cu(py)_2(H_2O)_2SO_4$ | $-2\,H_2O$ | 164±8 |
| $(NH_4)_2CuCl_4 \cdot 2\,H_2O$ | $-2\,H_2O$ | 90±3 |
| $K_2CuCl_4 \cdot 2\,H_2O$ | $-2\,H_2O$ | 112±4 |
| $Rb_2CuCl_4 \cdot 2\,H_2O$ | $-2\,H_2O$ | 145±2 |
| $CuCl_2 \cdot 2\,H_2O$ | $-2\,H_2O$ | 125±5 |

**Table 2** Some structure data of the studied complexes

| Complex | $r$(Cu – OH$_2$), Å | $U_{mean}$(O) · $10^4$, Å$^2$ | Hydrogen bonds lengths, Å | Ref. |
|---|---|---|---|---|
| $Cu(NH_3)_4(H_2O)SO_4$ | 2,339<br>(3.479) | 776<br>(242)$^a$ | 2.779 | 11 |
| $Cu(en)_2(H_2O)Cl_2$ | 2.62 | 583$^b$ | 3.04<br>3.13 | 12 |
| $Cu(en)_2(H_2O)Br_2$ | 2.78 | | | 13 |
| $Cu(en)(H_2O)_2SO_4$ | 1.975 | 245 | 2.71<br>2.72 | 14 |
| $Cu(py)_2(H_2O)_2SO_4$ | 2.04 | | | 15 |
| $Cu(H_2O)_3SO_4$ | $W_1$ 1.976 | 128 | 3.126<br>2.751 | 16 |
| | $W_2$ 1.855 | 121 | 2.678<br>2.595 | |
| | $W_3$ 1.965 | 143 | 2.697 | |
| | | $\Delta U_{ii}^{1/2} \cdot 10^3$, Å | | |
| $(NH_4)_2CuCl_4 \cdot 2\,H_2O$ | 1.954 | 54 | 2.186<br>2.186 | 17 |
| $K_2CuCl_4 \cdot 2\,H_2O$ | 1.971 | 35 | 2.165 | 18 |
| $Rb_2CuCl_4 \cdot 2\,H_2O$ | | | | 19 |
| $CuCl_2 \cdot 2\,H_2O$ | 1.957 | 13 | 3.216 | 20 |

a – value of $\Delta U_{ii}^{1/2}$ approximately in direction of the Cu – OH$_2$ bond
b – isotropic temperature factor

$W_3$) and from $Cu(en)(H_2O)_2SO_4$, where they are coordinated to Cu(II) by approximately equally long bonds [14, 16], appreciably different activation energies were found (199 and 108 kJ mol$^{-1}$, respectively); for the latter complex a value of 121 kJ mol$^{-1}$ has also been reported [21]. Such great differences in the activation energies of these two complexes do not follow unambiguously either from the number and lengths of the hydrogen bonds formed by the water molecules. For these complexes, however, considerable differences were observed in the anisotropic temperature factors of the oxygen atoms in the coordinated water molecules, the mean values ($U_{mean}$) of which are listed in Table 2. However, for $Cu(en)(H_2O)_2SO_4$, for which a lower activation energy value was found, $U_{mean}$ was markedly higher than the values for the oxygen atoms in the water molecules $W_1$ and $W_3$, the release of which is assumed in the dehydration of $CuSO_4 \cdot 3\,H_2O$ [3]. On the other hand, for the dehydration of $Cu(NH_3)_4(H_2O)SO_4$, connected with a partial release of the coordinated ammonia molecules, the $E^*$ value found was the same as for $Cu(en)(H_2O)_2SO_4$, though the $U_{mean}$ value of the oxygen atom in the released water molecule was about 3 times higher for the former complex. The comparatively high $E^*$ value with respect to the above facts, for the decomposition of $Cu(NH_3)_4(H_2O)SO_4$ is probably caused by the partial release of the ammonia molecules, since a value of $E^* = 66.3$ kJ mol$^{-1}$ was determined for the elimination of the water molecule only from this complex [22]. From study of the results of X-ray structure analysis of $Cu(NH_3)_4(H_2O)SO_4$, the temperature factor of the oxygen atom proved to be anomalous, since its component was the highest in the direction of the axis of the Cu–O bond. According to [23], such cases occur either for the superimposition of two or more structural states, or for "fluxional" complexes, which considerably change their structures, mainly the bond lengths in the Cu(II) coordination polyhedra, with varying temperature. In such a case the structure determined at laboratory temperature cannot be taken as basis for comparison with the $E^*$ values determined at considerably higher temperatures.

In comparing the $E^*$ and $U_{mean}$ values for the complexes under study, as given in the first part of Table 2, a trend can be observed: the activation energies of complex dehydration decreases with increasing $U_{mean}$ values. The only exception from this is the complex $Cu(en)_2(H_2O)Cl_2$, which should exhibit a lower $E^*$ value than $Cu(en)(H_2O)_2SO_4$. With respect to the fact that the structure of $Cu(en)_2(H_2O)Cl_2$ was only refined in the isotropic cycle and its solution was finished at $R = 0.115$, i.e. regarding the up-to-date requirements with a low degree of reliability, this fact cannot lead to unambiguous conclusions.

$M_2CuCl_4 \cdot 2\,H_2O$ and $CuCl_2 \cdot 2\,H_2O$ are isostructural and the $Cu{-}OH_2$ bonds lie in the direction of some of the crystallographic axes. Therefore, for comparison with the $E^*$ values of dehydration, the value of $\Delta U_{ii}^{1/2}$ along the respective crystallographic axis was chosen, which actually reflects the temperature displacement of the whole bond (Table 2). For these complexes the decrease in the activation energy with increasing $\Delta U_{ii}^{1/2}$ appears still more distinctly. Taking into account that temperature factors are functions of force constants, particle weight and temperature [6], it is logical that $\Delta U_{ii}^{1/2}$ must reflect the energetic situation in the coordination polyhedron more comprehensively than the $U_{mean}$ value of the donor oxigen atom.

## Conclusions

Though the results point to the existence of a qualitative relationship between $E^*$ and the thermal motions of atoms in the crystal structure. Further study of this relationship appears necessary. However, the results unambiguously indicate that, in studying the relations between the structures of Cu(II) complexes and the course of their thermal decomposition, it is necessary to consider the complex structure as a whole, since the course of decomposition is influenced by the overall energy of the compound and not by the partial energies of the broken bonds. The results of the present study indicate that the degree of tetragonal distortion of Cu(II) complexes, which was used for comparison with the $E^*$ values for decomposition of Tutton's salts [4], can not express sufficiently the differences in the energy contents of the Cu(II) complexes.

## References

1 H. Langfelderová, J. Thermal Anal., 12 (1977) 413.

2 H. Langfelderová, M. Linkešová, M. Serátor and J. Gažo, J. Thermal Anal., 17 (1979) 107.

3 H. Langfelderová, M. Linkešová and E. Jóna, J. Thermal Anal., 19 (1980) 117.

4 H. Langfelderová, F. Foret, P. Ambrovič and J. Gažo, J. Thermal Anal., 19 (1980) 357.

5 J. H. Ammeter, H. B. Burgi, E. Gamp, V. Meyer-Saundrin and W. P. Jensen, Inorg. Chem., 18 (1979) 733.

6 W. H. Zachariasen, Acta Cryst., A25 (1969) 276.

7 J. J. Berzelius, Ann. Chim., 82 (1812) 225, cited according to Gmelins Handbuch der anorg. Chemie, Kupfer, Syst. N. 60, Teil B, Lief. 1, 1958, p. 563.

8 C. H. Johnson and S. A. Bryant, J. Chem. Soc., (1934) 1783.

9 T. H. Changand and P. P. Hu, J. Chinese Chem. Soc., 10 (1943) 113, cited according to Gmelins Handbuch der anorg. Chemie, Kupfer, Syst. N. 60, Teil B, Lief. 1, 1958, p. 573.

10 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.

11 B. Morosin, Acta Cryst., B25 (1969) 19.

12 R. D. Ball, D. Hall, C. E. F. Rickard and C. E. P. Waters, J. Chem. Soc., A (1967) 1435.

13 J. M. Procter, B. J. Hathaway and P. Nicholls, J. Chem. Soc., A (1968) 1678.

14 M. Dunaj-Jurčo, Thesis, Bratislava, 1972.

15 E. Cunnillo and G. Giuseppetti, Atti Accad. Naz. Lincei Rend. Classe, Sci. Fis. Mat. Nat., 36 (1964) 878.

16 R. F. Zahrobsky and W. H. Baur, Acta Cryst., B24 (1968) 508.

17 S. N. Blahay-Taurhane, A. Sequeira and R. Chidambaram, Acta Cryst., B36 (1980) 2925.

18 R. Chidambaram, O. O. Navarro, A. Garcia, K. Linggoatmodjo, L. S. Chien, J. H. Suh, A. Sequeira and S. Srikanta, Acta Cryst., B26 (1970) 827.

19 B. D. Stepin, L. D. Ischarova, G. M. Serebrennikova, L. A. Starikova and V. K. Trunov, Zh. Neorgan. Khim., 21 (1976) 2783.

20 A. Engberg, Acta Chem. Scand., 24 (1970) 3510.

21 W. W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 833.

22 E. Segal, Studii Cercet. Chim., 11 (1963) 175.

23 B. J. Hathaway, M. Duggan, A. Murphy, J. Mullane, Ch. Power, A. Walsh and B. Walsh, Coord. Chem. Rev., 36 (1981) 267.

**Zusammenfassung** — Die Aktivierungsenergien ($E^*$) der Dehydratisierung von $Cu(NH_3)_4(H_2O)SO_4$, $Cu(en)_2(H_2O)X_2$ ($X = Cl^-, Br^-$), $Cu(en)_2(H_2O)_2SO_4$, $Cu(py)_2(H_2O)_2SO_4$, $CuCl_2 \cdot 2\,H_2O$ und $M^I_2CuCl_4 \cdot 2\,H_2O$ ($M^I = NH_4$, K, Rb) wurden experimentell aus den nicht-isothermen thermogravimetrischen Kurven unter Verwendung der Coats—Redfern-Methode erhalten. Diese $E^*$-Werte wurden mit bekannten Daten der Strukturen der in den angeführten Verbindungen vorliegenden Cu(II)-Koordinationspolyeder verglichen. Die $E^*$-Werte hängen weder von der Bindungslänge Zentralatom-Ligand noch von Zahl und Länge der von den Wassermolekülen gebildeten Wasserstoffbrückenbindungen ab. Es wurde jedoch festgestellt, dass es gerechtfertigt ist, nach Zusammenhängen zwischen den $E^*$-Werten und anisotropen Temperaturkoeffizienten der Donoratome der abgespaltenen Liganden zu suchen.

**Резюме** — Экспериментальные энергии активации $E^+$ реакции дегидратации $Cu(NH_3)_4(H_2O)SO_4$, $Cu(эда)_2(H_2O)X_2$ с $X = Cl^-$ и $Br^-$, $Cu(эда)_2(H_2O)_2SO_4$, $Cu(пир.)_2(H_2O)_2SO_4$, $CuCl_2 \cdot 2\,H_2O$ и $M^I_2CuCl_4 \cdot 2\,H_2O$, где $M^I = NH_4$, K, Rb — были определены из неизотермических термогравиметрических кривых, используя метод Коутса—Рэдферна. Полученные значения $E^+$ были сопоставлены с известными данными о структуре Cu(II) координационного полиэдра в вышеупомянутых комплексах. Не была найдена зависимость между $E^+$ и длиной связи центральный атом — выделяющийся лиганд, ни между числом и длиной водородных связей, образованными выделяющимися молекулами воды. Однако, было найдено, что оправданным является поиск некоторой взаимосвязи между значением $E^+$ и анизотропными температурными факторами донорных атомов лигандов.