

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

### IV. THE THERMOCHROMISM OF $M_2^I M^{II}(\text{SO}_4)_2$ COMPOUNDS ( $M^I = \text{K, Rb, Cs}$ or $\text{Tl}$ ; $M^{II} = \text{Ni}$ or $\text{Cu}$ )

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The paper presents the results of a study of  $M_2^I M^{II}(\text{SO}_4)_2$  compounds with  $M^I = \text{K, Rb, Cs}$  or  $\text{Tl}$ , and  $M^{II} = \text{Cu}$  or  $\text{Ni}$ , in the interval from room temperature to the melting temperature. All the compounds studied show endo- or exothermic excursions in their DTA curves, corresponding to phase transitions connected with colour changes of the compounds. For  $M_2^I \text{Cu}(\text{SO}_4)_2$ , where  $M^I$  is  $\text{K}$  or  $\text{Tl}$ , several modifications could be prepared at laboratory temperature, probably distortion isomers. No modifications of this type could be prepared, however, for  $M_2^I \text{Ni}(\text{SO}_4)_2$  compounds.

Many complex compounds of Cu(II) and Ni(II) are characterized by a reversible thermochromism. Study of the structures of Cu(II) complexes at different temperatures showed that this thermochromism was connected with changes of the tetragonal distortion of the coordination polyhedra, and in some cases a change of the ligand conformation also took place [1–3].

It is known from older literature that, depending on the temperature of its preparation, potassium copper(II) sulphate forms three different coloured modifications. This compound is also characterized by thermochromism [5]. Since the literature contains only a few data on the thermochromism structure and other properties of compounds of the type  $M_2^I \text{Cu}(\text{SO}_4)_2$  and  $M_2^I \text{Ni}(\text{SO}_4)_2$ , or they are even entirely missing, this study was aimed at obtaining further experimental information.

### Experimental

*Synthesis of complexes.* The investigated complexes were prepared by two methods, viz. by dehydration of the corresponding Tutton salts, or by heating a mixture of  $\text{CuSO}_4$  and  $M_2^I \text{SO}_4$  in a molar ratio of 1 : 1 until melting, with subsequent cooling.

*Analytical methods.* The Cu(II) or Ni(II) content in the prepared compounds was determined by complexometric titration with murexide as indicator. The results of Cu(II) determination in the different compounds were:

	found	calc.
$K_2Cu(SO_4)_2$	19.00%	19.03%
$Rb_2Cu(SO_4)_2$	14.78%	14.89%
$Cs_2Cu(SO_4)_2$	12.10%	12.18%
$Tl_2Cu(SO_4)_2$	9.42%	9.56%

The data of Ni(II) determination were:

$K_2Ni(SO_4)_2$	17.70%	17.84%
$Rb_2Ni(SO_4)_2$	13.81%	13.92%
$Cs_2Ni(SO_4)_2$	11.25%	11.36%
$Tl_2Ni(SO_4)_2$	8.74%	8.90%

*Apparatus and measuring conditions.* The thermal properties of the studied compounds were investigated with an OD 102 derivatograph (MOM, Budapest). The measurements were performed in the platinum crucibles supplied with the apparatus, with an upper diameter of 14 mm. The sample weight was 200 mg. As reference material  $Al_2O_3$  was used. The heating rate was 6°/min. Calorimetric measurements were made with a Perkin–Elmer DSC-2 calorimeter, in closed aluminium dishes, with a sample weight of  $\approx 10$  mg, the heating rate being 8°/min. The spectral properties of the compounds under investigation were studied using IR-75 (400–1300  $cm^{-1}$ ), UV–VIS (13.000–25.000  $cm^{-1}$ ) (Carl Zeiss, Jena) and Unicam SP 700 (7.000–15.000  $cm^{-1}$ ) spectrophotometer using the nujol suspension technique. The diffraction properties of the complexes were studied with a GON-2 powder goniometer (Czechoslovakia);  $CuK_{\alpha}$ -radiation and a Ni filter were used.

## Results and discussion

### *a. Potassium copper(II) sulphate and potassium nickel(II) sulphate*

Potassium copper(II) sulphate prepared by the dehydration of  $K_2Cu(SO_4)_2 \cdot 6 H_2O$  until 130° is reported [4, 5] to be light-blue ( $\alpha$ -modification). On heating, its DTA curve shows a small exothermic excursion at 180° and two endothermic excursions with maxima in the regions of 350–370° and 470–500°, respectively (Fig. 1). The melting temperature was 495–500°. Observation of the heated sample revealed a perceptible thermochromism, since the originally light-blue substance successively changed its colour to white, yellow, green, blue and dark-green. The melt was brown. On cooling of the melt, these colour changes were observed in the reverse order with the exception of the formation of the white colour. Formation of the white modification was not observed on repeated heating of the cooled melt. On cooling, the melt yields long needle-shaped crystals, which at  $\approx 30^\circ$  de-

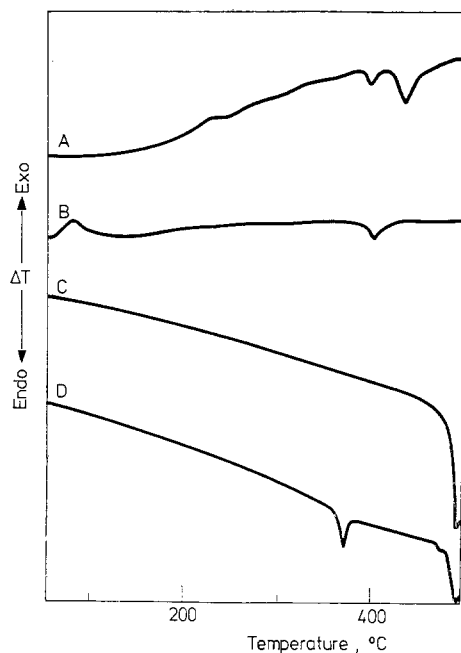


Fig. 1. DTA curves of  $K_2Cu(SO_4)_2$  modifications: A —  $\alpha$ , B —  $\beta$ , C —  $\gamma$ , D —  $\delta$

compose to a microcrystalline powder. This conversion is accompanied by a marked volume change; it appears as an exothermic excursion in the DTA curve during cooling of the melt (Fig. 2). When  $K_2Cu(SO_4)_2$  was heated only to the melting temperature, the powder formed was light-blue in colour ( $\gamma$ -modification); if the heating was continued gently above the melting temperature, but still below the decomposition temperature (rapid decomposition took place at  $\approx 700^\circ$ ), on cooling a green microcrystalline powder ( $\delta$ -modification) was obtained. On heating, the  $\gamma$ - and  $\delta$ -modifications do not yield any white  $\beta$ -modification and the entire courses

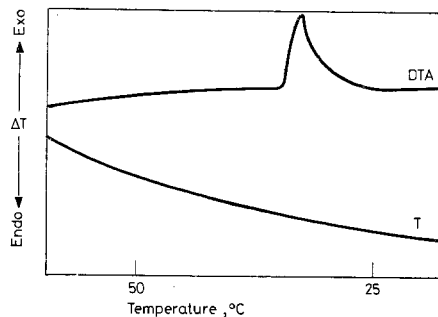


Fig. 2. DTA curve of cooling the melt of  $K_2Cu(SO_4)_2$

of their DTA curves also differ from those of the  $\alpha$ - and  $\beta$ -modifications (Fig. 1).

The powder diffractograms of the  $K_2Cu(SO_4)_2$  modifications (Fig. 3) indicate that the crystal structures of the  $\alpha$ -,  $\beta$ - and  $\gamma$ -modifications differ considerably. It must be noted here that  $\alpha$ - $K_2Cu(SO_4)_2$  gives rather poorly developed crystals immediately after thermal dehydration and the powder diffractogram exhibits broad lines of low intensity for angles of  $2\theta = 9.7, 13, 13.30^\circ$  and also  $21, 21.5$  and  $22^\circ$ . Somewhat more marked maxima are found for angles of  $2\theta = 28.3, 29.2, 30.5$  and  $32.4^\circ$ ; for a slowly performed dehydration (in a desiccator over  $P_2O_5$ ), the  $\alpha$ -modification obtained shows an evidently better developed crystal structure (Fig. 3a). The powder diffractograms of  $\gamma$ - and  $\delta$ - $K_2Cu(SO_4)_2$  are practically identical.

From the IR spectra of the  $K_2Cu(SO_4)_2$  modifications (Table 1) it may be stated that the sulphate groups in them are not coordinated to the Cu(II) in the same way. Though the powder diffractograms of the  $\gamma$ - and  $\delta$ -modifications show minimal differences, those in the vibrations of the  $SO_4^{2-}$  groups are rather expressive. A comparison of the obtained results with the vibrations of the  $SO_4^{2-}$  groups in  $K_2Cu(SO_4)_2 \cdot 6H_2O$  [6] leads to the conclusion that the interaction of the oxygen

Table 1  
Vibrations of  $SO_4^{2-}$  group in  $K_2Cu(SO_4)_2$  modifications

	$\tilde{\nu}_1, \text{cm}^{-1}$	$\tilde{\nu}_2, \text{cm}^{-1}$	$\tilde{\nu}_3, \text{cm}^{-1}$	$\tilde{\nu}_4, \text{cm}^{-1}$
$K_2Cu(SO_4)_2 \cdot 6H_2O$ [6]	980	440	1050 1030 1145 1165 1185	605 620 650 660
$\alpha$ -	977	437	1040 1120 1140 1163 1187	603 620 647 666
$\beta$ -	975	437 470 506	1027–1050 1120 1170 1200	606 640 650
$\gamma$ -	977	437 506	1040 1120 1140 1206	606 620 633 660
$\delta$ -	973	437 506	1033 1127 1206	606 620 633 660

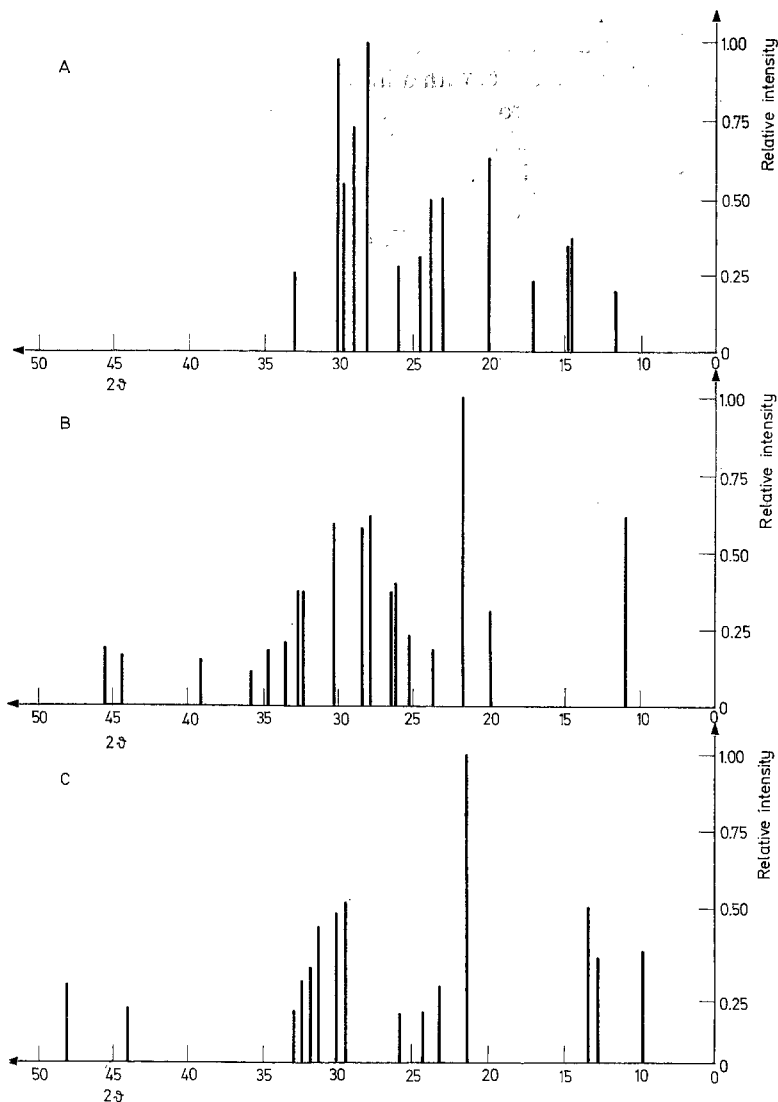


Fig. 3. Powder diffractograms of  $K_2Cu(SO_4)_2$  modifications: A -  $\alpha$ , B -  $\beta$ , C -  $\gamma$  modification

atoms from the sulphate groups with the hydrogen atoms from the water molecules by means of hydrogen bridges was substituted in the modifications of  $K_2Cu(SO_4)_2$  by an interaction with the Cu(II) atoms; this fact mainly reflected itself in the wavenumbers of the vibrations  $\nu_3$  and, for the  $\gamma$ - and  $\delta$ -modifications, in the splitting of this vibration of the sulphate group too. For the  $\beta$ -,  $\gamma$ - and  $\delta$ -modifications a strong band was observed with  $\nu_{max}$  at  $506\text{ cm}^{-1}$ . On the analogy of cobalt complexes [7] of this type, this band may be suggested to be caused by a chelate coordination of  $SO_4^{2-}$  to the central atom.

The electronic spectra of the  $\text{K}_2\text{Cu}(\text{SO}_4)_2$  modifications indicate that the Cu(II) atom has coordination number 6, with different degrees of distortion of the coordination polyhedron. The electronic spectra of the  $\alpha$ - and  $\beta$ -modifications show, in addition to a shift of the main band of the  $d-d$  transition ( $\alpha$ :  $13.200\text{ cm}^{-1}$ ,  $\beta$ :  $12.500\text{ cm}^{-1}$ ), differences in the near UV region, since for the  $\alpha$ -modification a band was observed at  $23.800\text{ cm}^{-1}$  (as a shoulder on the CT band), while for the  $\beta$ -modification the band was at  $20.000\text{ cm}^{-1}$  [5]. In spectra of the  $\gamma$ - and  $\delta$ -modifications in this work, no absorption bands were observed in the near UV region. For the wavenumbers of the  $d-d$  transition band maxima, the value obtained for the  $\gamma$ -modification was  $12.200\text{ cm}^{-1}$ , while for the  $\delta$ -modification it was  $12.000\text{ cm}^{-1}$  with a shoulder at  $8.500\text{ cm}^{-1}$ .

In connection with the method of preparation of  $\delta\text{-K}_2\text{Cu}(\text{SO}_4)_2$  it appeared necessary to determine whether partial decomposition of the melt occurred, though the analytical results did not indicate this possibility. Microscopic investigation of this modification did not show the presence of CuO grains. They can not be observed in the cooled melt, however, even when the decomposition temperature is exceeded. The results of further experiments support the suggestion that the green colour of  $\delta\text{-K}_2\text{Cu}(\text{SO}_4)_2$  is not caused by a CuO admixture in this compound. If this compound is exposed to the action of water vapour, green  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  is formed, differing from the light-blue Tutton salt (also formed in reactions of the other  $\text{K}_2\text{Cu}(\text{SO}_4)_2$  modifications with water vapour) in its powder diffractograms, electronic spectra and broad-band H-NMR spectra. The electronic spectrum of the green  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  modification exhibits, in addition to the main band of the  $d-d$  transition with its maximum at  $12.300\text{ cm}^{-1}$  (blue hexahydrate at  $12.400\text{ cm}^{-1}$ ), a distinct shoulder on the CT band in the near UV region at  $22.000\text{ cm}^{-1}$ . The broad-band H-NMR spectra indicate differences in the hydrogen bonds in both the modifications, since the blue  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  yields a split signal, pointing to the presence of water molecules not bonded by hydrogen bonds. The green  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  yields a single band. These results are in agreement with those from the IR spectra, according to which the  $\text{SO}_4^{2-}$  groups in the  $\gamma$ - and  $\delta$ -modifications are differently coordinate. Their different positions are apparently also retained in reactions with water vapour, resulting in the formation of different hydrogen bridges in the two forms of  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . When heated in a sealed test tube, the green form changes irreversibly at  $\approx 85^\circ$  into the blue modification. An attempt to determine the enthalpy change in this conversion by the DSC method was not successful; this can be understood, considering the small energetic differences connected with the assumed structural differences between the two forms of this compound. Besides, the temperature of transition is very near that of the decomposition of  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The differences in the obtained values of  $\Delta H$  for the two forms of this compound are smaller than 0.5%.

On heating, potassium nickel(II) sulphate also shows thermochromism, since the originally light-yellow compound then changes through orange to dark-brown in the melt. From the DTA curves of  $\text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Fig. 4) nickel(II) complexes of this type also exhibit colour changes probably accompanied by phase

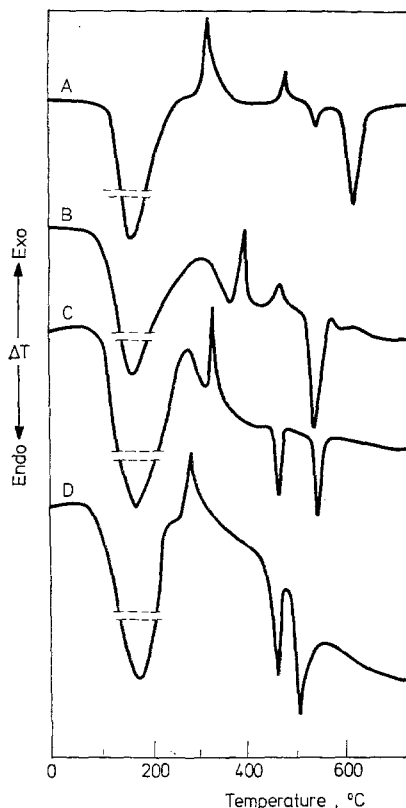


Fig. 4. DTA curves of  $M_2Ni(SO_4)_2 \cdot 6 H_2O$ , where  $M^I$  is A) K, B) Rb, C) Cs, D) Tl

transitions, being exothermic for  $K_2Ni(SO_4)_2$  at 325 and 485° and endothermic at 540 and 603° (melting) (Fig. 4). The attempts to separate different modifications of  $K_2Ni(SO_4)_2$  at laboratory temperature failed, however.

*b. Rubidium and cesium copper(II) and nickel(II) sulphates*

On heating, all these compounds show thermochromism, but so far all attempts to prepare different modifications of them able to exist at laboratory temperature have failed. The compounds of  $M_2Cu(SO_4)_2$  ( $M^I = Rb, Cs$ ) have the same powder diffractograms (Fig. 5) whether they were prepared by dehydration of the respective hexahydrates or by cooling of the melt. The thermochromism of these compounds containing Cu(II) is shown by the change in colour from light-blue through dark-blue and green to brown in the melt. The DTA curves of both the compounds are in agreement with the data [5].

The courses of the DTA curves of the nickel analogues of the discussed substances on dehydration are characterized for the rubidium salt by two comparatively marked exothermic excursions at 380 and 470° (Fig. 4B), while for the cesium

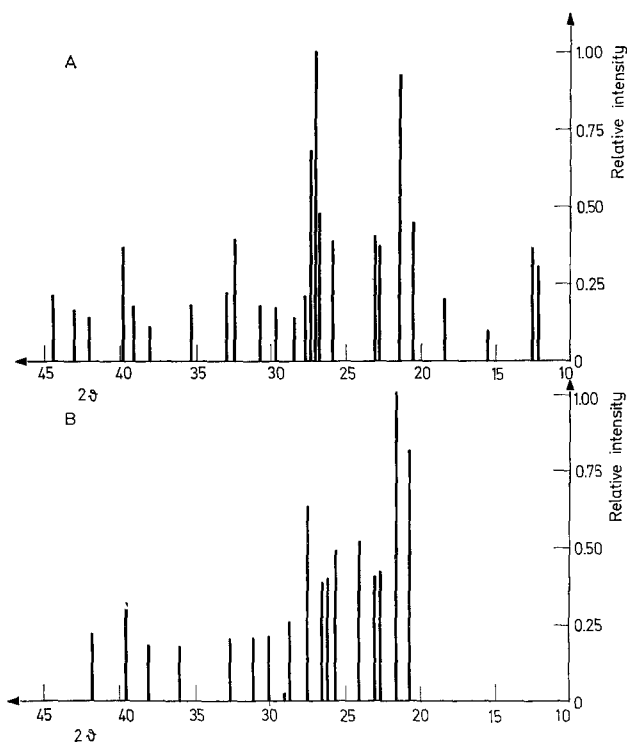


Fig. 5. Powder diffractograms of  $\text{Rb}_2\text{Cu}(\text{SO}_4)_2$  (A) and  $\text{Cs}_2\text{Cu}(\text{SO}_4)_2$  (B)

salt there is an exothermic excursion at  $350^\circ$  and an endothermic one at  $480^\circ$  (Fig. 4C). The melting temperatures are  $540^\circ$  and  $560^\circ$  for the rubidium and the cesium salt, respectively.

*c. Thallium(I) copper(II) and nickel(II) sulphate*

Thallium copper(II) sulphate, which as far as we know has not previously been described as an anhydrous compound in the literature, also exhibits strong thermochromism. On heating of this compound, its thermochromism becomes evident by colour changes from light-blue through green to brown in the melt. The DTA curve of the Tutton salt  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Fig. 6A) shows several phase transitions after dehydration. First, it is an exothermic excursion with its maximum at about  $200^\circ$  and two endothermic excursions, with maxima at  $320$  and  $330^\circ$ ; the melting temperature is  $345^\circ$ . On cooling, the formation of three modifications with different colours was observed. Under controlled cooling conditions it was possible to prepare all these three forms in the pure state. Slow cooling ( $\approx 10^\circ/\text{min}$ ) led to a blue-green flaky crystalline modification, denoted as  $\alpha\text{-Tl}_2\text{Cu}(\text{SO}_4)_2$ , the powder diffractogram of which (Fig. 7A) differs markedly from that of the brown-green  $\beta$ -modification (Fig. 7B). This is prepared by rapid cooling of the melt to  $\approx 100^\circ$  and by



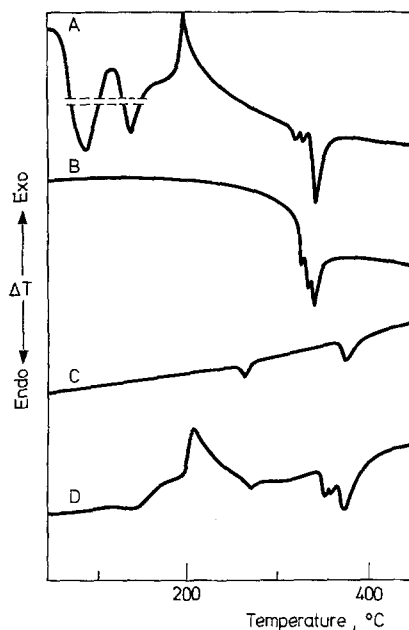


Fig. 6. DTA curves of the  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$  compound (A) and of  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  modifications: B)  $\alpha$ -, C)  $\beta$ -, D)  $\gamma$ -modification

slow gradual cooling to laboratory temperature. Intense cooling of the melt to laboratory temperature (or even lower) yields a green vitreous substance denoted as  $\gamma\text{-Tl}_2\text{Cu}(\text{SO}_4)_2$ , which does not diffract X-ray radiation, even after grinding. All three modifications are stable at laboratory temperature, but they undergo conversion into the  $\alpha$ -form on heating. The DTA curves of these  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  modifications are different (Fig. 6B, C, D). The DTA curve of the vitreous  $\gamma$ -modification exhibits an appreciable exothermic excursion with its maximum at  $215^\circ$ , a moderate endothermic excursion at  $270^\circ$ , and still other endothermic changes at  $360^\circ$  and  $380^\circ$ , the latter corresponding to sample melting. For the exothermic change corresponding to devitrification, the DSC method yields  $\Delta H = 7.4 \text{ kJ mol}^{-1}$ . From the DTA curves of the  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  modifications it is suggested that devitrification of the  $\gamma$ -form leads to  $\beta\text{-Tl}_2\text{Cu}(\text{SO}_4)_2$ , since no endothermic conversion with maximum at  $270^\circ$  was observed in the DTA curve of the  $\alpha$ -modification. Likewise, it is concluded that on dehydration of  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$  the amorphous  $\gamma$ -modification is formed, to which the exothermic excursion with maximum at  $\approx 200^\circ$  corresponds.

In the near IR and visible region of the spectra of these modifications, only one very broad absorption band of  $d-d$  transitions was found. The appropriate position of the maximum for the  $\alpha$ -compound is at  $11.200$ , for the  $\beta$ -form it is at  $10.000 \text{ cm}^{-1}$ , and for the  $\gamma$ -modification is at  $11.000 \text{ cm}^{-1}$ . A comparison of these values with those for the potassium and rubidium ( $13.000 \text{ cm}^{-1}$ ), cesium ( $12.800 \text{ cm}^{-1}$ )

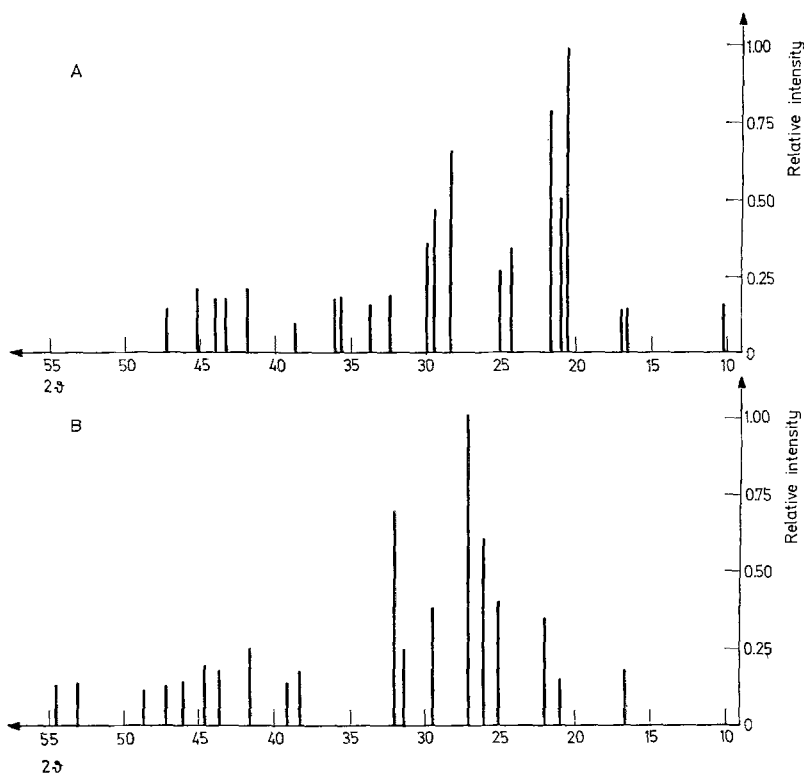


Fig. 7. Powder diffractograms of A)  $\alpha$ - and B)  $\beta$ - $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$

and sodium salts ( $13.000\text{ cm}^{-1}$ ) [5] shows that in the  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  modifications the sulphate group produces the weakest ligand field, with a retained coordination number of 6 of the central atom. The decrease of the ligand field strength of the  $\text{SO}_4^{2-}$  group in the thallium salt as compared with the salts containing the cations of the alkali metals may be due to its stronger interaction with the  $\text{Tl}^+$  ion, which exhibits a stronger polarizing effects than the alkali metal cations do.

The infrared spectra of the various modifications of  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  (Table 2) point to the fact that the interactions of the sulphate group are more various than in the potassium salt. In the spectra of  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  it appears almost impossible to distinguish the vibrations  $\nu_1$  and  $\nu_3$  (this is why they are listed in one column in Table 4). For  $\alpha$ - $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  all four vibrations of the  $\text{SO}_4^{2-}$  ion were observed to be split to different extents and notable shifts were also found for  $\nu_3$  and  $\nu_4$ , which are active in the IR spectrum of the free  $\text{SO}_4^{2-}$  anion [8]. This indicates significant bridging and netforming, respectively, by this anion in the crystal structure of this complex. In the other two  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  modifications vibration  $\nu_2$  was not observed, and the splittings of the other vibrations were less numerous; the wavenumber shifts of the bands with respect to the free  $\text{SO}_4^{2-}$  ion were also smaller. From an analysis of the

Table 2  
Vibrations of  $\text{SO}_4^{2-}$  group in  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  modifications

$\text{Tl}_2\text{Cu}(\text{SO}_4)_2$	$\tilde{\nu}_1$ and $\tilde{\nu}_3$ , $\text{cm}^{-1}$			$\tilde{\nu}_2$ , $\text{cm}^{-1}$	$\tilde{\nu}_4$ , $\text{cm}^{-1}$	
$\alpha$ -	930	950	990	(500)		590
	1020	1090	1173	430	627	660
$\beta$ -	947	973	1006			590
	1073	1146				630
$\gamma$ -	970	1020	1090			600
	1150					640

changes in the  $\text{SO}_4^{2-}$  vibrations owing to its coordination [8], it may be stated that, of the  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  modifications, it is the  $\alpha$ -form where the  $\text{SO}_4^{2-}$  anion is most strongly coordinated. This conclusion agrees well with the data of the electronic spectra of these modifications.

The most marked differences between  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  and  $\text{Tl}_2\text{Ni}(\text{SO}_4)_2$  are analogous to those in the potassium compounds, viz. in the inability of the latter to form modifications capable of existence at laboratory temperature, though on heating of these compounds excursions corresponding to phase transitions appear in the DTA curve below the melting temperature (Fig. 4D).

On the basis of the results obtained, we assume for all Cu(II) complexes studied a distorted octahedral coordination of the central atom, with the sulphate groups forming bridges between the Cu(II) atoms. The prepared  $\text{K}_2\text{Cu}(\text{SO}_4)_2$  and  $\text{Tl}_2\text{Cu}(\text{SO}_4)_2$  modifications probably represent still other examples of distortion isomers [9], since the research methods used indicate that these modifications differ in the degree of distortion of the coordination polyhedron.

Comparison of the influence of the outer sphere  $M^I$  cations on the degree of distortion of the Cu(II) coordination polyhedron in the Tutton salts and in compounds of type  $M_2^I\text{Cu}(\text{SO}_4)_2$  demonstrates that in these latter substances the situation is different and more complicated. Whereas in the Tutton salts the degree of distortion of the coordination polyhedron of the Cu(II) increases with the increasing atomic number of  $M^I$  [10], in the dehydrated substances no analogous trend could be observed.

According to the obtained results, the thermochromism found in the studied Cu(II) compounds is probably a manifestation of the temperature-dependence of the equatorial-axial interactions in the complexes; with respect to the assumed structures of these substances, the formation of different modifications, i.e. distortion isomer, is not surprising, since it is known that in compounds with chain structures there is a possibility for the fixation of unequally stable, differently distorted coordination polyhedra of Cu(II) [11].

The causes of the thermochromism of  $M_2^I\text{Ni}(\text{SO}_4)_2$ , as for other nickel complexes [3, 12], are so far unclarified.

## References

1. A. PAJUNEN, K. SMOLANDER and I. BELINSKIJ, Suomen Kemistilehti, B45 (1972) 317.
2. I. GRENTHE, P. PAOLETTI, M. SANDSTROM and S. GLIKBERG, Inorg. Chem., 18 (1979) 2687.
3. J. R. FERRARO, L. J. BASILE, L. R. GAREIA-INEGUES and L. FABRIZZI, Inorg. Chem., 15 (1976) 2342.
4. Gmelins Handbuch der anorganischen Chemie, Kupfer, S. N. 60, Teil B, Lief. 3, pp. 1032, 1072, 1110, 1184.
5. K. NAGASE, H. YOKOYASHI and K. SONE, Thermochim. Acta, 23 (1978) 283.
6. R. A. NYQUIST and R. O. KAGEL, Infrared Spectra of Inorganic Compounds, Academic Press, New York and London, 1971, Spectrum No. 496, p. 297.
7. W. P. GRIFFITH and R. COOMBER, J. Chem. Soc., (A) (1968) 1128.
8. N. NAKAMOTO, J. FUJITA, S. TANAKA and M. KOBAYASHI, J. Am. Chem. Soc., 79 (1957) 4904.
9. J. GAŽO, Pure Appl. Chem., 38 (1974) 279.
10. M. A. HITCHMAN and T. D. WAITE, Inorg. Chem., 15 (1976) 2150.
11. J. GAŽO, I. B. BERSUKER, J. GARAJ, M. KABEŠOVÁ, H. LANGFELDEROVÁ, J. KOHOUT, M. MELNIK, M. SERÁTOR and F. VALACH, Coord. Chem. Rev., 19 (1976) 253.
12. L. FABRIZZI, M. MICHELONI and P. PAOLETTI, Inorg. Chem., 13 (1974) 3019.

ZUSAMMENFASSUNG — Die Ergebnisse einer Untersuchung von  $M_2^I M^{II}(SO_4)_2$ -Verbindungen (Cs, Tl;  $M^{II} = Cu, Ni$ ) im Temperaturbereich von Raum- bis Schmelztemperatur werden beschrieben. Alle untersuchten Verbindungen zeigen in ihren DTA-Kurven mit Farbänderungen einhergehende, durch Phasenumwandlungen bedingte endo- und exotherme Peaks. Bei Laboratoriumstemperatur konnten verschiedene Modifikationen von  $M_2^I Cu(SO_4)_2$  (mit  $M^I$  gleich K oder Tl) hergestellt werden, wobei es sich wahrscheinlich um Distorsionsisomere handelt. Keine Modifikationen dieses Typs konnten jedoch für  $M_2^I Ni(SO_4)_2$  erhalten werden.

Резюме — Представлены результаты исследования соединений  $M_2^I M^{II}(SO_4)_2$ , где  $M^I$  — K, Rb, Cs и Tl, а  $M^{II}$  — Cu и Ni, в интервале температур от комнатной до температуры плавления. Все исследованные соединения показали эндо- и экзотермические отклонения на ДТА-кривых, что вызвано фазовыми переходами, сопровождающиеся изменением цвета. Для соединений  $M_2^I Cu(SO_4)_2$ , где  $M^I$  — K или Tl, при лабораторной температуре может быть получено несколько модификаций, которые, вероятно, являются нарушенными изомерами. Однако, в случае соединений  $M_2^I Ni(SO_4)_2$  модификации подобного типа не были получены.