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

X Double Cu(II) and Ni(II) selenates, their structure and thermal decomposition

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The structures of compounds $M^I_2M^{II}(SEO_4)_2$ (M^I = K, Tl; M^{II} = Cu and Ni), were studied using IR, electronic and EPR spectra. The results indicate a hexacoordination of both central atoms, and a bridging function of selenato groups, the mode of their coordination varies with M^I and M^{II}. The compound $Tl_2Cu(SeO_4)_2$ was prepared also in the amorphous glassy form, although with partial decomposition. It is presumed that in the homogeneous smaragd-green material —Cu—O—Cu—, —Cu—$OSeO_2$—Cu— and —Cu—$OSeO_3$—Cu— bridges are present simultaneously. The course of the thermal decomposition of the studied compounds depends on the nature of the M^I and M^{II} cations. According to powder X-ray patterns, the decomposition products do not contain individual oxides. Nearly complete removal of selenium was observed in the decomposition of hydrated ammonium double selenates of Ni(II) and Cu(II).

In our previous work we have found that compounds $M_2M^{II}(SO_4)_2$ have interesting chemical and physical properties [1, 2]. They are, for example, thermochromic, and exhibit semiconductivity. The amorphous glassy form of $Tl_2Cu(SO_4)_2$ is a semiconductor with electronic conductivity without appreciable contribution of ionic conduction to the transport of charge [3]. It was therefore of interest to find out what are the properties of the analogous selenate double salts. Here we present the results of the study of the compounds $M^I_2M^{II}(SeO_4)_2$, where M^I = K, Tl and M^{II} = Cu, Ni, regarding mainly their spectral properties and the possibility of the formation of amorphous glassy forms. The thermal decomposition of these compounds and of $(NH_4)_2[M^{II}(H_2O)_6](SeO_4)_2$ was studied because the double selenates are thermally less stable than the corresponding double sulphates and during the preparation of the glassy phases from the melts decomposition could take place. This study was also undertaken in order to answer the question of the possibility of selenium removal from the compounds as well as the question of the formation of the oxide mixtures, or double oxides as a final product of the decomposition.

Experimental

All the compounds studied were prepared by careful dehydration of the complexes $M^I_2[M^{II}(H_2O)_6](SeO_4)_2$, which were synthesized according to [4]. The ammonium compounds were used without dehydration. The content of M^{II} in the compounds prepared was found by complexometric titration and the results are summarized in Table 1. The analytical composition of the decomposition intermediates and products was established using an ICP 3510 spectrometer.

IR and electronic spectra of the studied compounds were measured in nujol mulls, using Specord IR–75 (Carl Zeiss, Jena), Specord M–40 (Carl Zeiss, Jena) and Unicam SP–700 spectrophotometers. The ESR spectra were gained on the Bruker spectrometer in the X-band with "Varian strong peak" as inner standard ($g = 2.0028$). The thermal decomposition of the compounds was carried out using a Derivatograph OD–102 (MOM Budapest). The sample weight was 70–100 mg in air atmosphere, heating rate ~ 10 deg min^{-1}, reference material α-Al_2O_3. The temperature was measured with Pt, Pt–Rh thermocouples.

Results and discussion

a) Spectral properties of the compounds studied

The dehydration of compounds $M_2[M^{II}(H_2O)_6](SeO_4)_2$ leads to the formation of anhydrous double salts $M_2M^{II}(SeO_4)_2$ which are pale blue when M^{II} = Cu and yellow when M^{II} = Ni. In contrast to the analogous sulphates, it is not possible to prepare double selenates from the melts of parent $M^I_2SeO_4$ and $M^{II}SeO_4$. It is also impossible to prepare anhydrous ammonium double selenates without partial decomposition. The crystal structures of anhydrous $M^I_2M^{II}(SeO_4)_2$ have not yet been elucidated, of the hexahydrates the crystal structures for $M^I = NH_4$ and K, M^{II} = Cu and $M^I = NH_4$, M^{II} = Ni [5–7] have been determined. The electronic spectra of both series of dehydrated compounds indicate close resemblance of the coordination polyhedra structures between hexahydrates and anhydrous $M^I_2M^{II}(SeO_4)_2$. It can be therefore concluded that the central atoms Cu and Ni are hexacoordinated and the selenato groups, bonded to them through their oxygen atoms form bridges between the neighbouring Cu^{II} and Ni^{II} atoms, respectively. The replacement of water molecules by selenato groups is reflected in the electronic spectra of studied compounds by the red shift of the $\tilde{\nu}_{max}(d-d)$ (Table 2). This is consistent with the lower ligand field strength of the selenato groups when compared with water molecules, but can be interpreted in terms of the reduction of the deformation of the Cu^{II} coordination polyhedra, as well. However, the changes in the electronic spectra of double selenates, connected with their dehydration are less pronounced than it was the case with the analogous sulphates [1]. Besides, the values of $\tilde{\nu}_{max}(d-d)$ for double Cu^{II} sulphates were shifted to the higher energies after their dehydration [2]. It can be concluded that the differences between the Cu^{II} coordination polyhedra in hydrated and dehydrated double copper selenates are very small. This is confirmed by the ESR spectra of $Tl_2Cu(H_2O)_6(SeO_4)_2$ and $Tl_2Cu(SeO_4)_2$ as shown in Fig. 1. Both spectra are axial, with $g_\perp = 2.15_3$ and $g_\| = 2.21_2$ for the hexahydrate, for the $Tl_2Cu(SeO_4)_2$ the values $g_\perp = 2.15_4$ and $g_\| = 2.21_6$ were found.

The coordination of selenato groups to the Cu^{II} or Ni^{II}, respectively lowers the T_d symmetry of non-coordinated SeO_4^{2-} to C_{3v} or C_{2v} symmetry of coordinated

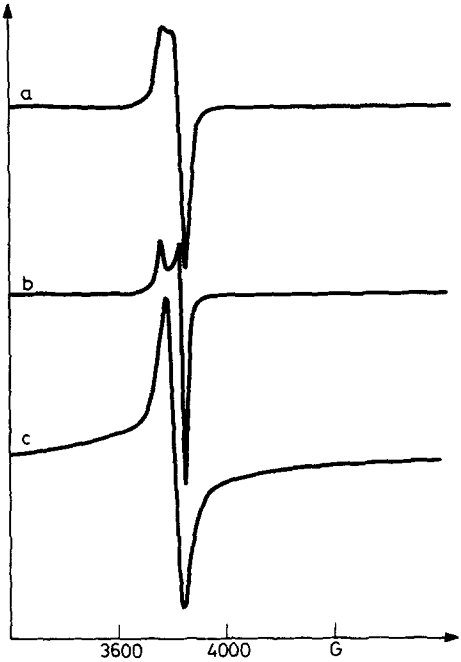

Fig. 1 The ESR specta of $Tl_2[Cu(H_2O)_6](SeO_4)_2$ (a); microcrystalline $Tl_2Cu(SeO_4)_2$ (b); glassy $Tl_2Cu(SeO_4)_n$ (c). Spectrum (c) was taken at 10_x higher sensitivity of the apparatus

selenates. The lower symmetry of SeO_4^{2-} in the anhydrous compounds, compared with their hexahydrates is reflected in the IR spectra. However, in the last compounds the effective symmetry of selenato groups is lower than T_d due to hydrogen bond formation. This is documented by the appearance of $\tilde{\nu}_1(SeO_4)^{2-}$ vibration in the IR spectra, although for T_d symmetry it is allowed only in the Raman spectra. Nevertheless, the $\tilde{\nu}_3$ vibration is not split in the spectra of hexahydrates and the $\tilde{\nu}_4$ was found to be split only for $Tl_2[Cu(H_2O)_6](SeO_4)_2$. For this compound also the $\tilde{\nu}_1$ absorption band was strong, therefore it can be concluded that the strongest hydrogen bonds are present in this compound. For dehydrated salts (Table 3) the $\tilde{\nu}_3$ vibration is three times split for $K_2Cu(SeO_4)_2$, which indicates the C_{2v} symmetry and bidentate mode of the selenato group coordination [8]. The corresponding splitting of $\tilde{\nu}_4$ was not found in our spectra, probably they lie below the measured range, or they are too weak. All other dehydrated compounds exhibit only double splitting of the $\tilde{\nu}_3$ vibration, which would suggest C_{3v} symmetry and monodentate mode of SeO_4^{2-} coordination [8]. However, considering the composition of the compounds and the electronic spectrum data, we assume that these symmetries are achieved in different manners, in $K_2Cu(SeO_4)_2$ being all four oxygen atoms of a selenato group coordinated (2+2), in all other compounds probably three oxygen atoms are coordinated from each SeO_4^{2-} group.

b) *Thermal decomposition of the compounds studied*

The heating of the compounds leads to different changes in the samples, depending on the nature of the cations M^I and M^{II}. The final weight loss corresponds to the formation of selenites or oxides of the atoms present. It was of interest to see whether the initial structure of the compounds influences the stoichiometry of the decomposition and the character of the product.

The thermal decomposition of $K_2Cu(SeO_4)_2$ proceeds in several steps (Fig. 2), which are all endothermic. At the beginning of the decomposition traces of water (~2%) are evolved. After that the slow decomposition to the $K_2Cu(SeO_3)_2$ takes place. This reaction is finished at ~400 °C and is accompanied by four endothermic peaks on the DTA curve. In the following two decomposition steps the weight loss corresponds to the decomposition of one SeO_3^{2-} group. At ~600° dark grey sintered material is formed. Chemical analysis of the decomposition intermediates and product, obtained under isothermal conditions confirm the decomposition stoichiometry as follows (Table 4):

$$K_2Cu(SeO_4)_2 \xrightarrow{-O_2} K_2Cu(SeO_3)_2 \xrightarrow{-0.7\ SeO_2} K_2O\cdot CuO\cdot 1.3SeO_2$$
$$\xrightarrow{-0.3\ SeO_2} K_2O\cdot CuO\cdot SeO_2$$

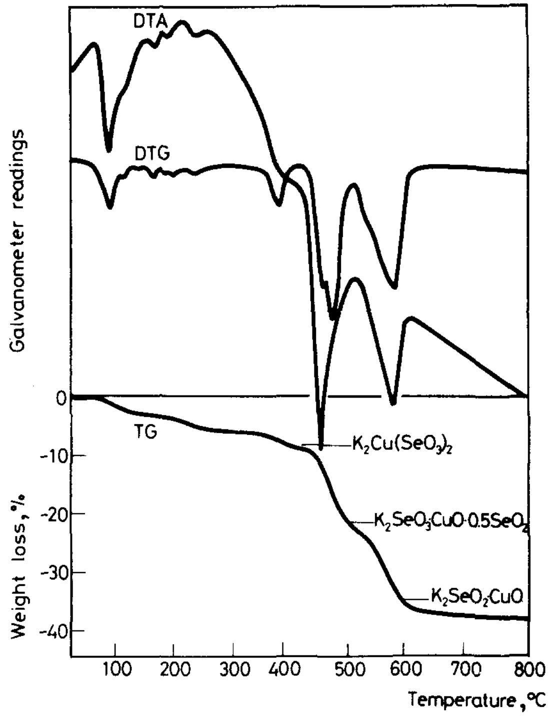

Fig. 2 The course of the thermal decomposition of $K_2Cu(SeO_4)_2$

The decomposition stoichiometry of $K_2Cu(SeO_3)_2$ differs under these conditions from that indicated by the TG curve of $K_2Cu(SeO_4)_2$ (Fig. 2). The product is not a simple mixture of the components, because microscopic observation showed no white particles of SeO_2 or K_2SeO_3. The course of the thermal decomposition of $K_2Cu(SeO_4)_2$ indicates the presence of nonequivalently bonded selenato groups. No endothermic peak corresponding to the melting of the sample was observed.

The decomposition of $Tl_2Cu(SeO_4)_2$ begins at 300° (Fig. 3). The weight loss is slow, and becomes faster at temperatures higher than 450°. The decomposition proceeds with different rates during further heating, but no well defined plateaus on the TG curve are formed. Under the decomposition conditions applied the melting of the sample took place at 490° (heating rate 9 deg min^{-1}). At this temperature, however, considerable decomposition occurred, the weight loss was ~7%. Using lower heating rate (3 deg min^{-1}) in an electrical oven, the sample melted at 420°. The quenching of the melt resulted in the formation of a smaragd green homogeneous transparent glassy material. According to chemical analysis (Table 5) its composition is $Tl_2Cu(SeO_4)_n$, where n is always smaller than 2. The nominal value of n depends on the duration of heating and on the temperature and its value

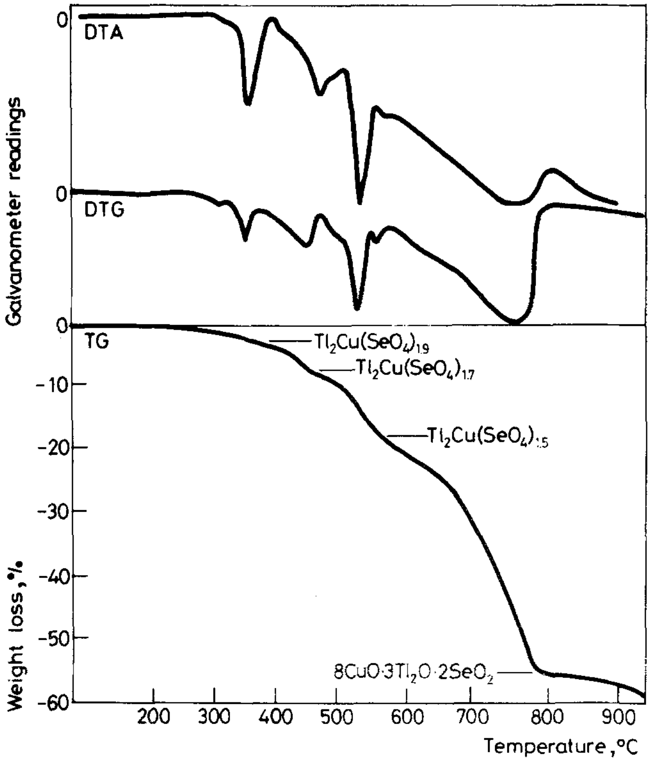

Fig. 3 The course of the thermal decomposition of $Tl_2Cu(SeO_4)_2$

varies between 1.75 and 1.5. The ESR spectrum of the glassy product is isotropic (Fig. 1c) with $g_{iso} = 2.18_0$ and the intensity of the signal is approximately 10 times lower than for microcrystalline $Tl_2Cu(SeO_4)_2$. The found g_{iso} value and the $g_\perp$ and $g_\parallel$ values of $Tl_2Cu(SeO_4)_2$ correspond to the equation

$$g_{iso} = 1/3(2g_\perp + g_\parallel)$$

We suppose therefore that the presence of considerable exchange interaction and/or greatly misaligned Cu^{II} coordination polyhedra could be responsible for this change. The lowering of the signal intensity could be connected with the actual lowering of the concentration of the ESR active compound. In the IR spectrum of this sample were found absorption bands corresponding to the $\tilde{\nu}_1$, $\tilde{\nu}_3$ and $\tilde{\nu}_4$ vibrations of SeO_4^{2-} (820, 840 and 460 cm^{-1}), $\tilde{\nu}$(Cu—O) at 530 cm^{-1} and a broad band between 650 and 740 cm^{-1}, corresponding to the $\tilde{\nu}_3$ vibration of SeO_3^{2-}, as well as a shoulder at 800 cm^{-1}, which can be attributed to the $\tilde{\nu}_1$ vibration of the selenite group [8]. We conclude, therefore, that the enhanced exchange interaction is due to the —Cu—O—Cu— bridge formation. Simultaneously bridges —Cu—

OSeO$_2$—Cu— and —Cu—OSeO$_3$—Cu— are present. According to the chemical analysis of the decomposition intermediates (Table 5), gained at higher temperatures, the oxygen content decreases more slowly than it was found for the potassium salt. The formation of $Tl_2Cu(SeO_3)_2$ was not analytically confirmed. The structural changes taking place during the decomposition are demonstrated in Fig. 4. The formation of individual oxides, however, was not confirmed in any decomposition step. This is true also for the final product, gained at 850°, with the somewhat puzzling composition 3 $Tl_2O \cdot 8\ CuO \cdot 2\ SeO_2$ (Table 5).

The comparison of our results with the data on the decomposition of $Cu(SeO_4) \cdot 5H_2O$ [10, 11] shows that outer-sphere cations influence markedly the

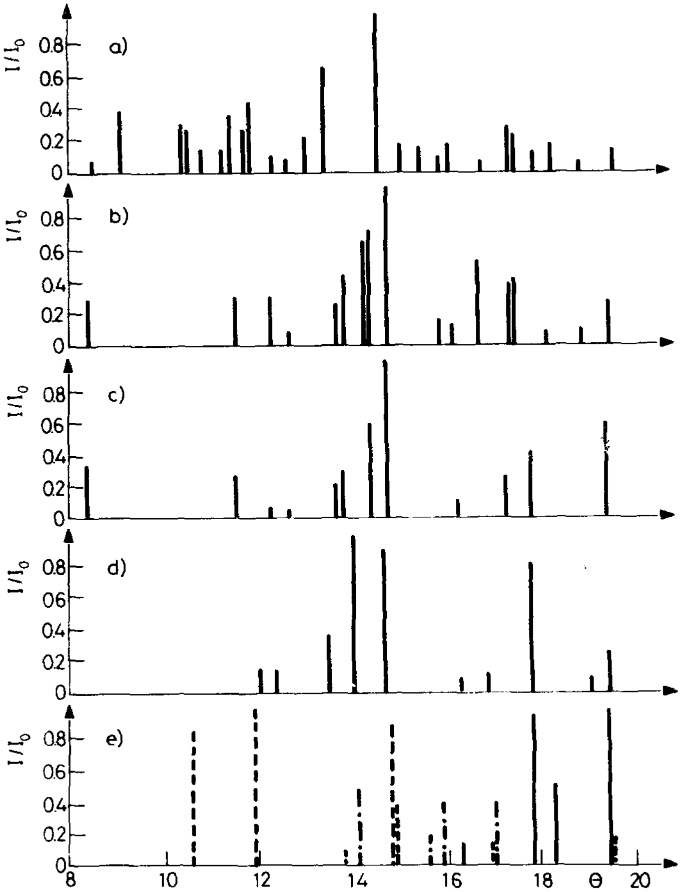

Fig. 4 Powder X-ray patterns of $Tl_2Cu(SeO_4)_2$ (a) and of its decomposition intermediates, gained at 480° (b), 560° (c) and 850° (d) in domparison with the patterns of CuO (——), Tl_2O (—·—·—) and SeO_2 (- - -) (e)

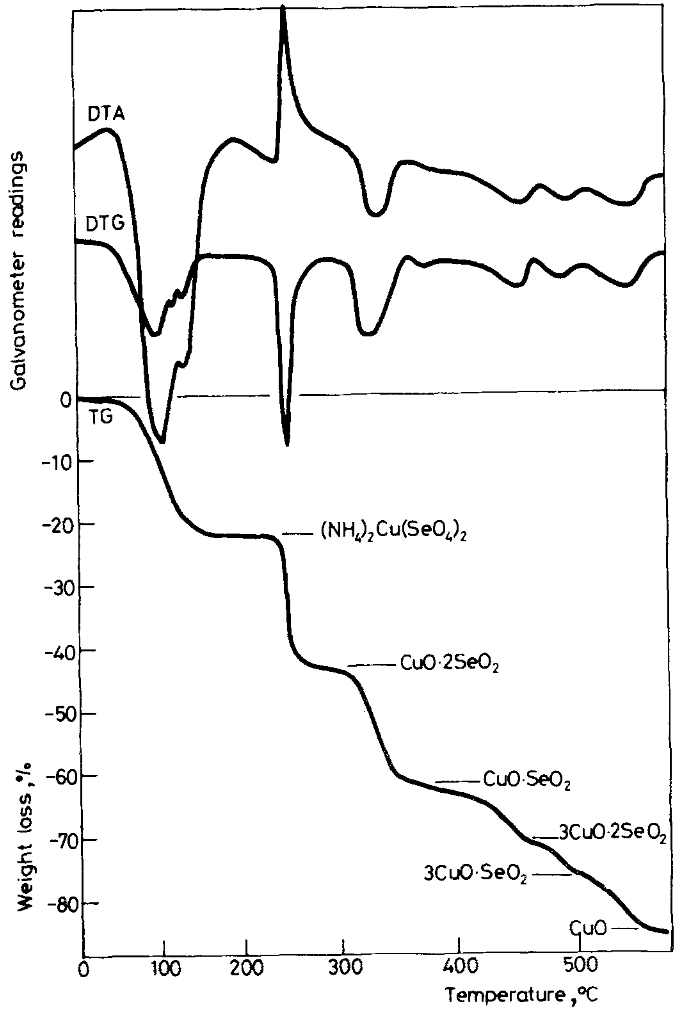

Fig. 5 The course of the thermal decomposition of $(NH_4)_2[Cu(H_2O)_6](SeO_4)_2$

thermal stability of the studied compounds, especially the reduction of Se(VI) to Se(IV) and the removal of SeO_2. In the decomposition product of copper(II) selenium hydrate no selenium was found at 700° [10]. Therefore we have studied the thermal decomposition of $(NH_4)_2[Cu(H_2O)_6](SeO_4)_2$. The weight loss corresponds in the first decomposition step to the dehydration (calc. 21.87%, found 22%) of the sample. The decomposition goes on slowly, until the temperature reaches 240°, then a sudden exothermic decomposition takes place. The weight loss corresponds to the formation of $CuO \cdot 2\ SeO_2$. Further decomposition leads to the formation of $CuO \cdot SeO_2$, $3CuO \cdot 2SeO_2$ (copper calc. 41.38%, found 40.97%; selenium calc. 34.29%, found 33.72%) as pale brown-green sintered body, and $3CuO \cdot SeO_2$. The decomposition is finished at 560°, copper(II) oxide containing traces of selenium being the product (Cu(II) calc. 79.88%, found 78.24%, Se found 1.1%). The decomposition of $(NH_4)_2[Cu(H_2O)_6](SeO_4)_2$ (Fig. 5) can be then described as follows:

$$(NH_4)_2[Cu(H_2O)_6](SeO_4)_2 \rightarrow (NH_4)_2Cu(SeO_4)_2 \rightarrow CuO \cdot 2SeO_2 \rightarrow$$

$$\rightarrow CuO \cdot SeO_2 \rightarrow 3CuO \cdot SeO_2 \rightarrow 3CuO \cdot SeO_2 \rightarrow CuO$$

The thermal decomposition of nickel(II) compounds, $M^I_2Ni(SeO_4)_2$, differ significantly from that of copper(II) compounds. However, the course of their decomposition depends on the outer sphere cation present as well. The compound $K_2Ni(SeO_4)_2$ is stable up to ~460° (Fig. 6). At higher temperatures it decomposes in one step into $K_2O \cdot NiO \cdot SeO_2$ (weight loss calc. 33.81%, found 33.9%) and only very slow further weight loss was observed between 680 and 1000°. Two small endothermic peaks, corresponding to phase transitions were registered on the DTA curve—at ~340 and ~460°. The last one could be attributed to the melting of the sample. The decomposition follows immediately, so the preparation of a glassy

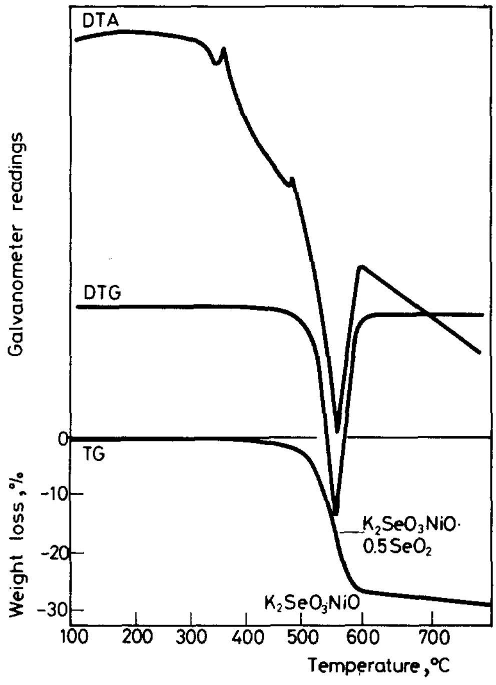

Fig. 6 The course of the thermal decomposition of $K_2Ni(SeO_4)_2$

phase is impossible. The decomposition of $Tl_2Ni(SeO_4)_2$ starts at ~530° (Fig. 7). In the first decomposition step the $Tl_2O \cdot NiO \cdot SeO_2$ is formed (weight loss calc. 18.98%, found 18.9%). This compound is thermally unstable and decompose immediately. The weight loss corresponds to the formation of $NiO \cdot SeO_2$ (calc. 75.4%, found 74%). On the DTA curve of this compound, two small endotherms appear, anyway the melting begins at ~660° after considerable decomposition of the sample. The quenching of the melts produces a brownish glassy material, but the recrystallization is very quick. The course of the thermal decomposition of $(NH_4)_2[Ni(H_2O)_6](SeO_4)_2$ is quite different. The product of the dehydration is unstable (Fig. 8) and decomposes, giving no well defined intermediates, to a mixture of Ni and NiO. The TG curve indicates the formation of $NiO \cdot 2SeO_2$ and $NiO \cdot SeO_2$, but we did not succeed in the preparation of intermediates.

The influence of the outer sphere cations, NH_4^+, K^+ and Tl^+ on the course of the thermal decomposition of both Cu^{II} and Ni^{II} double selenates is evident from our results. The role of outer sphere cations, however, is different for Cu^{II} and Ni^{II} compounds, respectively. In the case of nickel complexes these cations influence mainly the decomposition temperatures, the stoichiometry is controlled by the properties of M^I oxides or selenates. For copper(II) selenates we have to presume that the size and electrical charge density on the M^1 will affect the symmetry of the

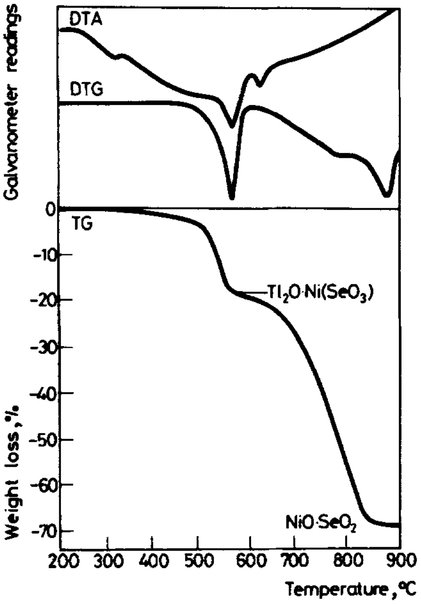

Fig. 7 The course of the thermal decomposition of $Tl_2Ni(SeO_4)_2$

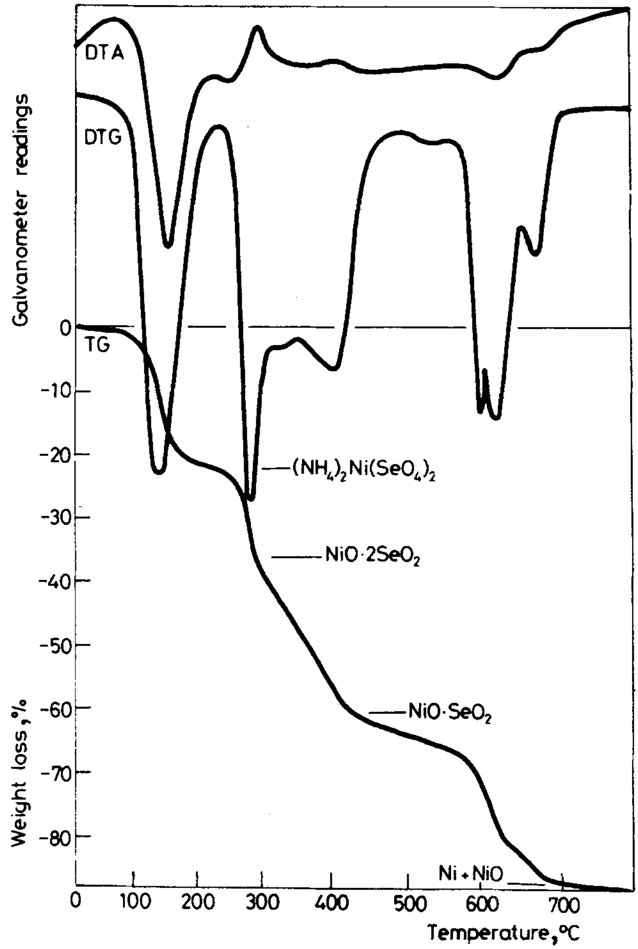

Fig. 8 The course of the thermal decomposition of $(NH_4)_2[Ni(H_2O)_6](SeO_4)_2$

plastic [12] Cu^{II} coordination polyhedra, as it was found for numerous compounds of this type. We conclude that the different binding of SeO_4^{2-} groups, indicated by the respective IR spectra, is responsible for the variability of decomposition stoichiometries of compounds $M^I_2Cu(SeO_4)_2$.

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Zusammenfassung — Mittels IR-, Elektronen- und EPR-Spektren wurden die Strukturen der Verbindungen $M^I_2M^{II}(SeO_4)_2$ mit M^I = K und Tl sowie M^{II} = Cu and Ni bestimmt. Die Ergebnisse zeigen eine Hexakoordination beider Zentralatome und eine Brückenfunktion der Selenatgruppen, deren Koordination sich mit M^I und M^{II} ändert. Die Verbindung $Tl_2Cu(SeO_4)_2$ wurde, wenn auch unter geringen Zerfalles, auch in einer amorphen Glasform hergestellt. Es wird angenommen, daß in den Smaragdgrün-Stoffen gleichzeitig —Cu—O—Cu—, —Cu—$OSeO_2$—Cu— und —Cu—$OSeO_3$—Cu—Brücken vorkommen. Der Verlauf der thermischen Zersetzung der untersuchten Verbindungen hängt von der Art der M^I und M^{II}-Kationen ab. In Bezugnahme auf Röntgenpulverdiffraktionsaufnahmen enthalten die Zersetzungsprodukte keine getrennten Oxide. Beim Zerfall von hydratierten Ammoniumdoppelselenaten von Ni(II) und Cu(II) wurde eine fast vollständige Abgabe von Selen beobachtet.

Резюме — Структура смешанных селенатов типа $M^I_2M^{II}(SeO_4)_2$, где M^I — калий, таллий, а M^{II} — медь и никель, была изучена методами ИК- и ЭПР спектроскопии, а также электронными спектрами поглощения. Полученные данные указывают на шестикоординационный характер обоих центральных атомов, мостиковый характер селенато-групп и тип их координации по отношению к M^I и M^{II}. Соединение $Tl_2Cu(SeO_4)_2$ было получено также и в аморфной стеклообразной форме, хотя и с частичным разложением. Предположено, что в синезеленом комплексе одновременно присутствуют мостиковые связи —Cu—O—Cu—, —Cu—$OSeO_2$— Cu и —Cu—$OSeO_3$—Cu—. Процесс термического разложения изученных соединений зависит от природы катионов M^I и M^{II}. Согласно данным порошкового рентгеноструктурного анализа, продукты разложения не содержат отдельных оксидов металлов. При разложений двойных аммоний селенатов никеля и меди наблюдалось почти полное удаление селена.