Journal of Thermal Analysis, Vol. 12 (1977) 91–95

HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES, XII.

PROBLEMS IN CORRELATING THE STRUCTURES AND THE STEPWISE THERMAL DECOMPOSITION REACTIONS OF COORDINATION COMPOUNDS

E. JÓNA and T. ŠRAMKO

Department of Inorganic Chemistry, Slovak Technical University, 880 37 Bratislava, ČSSR

(Received November 16, 1976)

The possibilities of correlating the structures and the stepwise thermal decomposition reactions of solid coordination compounds are discussed. The starting compounds were $Ni(NCS)_2(py)_4$, (py = pyridine), $CuSO_4 \cdot 5\,H_2O$ and $NiSO_4 \cdot 7\,H_2O$, for which correlations of the above type were studied. It was found that the structural data on the initial compound alone are not sufficient to predict the stepwise course of the thermal decompositions of coordination compounds.

Though the thermoanalytical study of crystalline compounds has long formed a part of the research into coordination compounds, up to now the literature contains only a few papers [1–4] in which the authors have tried to elucidate the stepwise character of thermal decomposition reactions (the stoichiometry of decomposition) of coordination compounds.

The different results of thermal analysis of coordination compounds, obtained by changing the experimental conditions [5], show only part of the given problem (some of the intermediates are not always identified). The other part covers the problem of whether it is possible to predict the stepwise course of thermal decomposition reactions from the structural data of the initial compound.

The object of the present paper is to discuss the possibilities of a correlation between the structure and the stepwise character of the thermal decomposition reactions for nickel(II) and copper(II) coordination compounds with volatile N- and O-molecule ligands.

Discussion

Most nickel(II) compounds with heterocyclic nitrogen ligands are of the type NiX_2A_4 (X = anion ligand, A = monodentate molecule ligand) and have the molecular structure $[NiX_2A_4]$. From this group of compounds the complex $Ni(NCS)_2$ (pyridine)$_4$ was taken as the starting substance, since its stoichiometry of decomposition is known [1, 2]:

$$Ni(NCS)_2py_4\ (s):\ 4 \rightarrow 2,\ 2 \rightarrow 0, \qquad (1)$$

as also its molecular structure is known [6]. The four pyridine molecules are in square coordination to the Ni(II) atom (the internuclear distance Ni–N(py) being=

= 2.03 Å), and with the two NCS groups form a distorted octahedron (Ni – N(NCS) = 2.12 Å). This information does not indicate, however, that the two pyridine molecules escaping in the first step (4 → 2) are less strongly bonded than the other two. Only the infrared spectra, viz. the differences in the γ(C – C) and γ(C – H) deformation vibrations of the pyridine molecules in the starting complex and the intermediate, indicated that the four pyridine molecules are not quite equivalent. There are fine structural differences concerning rather the region of the secondary coordination sphere (e.g. mutual interactions of structural units in the crystal), but this requires a knowledge of the full crystal structure of the starting compound. We, therefore, oriented our further studies to the hydrates $CuSO_4 \cdot 5\,H_2O$ and $NiSO_4 \cdot 7H_2O$ for which complexes these data are known.

Four-fifths of the water molecules of the pentahydrate of copper(II) sulfate form a coordination square around the Cu(II) atom, the coordination sphere of which is completed by two oxygen atoms from the SO_4^{2-} anions, in the axial positions to a distorted octahedron. Each water molecule from the remaining 1/5 is bonded through hydrogen bridges to two coordinated water molecules and to two oxygen atoms from different SO_4^{2-}. The X-ray structural data show [7] that the water molecules in the structure of $CuSO_4 \cdot 5\,H_2O$ are not equivalent. They may be divided into three groups: 2/5 of them form two hydrogen-bonds with the sulfate anions in addition to the coordinative bonds, i.e. each of the mentioned water molecules forms altogether three bonds. 2/5 of the water molecules belong to the second group; they also form a hydrogen-bond with the molecules of the lattice water, in addition to the three bonds already mentioned in the first group, i.e. each of the second group molecules of water forms 4 bonds. As already stated, the molecules of lattice water form 4 hydrogen bonds. Starting from the known stoichiometry of thermal decomposition:

$$CuSO_4 \cdot 5\,H_2O\ (s) : 5 \rightarrow 3,\ \ 3 \rightarrow 1,\ \ 1 \rightarrow 0 \qquad (2)$$

it appears acceptable [3] that the two water molecules of the first group (forming only three bonds) are evolved on heating in the first step (5 → 3). The water mole-

Table 1

Bonding possibilities of the H_2O molecules in $NiSO_4 \cdot 7H_2O$

Denotation	Number of bonds	Number and type of bonding interactions
A	3	Ni^{II}–, SO_4^{2-} <
B	3	Ni^{II}–, $2SO_4$–
C	3	Ni^{II}–, $2SO_4$–
D	3	Ni^{II}–, H_2O–(*F*), H_2O– (*G*)
E	4	Ni^{II}–, $2SO_4^{2-}$, H_2O– (*G*)
F	4	Ni^{II}–, SO_4^{2-}, H_2O– (*D*), H_2O– (*G*)
G	4	SO_4^{2-}, H_2O– (*D*), H_2O– (*E*), H_2O– (*F*)

cules of the second group, coordinated by four bonds, need more energy to be liberated than do those of group (1) and escape in the second step (3 → 1), while the lattice water molecules are expected to be evolved in the third step. The identity of the water molecules evolved in the three steps, however, was not proved in [3]. In the complex $NiSO_4 \cdot 7\ H_2O$ the water molecules show even more varied bonding possibilities, as listed in Table 1.

The TG curve of $NiSO_4 \cdot 7\ H_2O$ shows [3] four identifiable dehydration steps and its decomposition stoichiometry may be expressed by the scheme

$$NiSO_4 \cdot 7\ H_2O\ (s) : 7 \rightarrow 6,\ 6 \rightarrow 3,\ 3 \rightarrow 1,\ 1 \rightarrow 0 \qquad (3)$$

According to [3] these steps represent the following sequence:

1. 1/7 of the water molecules, denoted as "*A*", representing the most weakly bonded molecules;
2. 3/7 of the water molecules ("*B*, *C*, *D*"), each of which has to break bonds to three different partners;
3. 2/7 of the water molecules ("*E*, *F*"), breaking four bonds each; and
4. the molecules of lattice water ("*G*")

This interpretation cannot be accepted as satisfactory for several reasons:

a) If only the number of bonding interactions is considered, a two-step stoichiometry of thermal decomposition may be expected (7 → 3, 3 → 0).

b) Considering only the types of bonding interactions (6/7 of coordinated water molecules and 1/7 lattice water molecules) the stoichiometry of thermal decomposition could exhibit a minimum of two dehydration steps (7 → 1, 1 → 0) and a maximum of six (7 → 6, 6 → 4, 4 → 3, 3 → 2, 2 → 1, 1 → 0).

c) By the escape of 1/7 of the water molecules the α-modification of $NiSO_4 \cdot 6\ H_2O$ is formed, containing the coordination species $[Ni(H_2O)_6]^{2+}$ [7], and thus it has no structural water molecules at all.

d) In addition, several authors [9–12] support the following stoichiometry of thermal decomposition:

$$NiSO_4 \cdot 7\ H_2O\colon\ 7 \rightarrow 6\alpha,\ 6\alpha \rightarrow 6\beta,\ 6\beta \rightarrow 4,\ 4 \rightarrow 1,\ 1 \rightarrow 0. \qquad (4)$$

Analogously, the explanation of the stoichiometry of thermal decomposition found in the thermolysis of $CuSO_4 \cdot 5\ H_2O$ [3] can not be accepted as satisfactory either.

It follows from the above that in searching for correlations between thermal and structural data, it is necessary to analyze every reaction step separately, i.e. the full crystal structures of the different intermediates must be known (if the process exhibits several steps). An analogous situation is to be found in studying the mechanisms of substitution reactions of coordination compounds in solution, where every step of ligand substitution also has to be studied separately.

Conclusions

One of the significant problems of the chemistry of coordination compounds in solution is the stabilization of coordination species with a heterogeneous coordination sphere, during the substitution reactions. In the solid state the influence of the crystal structure, in addition to other factors, can result in the complex species known in solution not being stabilized in the solid state. Thus, the structural features of coordination compounds play an important part in thermal decomposition reactions with linear temperature increase and they can affect their stoichiometry (number of defined intermediates).

In addition to the structural factors, transport phenomena also play an important part here, above all, the diffusion of volatile ligands from the initial solid phase into the environment; they can cause the formation of a different number of intermediates, depending on the thermal decomposition conditions. A noteworthy example in this respect is the complex $Ni(NCS)_2(3\text{-methylpyridine})_4$, for which we found [13], depending on the experimental conditions, a thermal decomposition stoichiometry of three steps (for usual experimental conditions), one of two steps (microbalance), and also a one-step removal of the ligands (vacuum). It follows from the above that the structural data on the starting compound alone do not allow one to determine the stepwise character, and to predict the number of steps in the thermal decompositions of coordination compounds.

References

1. G. Liptay, Kémiai Közlemények, 32 (1969) 389.
2. G. Liptay, K. Burger, E. Papp-Molnár, S. Szebeni and F. Ruff, J. Inorg. Nucl. Chem., 31 (1969) 2359.
3. S. Sarig, Thermochim. Acta, 7 (1973) 297.
4. E. Jóna, T. Šramko and J. Gažo, J. Thermal Anal., 7 (1975) 551.
5. T. Šramko, E. Jóna and G. Liptay, Proceedings of the 5th Conference on Coordination Chemistry, p. 251. Smolenice—Bratislava 1974.
6. M. A. Poraj-Koshits and A. C. Antziskhina, Kristallografiya 3 (1958) 686.
7. R. C. Evans, An Introduction to Crystal Chemistry, p. 298. Cambridge University Press, London 1966.
8. C. A. Beevers and H. Lipson, Z. Krist., 83 (1932) 123.
9. R. Rabbering, J. Wanrooy and A. Scuff, Thermochim. Acta, 12 (1975) 57.
10. H. Chihara and S. Seki, J. Chem. Soc. Japan, 26 (1953) 88.
11. S. Caillère and T. Pobeguin, Bull. Soc. Chim. Franc., Minéral. Crist., 85 (1962) 48.
12. G. Pannetier, J. M. Brégeault, C. Laconturier and G. Djega-Mariadasson, Bull. Soc. Chim. France, (1964) 1141.
13. T. Šramko, G. Liptay and E. Jóna, J. Thermal Anal., (in press).

Résumé — On discute les possibilités d'établir une corrélation entre la structure et les réactions de décomposition thermique graduelle de composés de coordination solides. Les composés de départ étaient les suivants: $Ni(SCN)_2(py)_4$, (py = pyridine), $CuSO_4{\cdot}5\,H_2O$ et $NiSO_4{\cdot}7\,H_2O$ pour lesquels on a effectué le calcul des corrélations du type étudié. On a trouvé que les données relatives à la structure du composé de départ ne suffisaient pas pour prédire les étapes de la décomposition thermique des composés de coordination.

ZUSAMMENFASSUNG — Die Möglichkeiten der Korrelierung der Struktur und der stufenweisen thermischen Zersetzungsreaktionen fester Koordinationsverbindungen werden erörtert. Die Ausgangssubstanzen waren $Ni(NCS)_2(py)_4$, (py = Pyridin), $CuSO_4 \cdot 5\ H_2O$ und $NiSO_4 \cdot 7\ H_2O$, für welche Korrelationsberechnungen des untersuchten Typs durchgeführt wurden. Es wurde festgestellt, daß die Strukturangaben der Ausgangsverbindung allein nicht ausreichen, um den stufenweisen Verlauf der thermischen Zersetzung von Koordinationsverbindungen zu beschreiben.

Резюме — Обсуждены возможности коррелирования структуры и реакций ступенчатого термического разложения твердых координационных соединений. Исходными веществами были: $Ni(NCS)_2(py)_4$, (py = пиридин), $CuSO_4 \cdot 5H_2O$ и $NiSO_4 \cdot 7H_2O$, для которых и были выполнены корреляции такого типа. Найдено, что наличие только структурных данных об исходном соединении не является достаточным, чтобы установить ступенчатый характер термического разложения координационных соединений.