

Study of the effect of the structure differences of α -, β -, and γ -modifications of diammineoxalatocopper(II) complexes on their reactivity with gaseous and liquid ammonia

H. LANGFELDEROVÁ, J. GARAJ, and J. GAŽO

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

Received 21 January 1974

The aim of the present work is the investigation of the influence of structural differences of α -, β -, and γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ on the formation of $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ in reactions between the afore-mentioned substances with gaseous and liquid ammonia. It has been found that, under various conditions, each modification forms $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ with both gaseous and liquid ammonia. In these reactions three different modifications of $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ are formed. The preparation of the complex $\text{Cu}(\text{NH}_3)_6(\text{C}_2\text{O}_4)$ was vainly attempted. By thermal decomposition of the modifications of $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ that modification of $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ was obtained from which the complex $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ was originally prepared. The different reaction conditions under which α -, β -, and γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ react with gaseous and liquid ammonia are discussed with relation to differences in structure of the above modifications.

As we have shown in our previous work [1], the structural differences between α -, β -, and γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$, which we regard as distorted isomers of $\text{Cu}(\text{II})$ complexes [2], strongly influenced the course of their hydrolysis. For this reason it seemed interesting to study also the reactions of the above complexes with gaseous or liquid ammonia, especially since in this way new experimental data on the influence of relatively very small differences in structure on the reactivity of complexes in heterogeneous substitution reactions may be obtained.

The reactivity of modifications of $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ with regard to ammonia was discussed in some older papers as well. Thus, according to some of them [3], α - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ does not react with gaseous [3] and liquid NH_3 [4], while the second modification known at this time reacts with gaseous NH_3 already at room temperature [3]. Data reported in literature are incomplete.

We attempted the elucidation of relations between the structure of the modifications of $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ and penta-ammine complexes which arise from them.

Experimental

The modifications of diammineoxalatocopper(II) were prepared by methods reported in literature: α - and γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ according to [3, 4] and β -modification according to [5].

The starting materials and products of the individual substitution reactions were examined by the following analytical methods: copper was determined by complexometric method, the oxalato group by manganometric, and ammonia by distillation method.

The analytical composition of modifications of $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ is reported in [1].

The composition of the penta-amminecopper(II) oxalate prepared by any of the procedures under investigation was as follows.

For $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4) \cdot (236.66)$ calculated: 26.83% Cu, 35.97% NH_3 , 37.20% C_2O_4 ; found: 26.46% Cu, 35.90% NH_3 , 37.30% C_2O_4 .

Deviations of the individual determinations from the above values did not exceed $\pm 0.1\%$.

The X-ray powder diagrams were obtained with a goniometer GON II with $\text{CuK}\alpha$ radiation. For recording the X-ray diagrams, the penta-amminecopper(II) complexes were protected by PVC wrappings. The infrared absorption spectra were measured as Nujol mulls on a Perkin—Elmer 137 spectrophotometer.

Reactions of the diammineoxalatocopper(II) with gaseous ammonia were studied under isothermal conditions in the temperature range between 20 and 30°C in the intervals of 5°C. The sample was placed in a glass reaction vessel and the required temperature was adjusted with the aid of a cooling mixture of ethanol and dry ice. To the previously tempered sample the equally tempered dried gaseous ammonia was introduced at atmospheric pressure, and every thirty minutes the analytical determination of the composition of the specimen was performed. Reactions of α -, β -, and γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ with liquid ammonia were investigated under similar experimental conditions. To the sample cooled to -33°C liquid ammonia of the same temperature was added. The excess of liquid ammonia was allowed to evaporate under the given conditions.

A start of reaction of α - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ with gaseous ammonia can be observed at the temperature of -30°C . (At higher temperatures no reaction takes place.) A substance whose composition would correspond to the formula $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ was formed after five hours. The X-ray powder diagram of α - $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ formed by the above

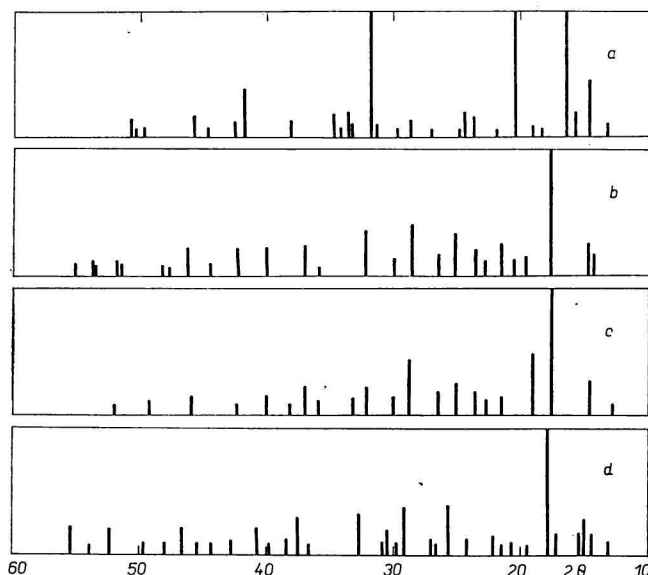


Fig. 1. X-Ray powder diagrams of $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ prepared from: a) CuC_2O_4 ; b) α - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$; c) β - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$; d) γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$.

procedure is shown in Fig. 1b. A specimen with identical composition and with identical physicochemical characteristics (X-ray powder diagram and i.r. spectrum; Table 1), was obtained by allowing the liquid ammonia to react with α - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ for 30 min at -33°C . β - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ reacts with gaseous ammonia at -10°C . A substance corresponding to the formula $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ was obtained after introducing the gaseous ammonia to β - $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ for two hours. With liquid NH_3 a substance with this composition and with identical physicochemical properties (X-ray powder diagram — Fig. 1c and i.r. spectrum) was formed virtually immediately after the reaction has started.

γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ reacts with gaseous ammonia noticeably at $+5^\circ\text{C}$, and after one-hour treatment with gaseous ammonia, $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ is formed. With liquid ammonia, γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ reacts vigorously and immediately a violet reaction product is formed, the composition of which is $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$. In this case too, γ - $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ prepared by two different methods has identical diffraction properties and i.r. spectrum (Fig. 1d, Table 1).

Table 1

Wavenumbers of the absorption bands and their correlation with i.r. spectra of the investigated penta-amminecopper(II) oxalate complexes

	Wavenumbers for the complexes [cm^{-1}]			
	I	II	III	IV
$\nu_{\text{as}}(\text{O}-\text{C}-\text{O})$	1674 1638	1653	1625	1652
$\nu_{\text{s}}(\text{C}-\text{O})$	1355 1290	1283	1290	1283
$\delta(\text{O}-\text{C}-\text{O})$	790 782	780 770	775	792
$\delta_{\text{d}}(\text{NH})$	1574	1558	1558	1563
$\delta_{\text{s}}(\text{NH})$	1250 1087	1240 1082	1240 1082	1240 1082
$\varrho(\text{NH}_3)$	759	750	748	750

I. δ - $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$; II. α - $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$;
III. β - $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$; IV. γ - $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$.

The decomposition of penta-amminecopper(II) oxalate complexes was studied at room temperature. The course of the curve of mass loss was practically identical for all three complexes. The release of ammonia is slowed down with samples in which the ratio of $\text{Cu} : \text{NH}_3 = 1 : 2.8-3.0$. Samples with such a composition react with gaseous ammonia already at room temperature.

Though the spontaneous transition from the intermediate products of the decomposition reactions to the diammineoxalatocopper(II) is rather slow (it may last even several days), we did not succeed to obtain data on their structure. The products of thermal decomposition of α -, β -, and γ -penta-amminecopper(II) oxalate complexes have an identical structure with that of the modification of $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ from which they have been prepared.

Discussion

Reactions between α -, β -, and γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ and ammonia take place only at lower temperatures. By lowering the temperature also the velocity of diffusion of NH_3 from the solid phase is decreased and the reaction equilibrium is shifted in favour of the formation of $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ since these are exothermic reactions [6].

If we take the known structure of the α -modification [7] and the assumed structure of β - [5, 8] or γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ [9], then the observed relations are understandable.

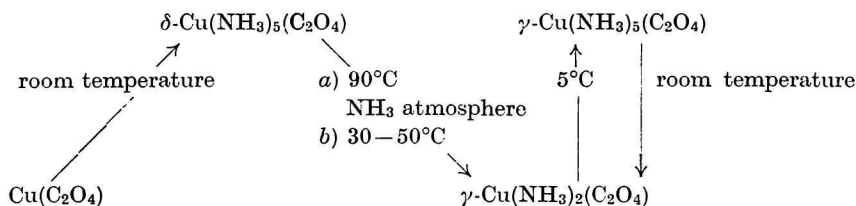
We assume that in α - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ the substitution reaction starts by substituting the oxygen atoms bonded by the weakest bonds on the so-called long coordinates by the molecules of ammonia. In this process, first a destruction of the whole three-dimensional system of bonding in the structure α - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ must take place, which, most probably, represents the greatest part of the energetic barrier in this reaction. The space arrangement of β - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ is most probably more favourable in that the substitution place is more easily accessible for the ammonia molecules, and, whereas in the α -modification there are two long bonds, in the β -modification the existence of four such bonds is supposed [5, 8].

A substantially higher reactivity of γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ when compared with that of α - and β -modifications of diammineoxalatocopper(II) complexes, with gaseous and liquid ammonia is in agreement with previous experimental results [1, 10]; this led to an assumption of a possible square planar coordination of the central atom in γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$.

The experimental results discussed in the present work are in good agreement with the i.r. spectra of the individual modifications of $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ [8], on the basis of which we may conclude that the weakest bonding $\text{Cu}-\text{O}$ occurs in the modification γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ and the strongest are in α - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$.

As it follows from the experimental results, we succeeded in preparing the complex $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ from all three modifications of diammineoxalatocopper(II) complexes by the action of both gaseous and liquid ammonia. The infrared spectra of the individual specimens show (Table 1) that in all cases $[\text{Cu}(\text{NH}_3)_5]^{2+}$ was formed [11]. The samples exhibit differences in stretching vibrations of NH groups, which is indicative of differences in the strength of the coordination of ammonia with regard to the central atom. The number and positions of the absorption bands of the oxalato groups do not agree perfectly with literature reports on the i.r. spectra of neither ionic nor covalent bonding of the oxalato group [12, 13]. By analogy with the known structures of the most of $\text{Cu}(\text{II})$ complexes we may assume that the oxalato group is linked to the central atom through the oxygen atom, occupies the sixth coordination position and thus completes the coordination of the central atom to a tetragonal bipyramidal coordination.

The structure differences between penta-amminecopper(II) oxalates are closely related to those between the modification of the diammineoxalatocopper(II) complex from which they have been prepared. This made us believe that the basic difference between penta-amminecopper(II) oxalate complexes consists in different space orientation of the oxalato group with regard to the pyramid $[\text{Cu}(\text{NH}_3)_5]$ (II). γ - $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$, which is a product of thermal decomposition of γ - $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ can be formed also by decomposition of penta-amminecopper(II) oxalate (δ) [5] prepared from $\text{Cu}(\text{C}_2\text{O}_4)$ [9], whose structure, however, is not identical with that of γ - $\text{Cu}(\text{NH}_3)_5(\text{C}_2\text{O}_4)$ (Table 1, Fig. 1). This apparent disagreement may be explained by different conditions of decomposition of both penta-ammine complexes, as it follows from the scheme:



In these relations it should be mentioned that, while the thermal decomposition of $\text{Cu}(\text{NH}_3)_6\text{Br}_2$ yields $\beta\text{-Cu}(\text{NH}_3)_2\text{Br}_2$ [14], by thermal decomposition of $\text{Cu}(\text{NH}_3)_5\text{Br}_2$ the α -modification of $\text{Cu}(\text{NH}_3)_2\text{Br}_2$ is formed, from which $\text{Cu}(\text{NH}_3)_5\text{Br}_2$ has been prepared [15].

On the basis of the above experimental results it may be concluded that the reactions start by substitution of the oxygen atom on the long coordinate in the modifications α - and $\beta\text{-Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ or, in the modification $\gamma\text{-Cu}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ by occupying the free coordination positions. Successively, NH_3 occupies further coordination positions. The penetration of the sixth molecule of ammonia into the coordination sphere of $\text{Cu}(\text{II})$ is most probably prevented by an, for this reaction, unfavourable steric position of the oxalato group.

References

- Langfelderová, H., Serátor, M., Garaj, J., and Gažo, J., *Chem. Zvesti* **28**, 180 (1974).
- Gažo, J., *Plenary Lectures of XV ICCO, Moscow 1973; Proc. of 4th Conf. on Coord. Chem.*, p. 144. Smolenice, 1974.
- Horn, D. W. and Graham, M. L., *Amer. Chem. J.* **39**, 505 (1908); cited *Gmelins Handbuch der anorganischen Chemie*, Syst. No. 60, Kupfer, Teil B, Lief. 2, p. 732. Verlag Chemie, Weinheim, 1961.
- Ephraim, F., *Ber.* **52**, 940 (1919).
- Garaj, J., Langfelderová, H., Lundgren, G., and Gažo, J., *Collect. Czech. Chem. Commun.* **37**, 3181 (1972).
- Langfelderová, H., unpublished results.
- Garaj, J., *Chem. Commun.* **1968**, 904.
- Melník, M., Langfelderová, H., Garaj, J., and Gažo, J., *Inorg. Chim. Acta* **7**, 669 (1973).
- Langfelderová, H., Garaj, J., and Gažo, J., *Chem. Zvesti* **28**, 173 (1974).
- Langfelderová, H., Mikovič, J., Garaj, J., and Gažo, J., *Thermochimica Acta* **5**, 303 (1973).
- Tomlinson, A. A. G. and Hathaway, B. J., *J. Chem. Soc. (A)* **1968**, 1905.
- Nakamoto, K., *Infrakrasnye spektry neorganicheskikh i koordinatsionnykh soedinenii.* (Infrared Spectra of Inorganic and Coordination Compounds.) P. 289. Mir, Moscow, 1966.
- Murata, H. and Kawai, K., *J. Chem. Phys.* **25**, 589 (1956).
- Gažo, J., Serátorová, K., and Serátor, M., *Chem. Zvesti* **13**, 5 (1959).
- Dunaj-Jurčo, M., Langfelderová, H., and Gažo, J., *Z. Chem.* **11**, 1268 (1971).

Translated by V. Šašková