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The Effect of High Pressure on Distortion Isomers of $CuBr_2(NH_3)_2$ and $CuCl_2(NH_3)_2$

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The effect of high pressures on isomerization of distortion isomers $CuX_2(NH_3)_2$, where X is Cl or Br, has been studied. Pressures of up to 5 GPa were applied using various kinds of equipment. X-ray diffractograms were used for identification of pressure-induced changes. Under pressure, from the monoclinic α-isomers $CuBr_2(NH_3)_2$ and $CuCl_2(NH_3)_2$, the cubic β-isomers were formed. After releasing the pressure the β-isomer $CuBr_2(NH_3)_2$ persisted for a certain time and its structure was found to be identical with that of the β-isomer prepared by chemical methods. The β-isomer $CuCl_2(NH_3)_2$ was transformed rather quickly to α-isomer on release of pressure. It was the first time that the existence of a β-$CuCl_2(NH_3)_2$ without admixtures of NH_4Cl could be demonstrated. Up till now this isomer has been known to exist in the matrix NH_4Cl.

Introduction

The coordination compounds of Cu(II) usually have a distorted coordination polyhedron. Several of these compounds form modifications which differ from each other in the mode of distortion of the coordination polyhedron of Cu(II). For this phenomenon observed in Cu(II) complexes the term distortion isomerism was coined [1, 2], and based on it the concept of plasticity of the coordination polyhedra of Cu(II) was introduced [3]. The distortion isomerism of Cu(II) complexes was theoretically explained as being based on the Jahn–Teller (or rather, pseudo-Jahn–Teller) effect by which several distorted states of the coordination polyhedron with the electron configuration d^9 of the central atom are stabilized [3].

The distortion isomers α-$CuCl_2(NH_3)_2$ and $CuBr_2(NH_3)_2$ are chain polymers in which the donor atoms form a tetragonal bipyramid. In the equatorial plane the halogen atoms are placed at the apices of the rhombus, the interatomic distances Cu–Cl being 0.266 and 0.291 nm, the distances Cu–Br equal to 0.254 and 0.308 nm. The coordination polyhedron is completed by two ammonium molecules bonded on a vertical [4, 5]. The above α-isomers are not isostructural, and were prepared in microcrystalline form only.

The β-isomers were prepared as microcrystals in the matrix NH_4X, where X = Cl or Br. Single-crystal X-ray analysis of these cubic crystals showed that the halogen atoms are placed at the apices of a square; the distances Cu–Cl and Cu–Br are 0.276 and 0.288 nm respectively [6]. The β-isomer of $CuBr_2(NH_3)_2$ was prepared without the matrix NH_4Br in the form of microcrystalline powder which contained admixtures of α-isomer [7], which changes into α-isomer after a certain time. The isomerisation rate increases with rising temperature. Attempts to prepare the β-isomer $CuCl_2(NH_3)_2$ without the matrix NH_4Cl have failed.

In the paper [3] a model was described which gives a theoretical explanation of the effects of NH_4X as an extraneous factor on stabilisation of the discussed β-isomers. In [8] the quantum mechanical calculations and evaluation of spectral data led to the conclusion that the distortion isomers $CuBr_2(NH_3)_2$ differ from each other in the degeneration of the orbitals of their central atom. The authors of the paper [9] explained the occurrence of β-isomer in the matrix NH_4Br as a dilution of the α-isomer in NH_4Br. However, neither the exact composition of the reported compounds, nor their syntheses, were reported in detail. In an earlier paper [10] differences in magnetic susceptibilities of these isomers were found.

A tendency of the α-isomer $CuBr_2(NH_3)_2$ to change to β-isomer when at high pressure was reported in [11].

In the present work we attempted to find whether the stabilizing effect of NH_4X (X = Cl, Br) could be replaced by changes in state conditions. Thus an answer could be given to questions arising with

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TABLE I. Diffraction Lines and Lattice Parameters of Isomers $CuCl_2(NH_3)_2$.

α-isomer (microcrystalline pure) atm. press			β-isomer (macrocrystalline with admixture NH_4Cl) atm. press			Sample at high pressure 5 GPa (wihtout admixture NH_4Cl)	
h k l	$d_{obs.}$ [nm]	$d_{calc.}$ [nm]	h k l	$d_{obs.}$ [nm]	$d_{calc.}$ [nm]	$d_{obs.}$ [nm]	$d_{calc.}$ [nm]
1 1 0	0.629 43	0.627 99	1 0 0	0.389 85	0.390 26	0.389 34	0.390 75
1 1 1	0.427 86	0.427 82	1 1 0	0.275 74	0.275 95	0.275 82	0.276 30
2 0 0	0.389 68	0.389 02	1 1 1	0.225 12	0.225 31	0.225 29	0.225 60
1 3 0	0.322 72	0.322 63	2 0 0	0.195 17	0.195 13	0.195 21	0.195 38
0 0 2	0.292 52	0.292 21	2 1 0	0.174 45	0.174 53		
1 3 1	0.282 78	0.282 45	2 1 1	0.159 29	0.159 32		
2 2 1	0.276 65	0.276 59					
0 4 0	0.266 25	0.265 92					
3 1 0	0.252 18	0.251 96					
0 4 1	0.242 24	0.242 04					
2 0 2	0.233 41	0.233 64					
3 1 1	0.231 33	0.231 38					
2 4 0	0.219 61	0.219 53					
2 4 1	0.205 34	0.205 51					
0 4 2	0.196 73	0.196 67					
3 1 2	0.191 03	0.190 82					
a = 0.778 0 (6)			a = 0.390 3 (2)			a = 0.390 8 (7)	
b = 1.063 7 (7)							
c = 0.584 4 (5)							

regard to the paper [9] in which the existence of isomers was questioned. These were the reasons why we decided to study the effect of high pressure on isomerization of α-isomers $CuX_2(NH_3)_3$.

Results

The α-isomers were prepared from acetone solutions according to [7]. The β-isomers in the matrix NH_4X were prepared by crystallization from aqueous solutions [7].

The effects of high pressure were evaluated from the X-ray diffractograms recorded at ambient pressure from specimens after application of pressure (*ex post*), and from diffractograms recorded during application of high pressure (*in situ*).

For investigations *ex post* a piston-cylinder equipment for pressures up to 1.2 GPa, a Radcliff cell for pressures up to 2.7 GPa, and for pressures up to 5 GPa a Bridgman anvil apparatus made of tungsten carbide and diamond [12, 13] were used. The diffractograms were made with an X-ray goniometer GON 03 using Ni-filtered CuKα radiation with scan rate of 0.125 to 0.5 θ min^{-1}, or with a Philips PW 1049 using CuKα radiation with scan rate of 0.5 and 0.25 °θ min^{-1}. Data on $CuBr_2(NH_3)_2$ were collected in the range 3–33 °θ and those on $CuCl_2(NH_3)_2$ in the range 5–30 °θ. For an *in situ* investigation a universal optical and X-ray cell with diamond anvils of the 'squeezer' type was used. Zr-filtered MoKα radiation and pressure of 5 GPa was used. The diffracted radiation was recorded on a plane film in the shape of sectors of a circle. For comparison purposes, a diffractogram was made of the sampel prior to pressure application.

For grinding of samples a ball-vibrator was used in which steel grindling balls, 9.6 mm in diameter, were placed in a spherical vessel. With this technique phase changes could be detected. For exact measurements of lattice parameters and compressibility this method was unsuitable. For this reason the lattice parameters determined *in situ* under the pressure of 5 GPa were not used for compressibility calculations.

The Effect of High Pressure on α-$CuCl_2(NH_3)_2$

After application of pressures higher than 0.28 GPa at laboratory temperature, and of still lower pressures at 363 K, the samples of the α-isomer $CuCl_2(NH_3)_2$ changed their colour quite distinctly from a light blue to a light green, a colour similar to that of the β-isomer in the matrix NH_4Cl. The higher the applied pressure, the deeper the green

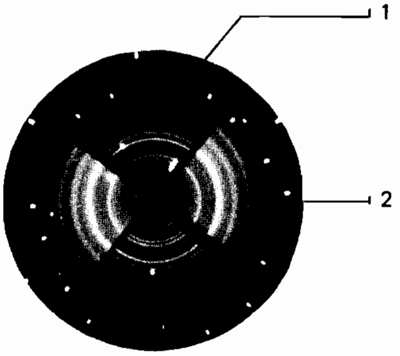

Fig. 1. Diffractograms of CuCl$_2$(NH$_3$)$_2$. Sector 1: α-isomer prior to pressure application. Sector 2: β-isomer under pressure of 5 GPa.

colour of the sample. After allowing to stand for several hours, the samples regained their original colour. For this reason the samples (in the form of pellets or flakes) were submitted to X-ray phase analysis immediately after release of pressure. X-ray runs on powdered samples were made later. There was rather low preferred-orientation in the pressed samples. For investigation the lines (111), (002), (221) and (042) of the α-isomer were used. After pressure application a certain decrease of lines pertinent to the α-isomer and a slight increase of lines pertinent to the β-isomer, (001), (111), and (002) were observed (Table I). Two to three hours after pressure application diffractograms identical with those of the starting α-isomer were obtained, consistent with the observed change of colour.

In order to obtain unambiguous results a diffractogram on the sample of the α-isomer was made *in situ* under a pressure of 5 GPa. In Fig. 1 the diffractogram of the α-isomer prior to pressure application (sector 1) and diffractogram of the β-isomer formed by high pressure (sector 2) are shown. The Laue spots are due to the diamond anvils. In Table I the following data are listed: the measured and calculated values of interplanar distances (d$_{obs}$, d$_{calc}$), the lattice para-

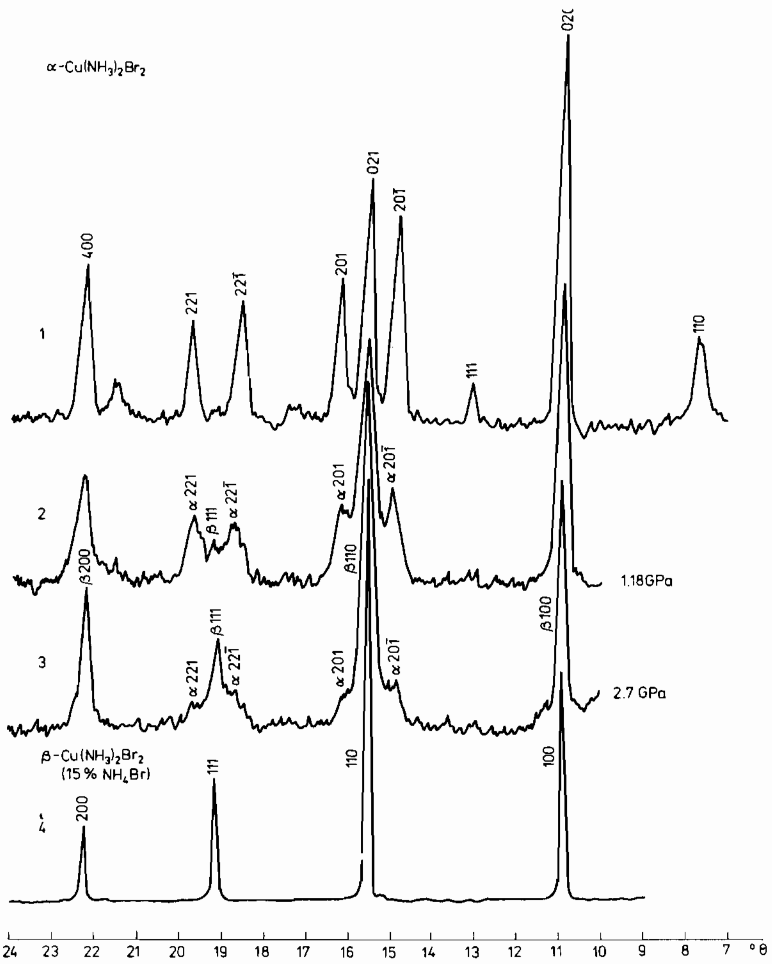

Fig. 2. Diffractograms of CuBr$_2$(NH$_3$)$_2$ (see text).

TABLE II. Lattice Parameters of Isomers $CuBr_2(NH_3)_2$.

Sample	Lattice parameters [nm]	Density calculated [g cm^{-3}]
α-isomer microcrystalline pure	a = 0.818 1 (5) b = 0.815 6 (8) c = 0.407 5 (5) β = 94.91(4)°	3.155 (9)
β-isomer (macrocrystalline with admixture 15% NH_4Br)	a = 0.407 2 (1)	
sample at pressure 2.7 GPa experiment *ex post* Fig. 2, curve No. 3	a = 0.407 3 (3)	3.163 (7)
sample at pressure 5 GPa experiment *in situ*	a = 0.409 (1)	

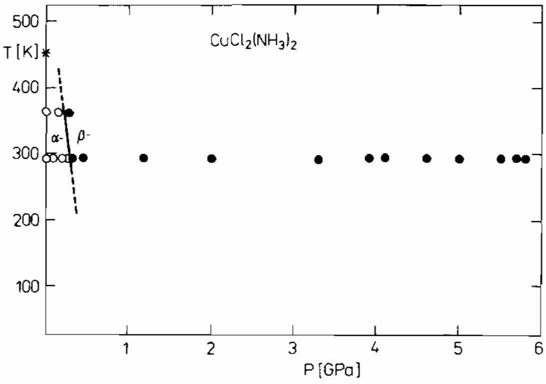

Fig. 3. Phase P–T diagram of $CuCl_2(NH_3)_2$.

meters of the chemically pure β-isomer formed under pressure (*in situ*) and of the β-isomer with the admixture of NH_4Cl, and finally those of the α-isomer at ambient pressure. Standard deviations are given in brackets.

The occurrence of a very weak line (111) pertinent to the α-isomer, together with intense lines of the β-isomer in Fig. 1 (sector 2) proves that even after application of a pressure of 5 GPa for 40 days it was impossible to prepare pure β-$CuCl_2(NH_3)_2$ without the admixture of NH_4Cl. The β-isomer containing admixtures of NH_4Cl was not changed by application of a pressure of 4.7 GPa (experiment *ex post*).

Effect of High Pressure on α-$CuBr_2(NH_3)_2$

By the action of high pressure between 1.18 to 5 GPa on chemically pure α-$CuBr_2(NH_3)_2$ substances were prepared whose diffraction patterns recorded at ambient pressure indicated formation of the β-isomer and presence of the α-isomer. A series of diffraction patterns in Fig. 2, recorded *ex post*, shows a successive transformation of chemically pure α-isomer (curve No. 1) to chemically pure β-isomer. At 2.7 GPa the α-isomer was transformed to β-isomer containing traces of α-isomer (curve No. 3). For comparison purposes a diffraction pattern of the β-isomer stabilized with 15 mass % NH_4Br is shown (curve No. 4).

The assumption that the chemically pure β-isomer $CuBr_2(NH_3)_2$, existing under high pressure, is identical with that which was identified after release of pressure, could be verified by an experiment *in situ* in the above mentioned X-ray cell. At 5 GPa, as well as on release of pressure, identical diffraction patterns of β-isomer with diffuse (110) and (111) lines were obtained. This is in agreement with the curve No. 3 in Fig. 2. Here, alongside the mentioned lines, traces of diffraction lines of the α-isomer occur, which proves that not even by application of a pressure of 5 GPa for more than two weeks was a pure β-isomer formed.

In greater quantities the chemically pure β-isomer can be prepared in a more convenient way by grinding the α-isomer in a ball mill at temperatures round 0 °C. Thus prepared β-specimens (with a certain content of α-isomer) gave in consequence of grinding for 0.5 to 1 hour diffuse diffraction lines. Allowed to stand for several days at ambient temperature they changed back to the starting α-isomer. Kept at temperatures of dry ice they persevered for several weeks. Similarly, the chemically pure β-isomer formed on application of high pressure changed back to the α-isomer at ambient temperature. Stability of chemically pure β-isomer is strongly impaired by humidity. In Table II the re-determined lattice parameters of the α-isomer are listed, together with parameters of chemically pure β-isomer formed on pressure, as these were found by experiments *ex post* and *in situ*. For comparison, parameters of the β-isomer in the matrix NH_4Br, which are identical with those of the chemically pure β-isomer, are also shown.

By the application of pressure (5.4 GPa) on β-isomer with the admixture of 15% NH_4Br no changes were induced (experiment *ex post*).

P–T Diagrams of $CuX_2(NH_3)_2$

Construction of P–T diagrams was attempted on the basis of which the ranges of stable existence of individual isomers could be approximatively established, and by which the energetical balance of the isomerization could be determined. The diagrams were constructed on the basis of high pressure experiments performed at ambient temperature, at 363 °K and at the temperature of liquid nitrogen [15]at ambient pressure. For identification X-ray, optical and DTA methods were used.

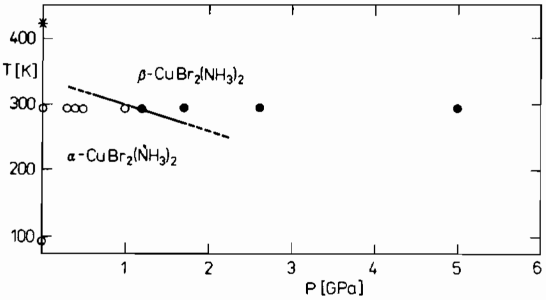

Fig. 4. Phase P–T diagram of $CuBr_2(NH_3)_2$.

From the phase P–T diagram of $CuCl_2(NH_3)_2$ (Fig. 3) the experimentally found gradient of the phase boundary dT/dP was 1.3×10^{-6} KPa^{-1} and the volume change $\Delta V_{(\beta \to \alpha)} = 1.23 \times 10^{-6}$ m^3 mol^{-1}. Then from the Clapeyron equation: $\Delta H_{(\beta \to \alpha)} = -280$ J mol^{-1}. From Fig. 3 it can be seen that the phase boundary lies at relatively low pressures (0.26 GPa) and consequently the compressibility can be neglected (Table I) in estimating the equilibrium volume changes.

The empty circles in Figs. 3 and 4 represent experiments in which only the α-isomer was identified. Experiments in which β-isomer was also determined are designated by full circles. The point * indicates temperature of decomposition of the α-isomer at ambient pressure.

From Fig. 4 it can be seen that the pressure of phase transition for $CuBr_2(NH_3)_2$ is higher. The enthalpy balance of transition from β to α-$CuBr_2$-$(NH_3)_2$ is also remarkably higher, $\Delta H_{(\beta \to \alpha)} = -1500$ J mol^{-1}.

Since β-$CuBr_2(NH_3)_2$ can be easily prepared by grinding, it was possible to check these important data with the aid of a Dupont 990 DSC thermoanalyzer cell at normal pressure, under which conditions it is a spontaneous β → α transformation accelerated by rising temperature. It can be assumed that under pressure the enthalpy balance of this isomerization will be only slightly lower [16] since the pressures of the equilibrium transitions are rather small.

It is not possible to determine the exact equilibrium change of volume which accompanies the phase transition on pressure because the compressibilities of isomers are not known. Instead we used data found at laboratory conditions ($\Delta V_{(\beta \to \alpha)} \sim 2.06 \times 10^{-7}$ m^3 mol^{-1}). Hence it follows that the gradient of the phase boundary $dT/dP = -4 \times 10^{-8}$ KPa^{-1} as it was calculated from the Clausius–Clapeyron equation can, with the exception of the sign, be rather erroneous (Fig. 4).

Conclusions

It has been unequivocally proved that high pressures (up to 6 GPa) cause transformation of α-isomers $CuCl_2(NH_3)_2$ and $CuBr_2(NH_3)_2$ into cubic β-isomers, without formation of any other modification. This transformation takes place in the absence of stabilizers NH_4Cl or NH_4Br, so that an interpretation of chemically stabilized β-isomers as mixed crystals NH_4X with α-isomers [9] is ruled out. On pressure release a transformation of β-isomers into α-isomers $CuX_2(NH_3)_2$ takes place. This is a rapid process in the case of $CuCl_2(NH_3)_2$ and for this reason it was necessary to prove that the isomerization (α → β) is pressure induced by an experiment *in situ*. The transformation of β-$CuBr_2(NH_3)_2$ into the α-isomer proceeds more slowly and consequently it was possible to prove the pressure induced α → β transformation by measurements made *ex post.*

Formation of β-$CuBr_2(NH_3)_2$ in a ball mill is explained by local action of high pressure. Heat formed in the course of milling must be abstracted since with rising temperature at normal pressure the rate of isomerization (β → α) increases.

An analysis of the P–T diagrams shows that, at temperatures which do not differ too much from the usual room temperature, and at pressures up to 6 GPa, only the discussed α and β-isomers can exist.

References

1 J. Gažo, *Proc. IVth Conf. Coord. Chem.*, Bratislava, Smolenice, 1973, p. 144.
2 J. Gažo, *Pure Appl. Chem.*, *38*, 279 (1974).
3 J. Gažo, *et al.*, *Coord. Chem. Rev.*, *19*, 253 (1976).
4 F. Hanic, *Acta Cryst.*, *12*, 739 (1959).
5 L. Zsoldos, *Magy. Fiz. Folyoirat*, *10*, 189 (1962).
6 F. Hanic, I. Čakajdová, *Acta Crystal.*, *11*, 610 (1958).
7 J. Gažo, K. Serátorová, and M. Serátor, *Chem. Zvesti*, *13*, 3 (1959).
8 T. Obert and I. B. Bersuker, *Proc. XIX ICCC, Vol. II*, 94, Praha, 1978.
9 T. Asai, H. Saheki, K. Hori and R. Kiriyama, *Bull. Chem. Soc. Japan*, *51*, 974 (1978).
10 J. Kohout and J. Gažo, *Chem. Zvesti*, *22*, 905 (1968).
11 J. Garaj and J. Gažo, *Chem. Zvesti*, *20*, 458 (1966).
12 R. H. Wentorf, 'Modern Very High Pressure Techniques', London, 1962.
13 W. Kleber, K. Th. Wilke, *Kristall. u. Technik*, *4*, 165 (1969).
14 J. R. Ferraro, *Coord. Chem. Rev.*, *29*, 1 (1979).
15 M. Serátor, H. Langfelderová, J. Gažo and J. Stracelský, *Inorg. Chim. Acta*, *30*, 267 (1978).
16 J. Klimovič, *Československý časopis pre fyziku*, *17*, 344 (1967).