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Temperature Dependent Stereochemical Transformations of Distortion Isomers of $CuBr_2(NH_3)_2$

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In the present work the influence of temperature on the deformation of the Cu(II) coordination polyhedron in the isomers of $CuBr_2(NH_3)_2$ *was studied. At temperatures of −180, 20 and 150 °C the changes of structure were followed with the aid of electronic spectra and at −180 and 20 °C also the powder diffraction patterns were taken. Although in both investigated isomers of* $CuBr_2(NH_3)_2$ *certain temperature dependent variations in the deformation of the coordination polyhedron were observed, these could not be interpreted as formation of a new isomer since the crystal structure did not change in such a manner as to lead to stabilization of a new coordination polyhedron. The results of investigation are discussed with regard to the present notions on the plasticity of the coordination polyhedron of Cu(II) complexes.*

Introduction

The existence of quite a number of structure modifications of copper(II) compounds that differ in the deformation of their coordination polyhedron and the analysis of causes of their existence made us to introduce the term *distortion isomerism* [1] and the notion of *plasticity* [2] of Cu(II) coordination polyhedra.

The existence of distortion isomerism in Cu(II) complexes was theoretically accounted for by the possibility of stabilizing various states of the plastic polyhedron, these states having been caused by the Jahn–Teller or pseudo Jahn–Teller effect [2]. Consequently those Cu(II) complexes can be regarded as distortion isomers with identical stoichiometric composition which differ from each other by the degree of deformation of their coordination polyhedron. The question is how one should estimate, with regard to the definition of distortion isomerism, the possible changes in the degree of deformation that were caused by changes in state conditions. As has been reported [3], tetragonality of some Cu(II) complexes is temperature dependent. For our investigation we took the distortion isomers [4] of the complex $CuBr_2(NH_3)_2$, the crystal structure of which is known [5, 6]. From the two isomers the α-$CuBr_2(NH_3)_2$ is thermodynamically stable under normal conditions, while the β-isomer represents, under identical conditions, the metastable phase which slowly changes to the α-isomer.

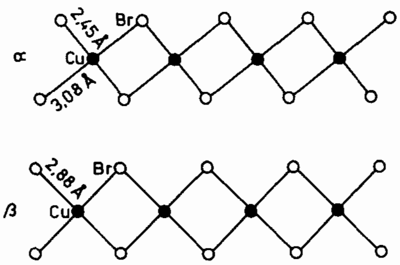

Figure 1. Schematic representation of Cu–Br bonds in the isomers of $CuBr_2(NH_3)_2$.

The structure differences between the α- and β-isomer of $CuBr_2(NH_3)_2$ are especially the differences in interatomic distances Cu–Br, where each bromine atom is bidentate and forms a polymeric chain indicated in Fig. 1. The bonds Cu–NH_3 approximately identical in both isomers, are perpendicular to the plane of the above chain. The equatorial plane in the coordination polyhedron of the copper atom is formed by four bromine atoms in both isomers. In the α-isomer which crystallizes in the monoclinic system these atoms form a rhomb, in the β-isomer which crystallizes in the cubic system they form a square [5, 6]. Since the structure differences between the isomers of $CuBr_2(NH_3)_2$ are to be found chiefly in the equatorial plane of the distorted octahedron, we assume that the temperature dependent variations in the degree of distortion of the coordination polyhedron will be also related to this plane. For experimental check of these changes the electronic spectra were used, which give us information on the interactions between the central atom and the ligands. Further powder diffraction patterns were taken from

TABLE I. Maxima of d–d Absorption Bands of Isomers $CuBr_2(NH_3)_2$.

Sample $CuBr_2(NH_3)_2$	$\tilde{\nu}_{max}$ [cm^{-1}] at temperature			Δ_1[a]	Δ_2[a]
	−180 °C	20 °C	150 °C		
α-Isomer	15200	14800	14650	400	150
β-Isomer prepared by grinding α-isomer	15100	14450	b	650	. . .
β-Crystalline with the admixture of NH_4Br	14800	14100	13700	700	400
β-Crystalline with the admixture of NH_4Br, ground for 1 hr	14900	14300	14000	600	300

[a] Δ_1 = (maximum at −180 °C) − (maximum at 20 °C). Δ_2 = (maximum at 20 °C) − (maximum at 150 °C). [b] Only the arm was observed, position of the peak could not be found exactly.

which information on the symmetry of the crystal structure can be derived.

Experimental

The isomers of $CuBr_2(NH_3)_2$ were prepared by the following procedures: the α-isomer and the β-isomer containing about 15% NH_4Br as reported previously [4], the β-isomer without NH_4Br was prepared by grinding in a vibrator with steel balls for one hour. In the latter method of preparation the action of high pressures for a short time brings about transformation of the α-isomer to the β-isomer [7]. The electronic spectra were recorded as Nujol mulls on the UV–VIS Specord spectrophotometer in the region of 30000–13000 cm^{-1}. Up to 150 °C silicone oil was taken instead of Nujol. Cells of our own construction were used for recording of spectra at the boiling point temperature of liquid nitrogen and at 150 °C. The optical properties of these cells were checked both at laboratory temperature and at temperatures of the experiment. The X-ray diffraction patterns in the region 3–33°θ were recorded with the goniometer GON 03 (of Czechoslovak make) using Ni-filtered CuKα radiation with the arm step of 0.25°θ/min. The diffraction patterns were recorded at the temperature of liquid nitrogen and with a cell of our own construction made from methylmetacrylate. On the side opposite to the incident radiation, the sample was cooled by liquid nitrogen. The evaporated nitrogen was then brought to the front side of the sample so that this should not be heated by the ambient air. For control purposes a diagram was taken with the same sample and with the same cell at room temperature. The cell was calibrated for powder silicon at room temperature.

Results

The electronic spectra of all samples taken at room temperature show one absorption band due to d–d transition of the central atom in the region between 14000 and 15000 cm^{-1} the evaluation of which will be discussed later. A broad plateau is observed between 20000–30000 cm^{-1} which is not evaluated. For the peaks of the d–d bands of the α-isomer and of the crystalline β-isomer (15% NH_4Br) at room temperature we obtained identical data with those reported [8]. As can be seen from Table I, with all investigated samples of both isomers a shift of peaks towards higher wavelengths with decreasing temperature, and *vice versa,* a shift towards lower wavelengths with increasing temperature, took place.

These changes were found to be perfectly reversible on cooling up to −180 °C. Further it was found that, when heating lasted 2–3 minutes, the observed changes on all samples are reversible. When the heating to 160 °C lasted 10 minutes and more, then the β-isomer which did not contain the admixture NH_4Br was observed to isomerize irreversibly to the α-isomer. This is proved also by the irreversible shift of the original peak from 14500 cm^{-1} to 14800 cm^{-1} which belongs to the sample that has been cooled to room temperature. The β-isomer with the isomorphous admixture of NH_4Br (ground for one hour) when heated in the same manner as above is irreversibly changed in such a manner that original peak is shifted from 14300 to 14100 cm^{-1}, which is identical with the d–d transition of the unground β-isomer with the admixture of NH_4Br.

The powder diffraction patterns of samples cooled to −180 °C do not show, when compared with the control patterns recorded at room temperature, any changes in the number of diffractions: just shifts towards higher values of the angle θ took place. Hence it follows that on cooling the symmetry of the crystal lattice, monoclinic α-isomer and cubic β-isomer, remains unchanged. In Table II the lattice parameters calculated from the diffraction patterns taken in the present investigation are given. For both the α- and β-isomer the diffractions from the area of 3–33°θ were evaluated. Those values were calculated also from the control patterns taken at room temperature so that in this way possible systematic errors of the applied method should be eliminated.

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

Lattice Parameters	At 20 °C	At −180 °C
α-Isomer		
a [Å]	8.180 ± 0.004	8.15 ± 0.01
b [Å]	8.15 ± 0.01	8.12 ± 0.01
c [Å]	4.070 ± 0.004	4.07 ± 0.02
β [°]	94.90 ± 0.04	95.27 ± 0.15
Coefficient of volume expansion $0.35.10^{-4}$ K^{-1}		
β-Isomer (the ground sample)		
a [Å]	4.088 ± 0.002	4.057 ± 0.002
Coefficient of volume expansion $1.2.10^{-4}$ K^{-1}		

Discussion

From the powder diffraction patterns of samples after short temperature changes between −180 and 150 °C it follows that no such overall changes in the symmetry of crystal lattice take place that would be related with the transformation of the β-isomer to α-isomer and *vice versa.* We suppose that the changes in the electronic spectra are caused by changed interatomic distances in the coordination polyhedra within the given crystal symmetry and that these changes are temperature dependent.

With regard to the fact that the essential differences in distortion isomers α- and β-$CuBr_2(NH_3)_2$ are those of interatomic distances of the Cu–Br bonds we assume that the above discussed temperature dependent changes will regard especially the Cu–Br bonds and, to a first approximation, the changes in the bond distances Cu–NH_3 can be neglected.

As follows from the structure of the Cu(II) coordination polyhedron in the α-isomer, the distance between copper atom and two bromine atoms is relatively large (3.08 Å at 20 °C). Evidently changes in thermal vibrations of these atoms will affect but slightly their ligand field strength, even when changes in the atomic distances are relatively large. On the other hand, the distance from the other two bromine atoms to the copper atom (the bond between the bromine and copper atoms being relatively short and strong, 2.45 Å at 20 °C), cannot be considerably changed under the influence of lowered temperature. In agreement with this argument, the observed changes in position of d–d bands in the α-isomer induced by temperature changes are relatively small. In the β-isomer all bromine atoms are at an equal distance, the value of this distance (2.88 Å) lying between those found for the α-isomer. Temperature changes manifested themselves more strongly in the electronic spectra. On lowering the temperature the cubic structure of the β-isomer remained unchanged which can be seen from the diffraction patterns. Since the copper and bromine atoms are in special positions [5], by temperature changes all four interatomic distances must change in the same manner. The interatomic distance Cu–Br calculated from the powder diffraction diagrams of β-$CuBr_2(NH_3)_2$ at the temperature of liquid nitrogen is 2.869 Å (at room temperature it is 2.891 Å). We account for the increase in the ligand field strength manifested by the shift of the d–d band towards shorter wavelengths as a consequence of simultaneous shortening of all four interatomic distances Cu–Br. The extent of the shift of the d–d absorption band in relation to the interatomic distances can be calculated on the basis of the crystal field theory as follows [9]:

$$d\Delta = -\frac{5(R_1 - R)}{R}\Delta$$

where dΔ is the shift of the d–d absorption band in cm^{-1}, when the interatomic distance is changed from R to R_1, Δ is the wavenumber of d–d absorption band maximum in cm^{-1}, the interatomic distance being R.

After inserting the respective values for R, R_1 and Δ, we obtain for dΔ the value 495 cm^{-1} which agrees, as to the order of magnitude, with the experimental value of the shift of peak of the β-isomer (650 cm^{-1}). This result supports our assumption that the temperature shift of the d–d band in $CuBr_2(NH_3)_2$ is caused by the change in the ligand field strength in the neighbourhood of the central atom.

There are considerable differences in the coefficients of the volume expansion (Table II). The coefficient of the volume expansion of the α-isomer corresponds in the order of magnitude to that of substances that can be designated as covalent polymers (*e.g.* SiO_2). On the other hand, the coefficient of the β-isomer corresponds to that of substances with ionic structure [10]. This fact suggests again that the differences between the α- and β-isomer are in chemical structure and not only in symmetry of crystal lattice.

Comparing the coefficients of volume expansion of the two isomers we can see that that of β-isomer is about four times that of α-isomer. Similarly, the temperature dependent shift of the absorption band of d–d transition is greater for the β-isomer than that for the α-isomer (Table III). The differences in the electronic spectra of the α- and β-isomer, which are smaller at lower than at higher temperatures, are in agreement with this.

On the basis of results of the present investigation we came to the conclusion that, as a consequence of temperature changes, a reversible change in the geometry of the coordination polyhedra of the distortion isomers $CuBr_2(NH_3)_2$ took place which is not accompanied by changes in the crystal symmetry of the individual isomers. These findings make it possible to

TABLE III. Shifts of maxima of d-d absorption band [cm^{-1}] of Isomers $\mathrm{CuBr_2(NH_3)_2}$.

	$\tilde{\nu}_{\mathrm{max}}$ − 180 °C	$\Delta\tilde{\nu}_{\mathrm{max}}$ Temperature shift	$\tilde{\nu}_{\mathrm{max}}$ 150 °C
α-isomer	15 200	550	14 650
$\Delta\tilde{\nu}_{\mathrm{max}}$ isomer shift	400		950
β-isomer	14 800	1 100	13 700

explain the phenomenon of distortion isomerism on the basis of experimental results. A theoretical explanation of distortion isomerism was given in a previous paper [2] in relation with a possibility of stabilizing different states of the plastic Cu(II) polyhedron brought about by Jahn–Teller or pseudo-Jahn–Teller effect evoked by the electron degenerated (or pseudo-degenerated) ground states of the central Cu(II) atom.

The above results show that the distortion isomerism should not be connected with any change in degree of coordination polyhedron distortion, except such discrete change which is due to Jahn–Teller effect and which manifests itself as a consequence of a qualitatively different influence of the surroundings on the coordination polyhedron with plastic properties (*e.g.* as a consequence of the influence of different symmetry of the crystal as a whole). We see the importance of this statement also in connection with the evolution of views and opinions regarding the phenomenon of isomerism which are due to development of theoretical and experimental structure research.

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