

STRUCTURE AND PROPERTIES OF SOME COPPER (II) COORDINATION COMPOUNDS DISTORTION ISOMERISM OF COPPER (II) COMPOUNDS

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ABSTRACT

Starting from information on the structural differences in the coordination polyhedra of different modifications of a number of copper(II) compounds, the present paper shows the possibility of the existence of a so-called distortion isomerism of copper(II) compounds. By 'distortion isomerism' is meant the occurrence of copper(II) compounds in different structures, caused by varying degrees of distortion of the coordination polyhedron, which have different physical and chemical properties (colour, spectral properties, magnetic behaviour, thermal stability, conditions of preparation and chemical reactivity). A knowledge of the interconversion of this type of isomer, and of the existence of the so-called intermediates, completes the concept of distortion isomerism of copper(II) compounds with regard to its dynamic aspect. The paper discusses questions of distortion isomerism of copper(II) compounds referring to the definition of isomerism in general, to the relationship between crystal structure, ligand conformation and distortion isomerism, as well as to the specific properties of the central atom causing this type of isomerism.

INTRODUCTION

Even though an enormous number of copper(II) compounds are known, the problem of isomerism of these compounds as a whole is still an open question. Classical coordination chemistry could only state that for Cu^{II} compounds it appears impossible to prepare *cis-trans* isomers with monodentate ligands, though the square-planar ligand arrangement around the Cu^{II} atom allows of the possibility of such space isomerism. There is some evidence of the existence of *cis-trans* isomers of Cu^{II} compounds, as, e.g., for $[\text{Cu}(2,2'\text{-bipyridyl})_2(\text{H}_2\text{O})_2]^{2+}$ and $\text{Cu}(\text{glycine})_2 \cdot \text{H}_2\text{O}^1$, and it is possible that there is a *cis*-arrangement of ligands in the coordination sphere of copper(II) in, for example, $\text{Cu}_3(\text{CN})_4(\text{NH}_3)_3^2$. It appears justified to suggest a preferential formation of *trans*-isomers of heterogeneous Cu^{II} compounds in connection with their kinetic properties and especially by preferential ligand

substitution in the places of longer bonds being mutually in *trans*-positions in the distorted coordination polyhedra of Cu(II) compounds³.

Until now there have been no experimental results which would prove the existence of space isomerism of this kind.

The utilization of modern techniques of structure research in the last fifteen years has brought interesting information on structure differences causing the occurrence of several copper(II) compounds in different modifications which may be considered as a special case of space isomerism, or as we call it, distortion isomerism†. Since the number of known copper(II) compounds occurring in different modifications has increased, it appears timely to gather that knowledge and to try to evaluate it even though it is clear that the phenomenon dealt with below has until now had no satisfactory theoretical explanation. In our opinion the phenomenon of distortion isomerism is interesting not only with respect to the elucidation of the causes of distortion of the coordination polyhedra for the large majority of Cu^{II} compounds, but also with respect to the evolution of the conception of isomerism in coordination chemistry and to its utilization in the research of the chemical reactivity of compounds.

EXPERIMENTAL DATA FOR THE FORMULATION OF THE CONCEPT OF 'DISTORTION ISOMERISM' OF COPPER(II) COMPOUNDS

In the thirties Pfeiffer and his co-workers occupied themselves with the chemistry of copper(II) coordination compounds with different organic ligands⁴. For some compounds they found several modifications and studied their interconversion and the possibility of preparation using different solvent media from which those modifications were separated. Pfeiffer *et al.* did not succeed, however, in determining the character of the differences by chemical methods. In 1947 Stackelberg⁵ published the results of his investigations over several years; based on x-ray analysis he showed that those by Pfeiffer *et al.* presented α -, β - and γ -modifications of Cu^{II} compounds with two anions of salicylaldehydemethylimine. In addition, the α - and β -modifications of copper(II) compounds with two anions of β -oxy- α -naphthaldehydemethylimine as ligands have *trans*-configuration and thus, according to him, the differences arise from the different arrangements of the molecules in the crystal. Regarding our considerations it appears interesting that even when Stackelberg considered all the cases for Cu^{II} with coordination number four, based on merely geometrical analysis of the structure, he emphasized the 'extraordinarily strong secondary valencies' between the layers and he points out that with respect to the above, it would be interesting to reinvestigate some of the studied compounds⁵. More than ten years later the spectra of these modifications were studied in different solvents⁶. These studies

† This isomerism of Cu^{II} complexes that we discussed in 1966 in our contribution²¹ has got in the course of time different names (affinity isomerism⁶⁰, conformation isomerism³). Now we think 'distortion isomerism' to characterize best this phenomenon. A similar term has been used by J. Chatt, R. Manojlović-Muir, K. W. Muir (*Chem. Comm.* 1971, 655) for the existence of two compounds of different stoichiometric composition, viz., the blue *cis-mèr*-[MoOCl₂(PMe₂Ph)₃] and the green *cis-mèr*-[MoOCl₂(PEt₂Ph)₃].

suggest for the green modifications a coordination number higher than four, while for brown or violet forms it is four.

Besides the works of Pfeiffer *et al.* we mention from that time also the preparation of two forms of sodium copper(II)tetracyanoureate, $\text{Na}_2[\text{Cu}(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_4]$, namely the stable red-violet α -modification and the unstable steel-blue β -modification⁷. Recently on the basis of the differences in colours, infrared spectra, and EPR studies it has been suggested that both modifications have a planar tetragonal structure with differences in association (β -state associated form, α -state unassociated form) and that they are examples of crystalline dimorphism.⁸

In studying the analogy between the mutual influence of ligands for Cu^{II} and Pt^{II} compounds in 1959 we published data on the preparation of α - and β -modifications of $\text{Cu}(\text{NH}_3)_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$)⁹. The prepared compounds were subjected to x-ray analysis¹⁰. Figure 1 shows that the differences between α - and β - $\text{Cu}(\text{NH}_3)_2\text{Br}_2$ may be considered as the two types of distortion of octahedral arrangements of the coordination polyhedron.

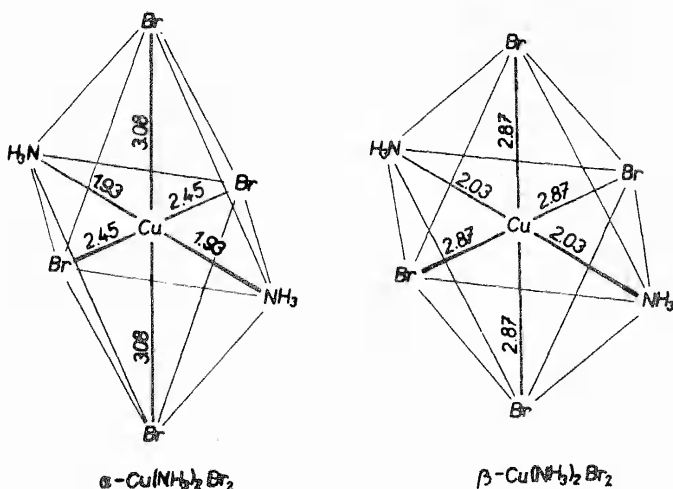


Figure 1. Schematic representation of the coordination sphere around Cu^{II} in $\alpha\text{-Cu}(\text{NH}_3)_2\text{Br}_2$ (I) and $\beta\text{-Cu}(\text{NH}_3)_2\text{Br}_2$ (II). Data from ref. 10.

Some experimental data can be also explained on the assumption of the existence of so-called intermediates: compounds occurring between the two limiting states of distortion of the octahedral ligand configuration¹¹. We also could present information on spontaneous interconversion of different modifications and on the influence of pressure and temperature on these transformations^{9,12}. We have found evident differences in some physical properties of these modifications (colour, magnetic moments, thermal decomposition, IR spectra)^{9,13,14}.

Using analogous methods as in the preparation of $\text{Cu}(\text{NH}_3)_2\text{Br}_2$ (applying the so-called Peyron and Jörgensen rules¹⁵ for the preparation of *cis-trans* isomers of PtA_2X_2), we succeeded in preparing different modifications of $\text{Cu}(\text{NH}_3)_2(\text{NCS})_2$ ¹⁶. Also for this compound the so-called intermediates

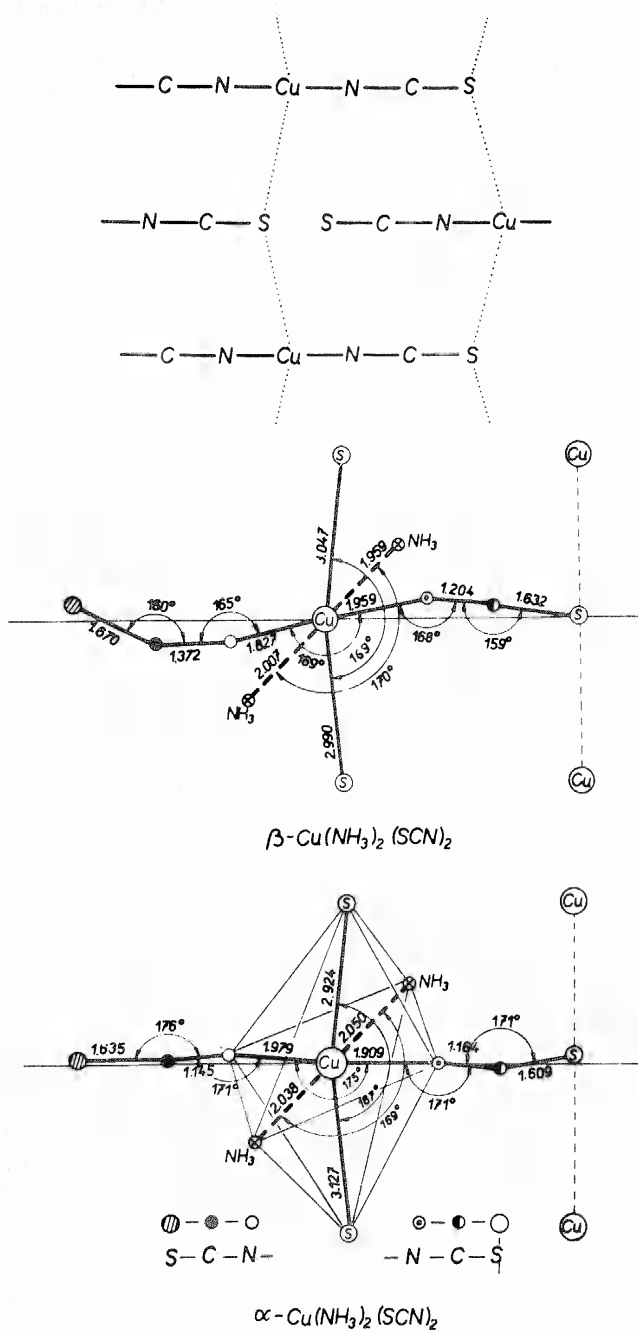


Figure 2. Schematic representation of the coordination sphere around Cu^{II} in $\alpha\text{-Cu}(\text{NH}_3)_2(\text{SCN})_2$ (I) and $\beta\text{-Cu}(\text{NH}_3)_2(\text{SCN})_2$ (II) and their structural fragment. Data from refs. 19 and 20.

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were found to be typical¹⁷. The preparation of different modifications from solutions is influenced by temperature and the ratio of concentration of the components in solution¹⁸. The modifications differ in several physical properties¹⁹. X-ray analysis showed that the differences between the modifications are caused by differences in the NCS group's deviation from linearity and in some interatomic distances central atom–ligand, maintaining the distorted octahedral ligand arrangement with the sulphur atoms in *trans*-positions in the more distant axial places²⁰ (Figure 2).

Considerations that the phenomenon found for the above complexes of the composition $\text{Cu}(\text{NH}_3)_2\text{X}_2$ could occur more commonly and could represent an example of a new-type isomerism of copper(II) compounds²¹ stimulated us to devote appropriate attention to this problem. Thus it has been found²² that the different modifications of the $\text{Cu}(\text{NH}_3)_2(\text{ox})$ probably also may be interpreted on the basis of different degrees of distortion of octahedral arrangement of donor atoms around the central atom, even though certain differences in the chelate bonding of the oxalate group of course also play a role (Figure 3).

More detailed study also showed that still other copper(II) compounds of the composition CuA_2X_2 occur in different modifications. This is the case, e.g., for $\text{Cu}(\text{py})_2\text{X}_2$ ^{23–25} ($\text{X} = \text{Cl}^-$, Br^- , NCS^- , CH_3COO^- , $\text{C}_6\text{H}_4\text{OHCOO}^-$) as well as for $\text{Cu}(\text{CHA})_2\text{Cl}_2$ ($\text{CHA} = \text{cyclohexylamine}$)²⁶ and $\text{Cu}(2,4\text{-lut})_2$

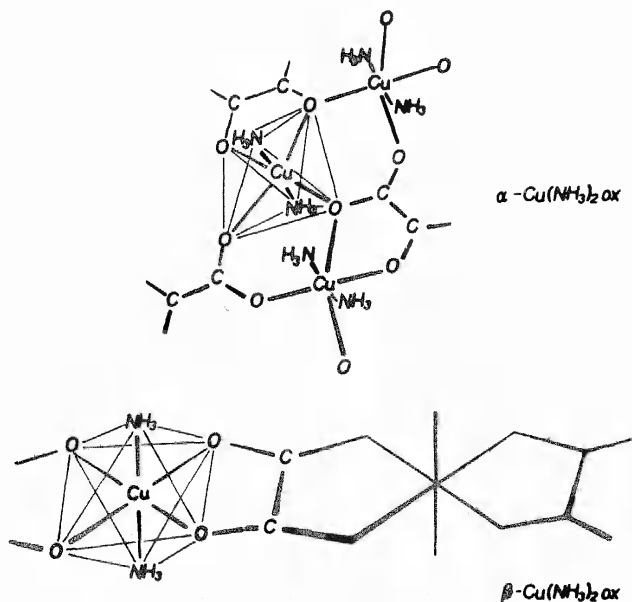


Figure 3. Schematic representation of the coordination sphere around Cu^{II} and structural fragment of $\alpha\text{-Cu}(\text{NH}_3)_2\text{ox}$ (I) and suggested structural fragment of $\beta\text{-Cu}(\text{NH}_3)_2\text{ox}$ (II). Data from ref. 22.

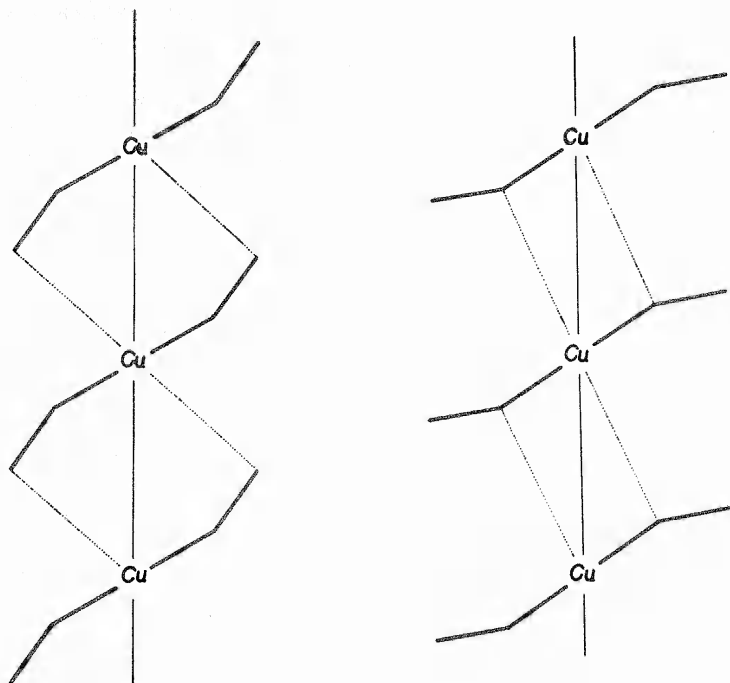


Figure 4a. Structural fragments of bis-(salicylaldehyde)-copper(II) form(I) and form(II).

(NCO)₂ (lut = lutidine), Cu(pyrazole)₂ (NCO₂)²⁷. We also observed the occurrence of different modifications for copper(II) compounds of another composition than CuA₂X₂, namely Cu(2,4-lut) (NCO)₂, Cu(urtp) (NCO)₂ and Cu(urtp) (NCO)₂ · 2H₂O (urtp = urotropine). Though structural reasons for the differences between the modifications of these compounds are not definitely known, based on the research results obtained by indirect structural methods, we may suggest^{23, 24–27} that those differences again are caused only by a different degree of distortion from some certain ideal coordination polyhedron. This finding has been indirectly confirmed by other authors studying the nature of the structure differences between modifications of other copper(II) compounds.

The investigation of two forms of bis(salicylaldehyde)copper(II) compounds showed that they differ in different axial contact with the π-bonding system of the adjacent molecule²⁸. Figure 4b shows these differences and stimulates a more profound analysis of π-bonding interactions of the central atom.

The two modifications of bis(1,3-diaminobutane)copper(II) perchlorate exhibit very similar structures²⁹ (Figures 5a and 5b). The coordination polyhedron has the form of a distorted octahedron. The six-membered ring formed by coordination has in both cases a chair conformation with expressively

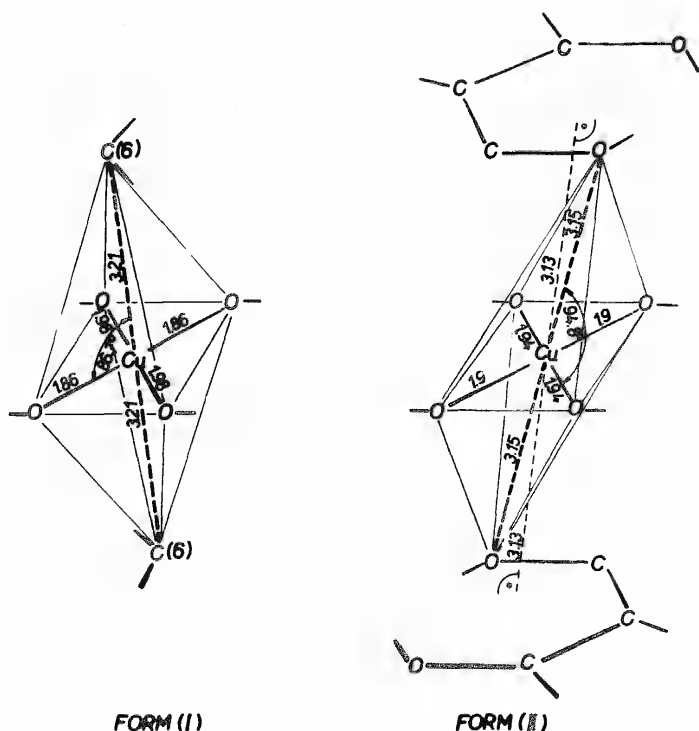


Figure 4. Schematic representation of the coordination sphere around Cu^{II} of bis(salicylaldehyde)copper(II) for form (I) and form (II). Data from ref. 28.

differing angles. The greatest differences in the interatomic distances have been observed in the $\text{Cu}-\text{O}$ bonds to the oxygen atoms of the perchlorate group in axial positions. This distance is 2.576 (6) Å for the blue-violet form and 2.676 (10) Å for the red one²⁹. The knowledge of the structure of these modifications is interesting, for the reason that they give an example of molecular crystal structures, where the molecules of both the modifications may be considered to a great extent separately.

In both forms of $\text{Cu}(\text{NH}_2\text{NHCONH}_2)\text{Cl}_2$ semicarbazide is bonded to Cu^{II} as a chelate³⁰. Besides the differences in the mutual positions of semicarbazide ligands in two subsequently arranged octahedra, greater differences have been found in the interatomic distances between the central atom Cu^{II} and the Cl atom in axial positions of the distorted octahedron. They are for one modification: $\text{Cu}-\text{Cl}$ (1): 3.144 (6) Å and $\text{Cu}-\text{Cl}$ (2): 2.792 (6) Å; and for the other: $\text{Cu}-\text{Cl}$ (1): 3.037 (6) Å and $\text{Cu}-\text{Cl}$ (2): 2.900 (5) Å (Figures 6a and 6b).

As to the different modifications of $\text{Cu}(\text{2-pic})_2(\text{NO}_3)_2$ it is, according to the authors³¹ an almost unique case of polymorphism, since both forms have the same space group and almost the same basic cell, but different

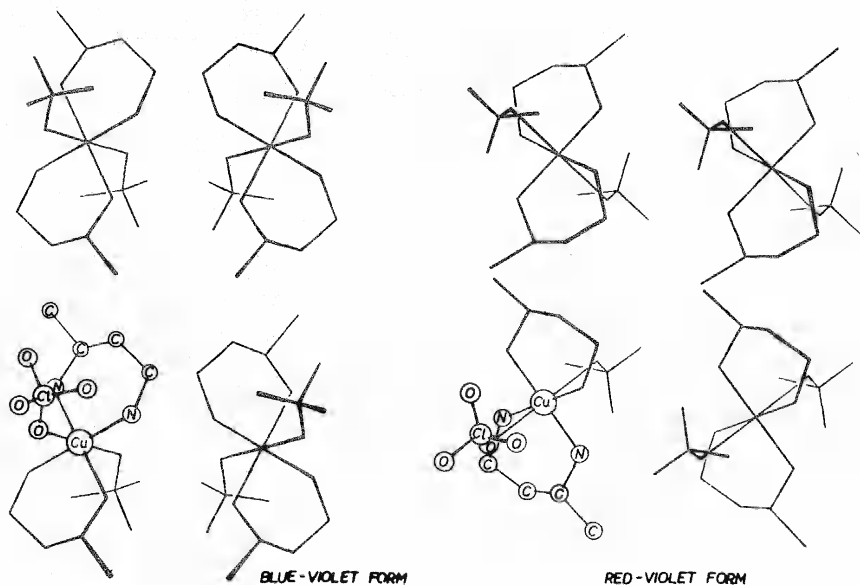


Figure 5a. Crystal structures of blue-violet and red-violet forms of bis(1,3-diaminobutane)copper(II) perchlorate.

crystal packing configurations. Both modifications have a monomeric structure. Above the basic square-planar arrangement, approximately in the middle of which the Cu^{II} atom is sited, there are on the longer distances two oxygen atoms of the nitrate group mutually in *cis*-positions (Figure 7). The most expressive differences are in the distances $\text{Cu}-\text{O}$ (oxygen atom of the nitrate group). For modification (I) this distance makes 2.307 (13) Å, while for modification (II) it is 2.517 (8) Å.

In connection with the structure differences between the two forms of $\text{Cu}(\text{2-pic})_2(\text{NO}_3)_2$, where differences have been observed in the bonding of the nitrate group, it would be interesting to know in detail the causes of the existence of two modifications of $\text{Cu}(\text{NO}_3)_2$, one of which readily turns into the other at increased temperature³². This is also interesting in connection with the finding that for $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ ³³ and $[\text{Cu}(\text{py})(\text{NO}_3)_2 \cdot 0.5\text{py}]_2$ ³⁴ the same somewhat unusual bonding of the nitrate group to the central atom was observed (two oxygen atoms of the nitrate group bonded on the longer bond distances in the *cis*-position, below the square-planar arrangement).

From three cases of Cu^{II} compounds with the general formula of CuL_2Cl_2 , where $\text{L} = 3\text{-picoline-NO}$, 4-picoline-NO , $2,6\text{-lutidine-NO}$, occurring in differently coloured modifications, as described by Kidd and co-workers³⁵, Johnson and Watson³⁶ studied with x-ray analysis the structure of both modifications of $\text{Cu}(4\text{-pic-NO})_2\text{Cl}_2$. They have found that the yellow unstable form changes at 73 °C to the stable green modification. The yellow form consists of coordination polyhedra, that may be considered as strongly distorted square-planar pyramids with chlorine atoms in axial positions (the

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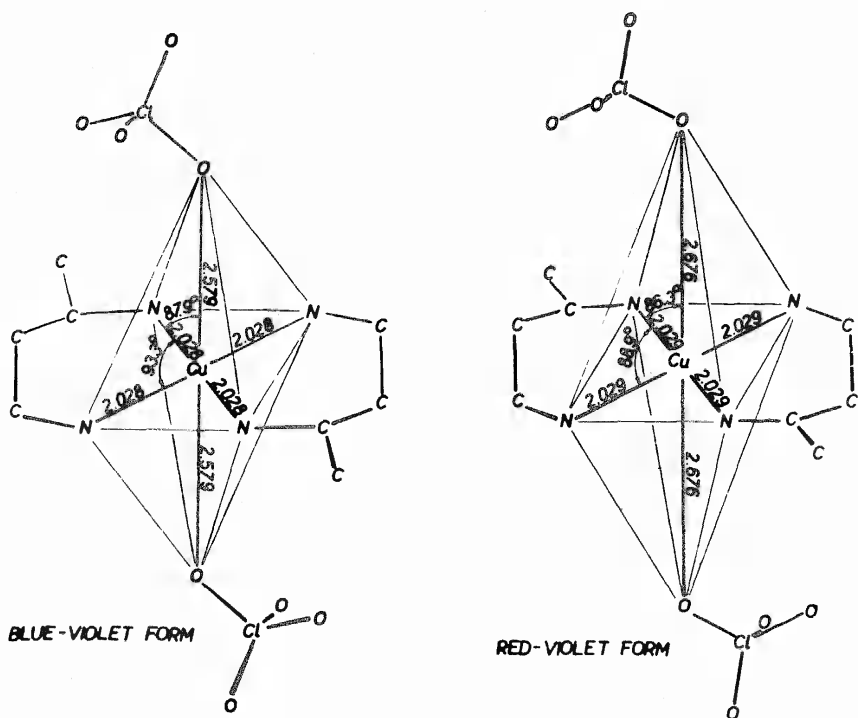


Figure 5b. Schematic representation of the coordination sphere around Cu^{II} of blue-violet form and red-violet form of bis(1,3-diaminobutane)copper(II) perchlorate. Data from ref. 29.

distance of $\text{Cu}-\text{Cl}$ being 2.354 (3) Å). The bridges $\text{Cu}-\text{O}-\text{Cu}$, which condition the formation of dimers, differ in their length (1.957 (6) and 2.153 (6) Å, respectively). In the green modification, formed by monomers, the copper atom is coordinated only with two chlorine and two oxygen atoms being transposed. In axial positions there is no atom sufficiently near for bond interaction; the nearest is the carbon atom from the methyl group at the distance of 4.11 Å (Figures 8a and 8b).

The structure of two forms of $\text{Cu}(\text{8-OQuin})_2$ (8-OQuin = 8-hydroxyquinoline) prepared by Fanning and Jonassen³⁷, was investigated by Palenik, Hoy and Morris³⁸. In the α -form, which is less stable, Cu^{II} has the coordination number six. The structure is formed by a chain of planar molecules $\text{Cu}(\text{8-OQuin})_2$ mutually linked together by the bonds $\text{Cu}-\text{O}$ of the length 3.32 Å. The β -form is formed by dimers. The copper atom in this form shows the coordination number five, the distance of $\text{Cu}-\text{O}$ in axial position being 2.83 Å. In both modifications the distance between the oxygen and the Cu^{II} atom in the square-planar configuration is almost the same (1.93 and 1.94 Å, respectively) (Figure 9).

As complementary methods to x-ray analysis, and as means to solve the structure problems under investigation, so-called indirect methods of structure research were also applied.

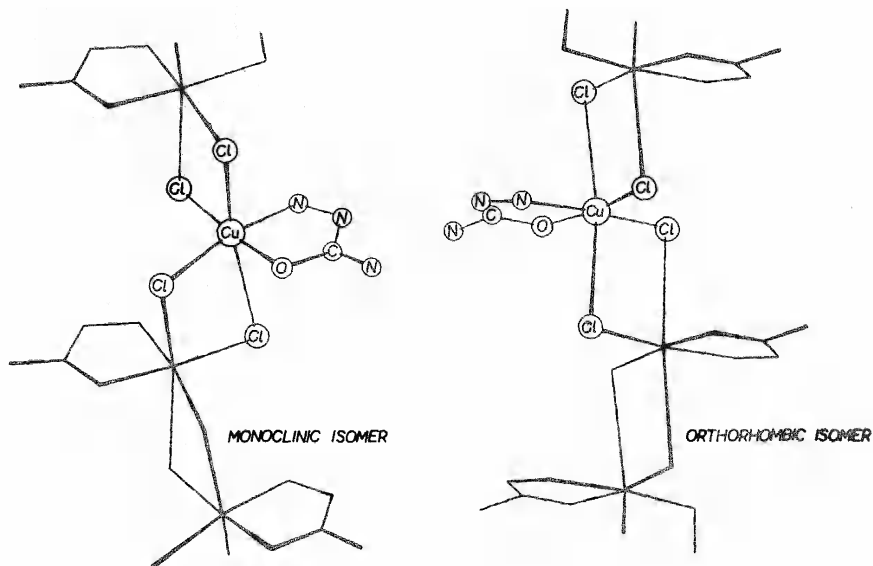


Figure 6a. Structural fragments of the monoclinic and orthorhombic isomers of $\text{Cu}(\text{NH}_2\text{NHCONH}_2)\text{Cl}_2$.

Lever *et al.*³⁹ studied the axial interaction between anions and the chromophore CuN_4 in the compounds $\text{Cu}(\text{asym}-(\text{C}_2\text{H}_5)_2\text{en})_2\text{X}_2$ ($\text{X} = \text{ClO}_4, \text{BF}_4, \text{NO}_3$) in dependence on the temperature. These compounds are described in different thermochromic forms and were of interest to others⁴⁰. The transformation at room temperature of the red $\text{Cu}(\text{asym}-(\text{C}_2\text{H}_5)_2\text{en})_2(\text{ClO}_4)_2$ to the blue form at 40°C is mentioned already by Pfeiffer and Glaser⁴¹. The complex salt of nitrate and that of tetrafluoroborate are thermochromically reversible. As is to be seen from the data³⁹, the maximum of the electron absorption bands, the magnetic moments and the stretching frequency metal–nitrogen clearly depend on the temperature. For example in the case of the nitrate salt differences in the metal–nitrogen stretching frequency were observed up to 22 cm^{-1} in the band energy between the purple and yellow-orange isomers, and up to 3 cm^{-1} between the red and yellow-orange isomers. The red isomer exhibits a single narrow sharp band at 1750 cm^{-1} , while the purple isomer shows two weaker bands at 1748 and 1760 cm^{-1} . The maxima of the electron absorption bands of $\text{Cu}(\text{asym}-(\text{C}_2\text{H}_5)_2\text{en})_2(\text{NO}_3)_2$ at 25°C are: $17\ 605\text{ cm}^{-1}$ for the purple isomer; $21\ 400\text{ cm}^{-1}$ for red isomer; and for the yellow-orange isomer $22\ 420\text{ cm}^{-1}$ at -196°C . Based on the results obtained together with some EPR data the authors suggest that the thermochromic properties of the investigated compounds are connected with the temperature dependence of the axial interaction between the anions and the plane CuN_4 . The authors assume that in cooling the sample the bonds in the plane shorten thus weakening the axial interaction. In connection with this, investigations of the changes in monocrystal diffractograms of Cu^{II} formate tetrahydrate in dependence on temperature are interesting⁴². Similar temperature dependences of magnetic moments of some compounds under investigation have been observed by Lever *et al.*,

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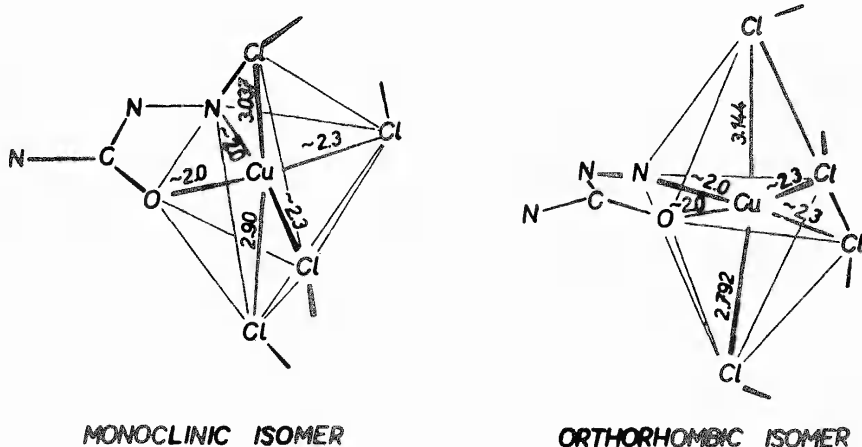


Figure 6b. Schematic representation of the coordination sphere around Cu^{II} of the orthorhombic and monoclinic isomers of $\text{Cu}(\text{NH}_2\text{NHCONH}_2)\text{Cl}_2$. Data from ref. 30.

as well as also for some compounds studied in our laboratory, as e.g. for CuA_2X_2 (Figure 10).

Based on direct methods Lever *et al.*⁴³ assume also that the two forms of CuRCl_2 ($\text{R} = \text{bis}(2\text{-pyridyl})\text{disulphide}$), the yellow-green and the blue compounds, are conditioned by the circumstance that the first exhibits a tetragonal octahedral coordination while the second is square.

It may be assumed that also in other cases of different modifications of copper(II) compounds, differing e.g. in their magnetic properties⁴⁴, or expressively in colour in dependence on the temperature⁴⁵, the differences mentioned will be in connection with different possible degrees of distortion of the coordination polyhedron around the central atom. The effect of this distortion may then be also shown in different degrees of polymerization, magnetic super-exchange, different interactions between the atoms in axial positions and the equatorial plane of the coordination polyhedron, etc.

There are, however, many more similar cases of the existence of different modifications of Cu^{II} compounds and we are persuaded that their number will increase in the near future partly due to application of modern techniques and partly also as a consequence of purposeful research of this phenomenon.

Hitherto existing knowledge has shown that the occurrence of different forms of copper(II) compounds in most cases may not be attributed to *cis-trans* space isomerism.

A considerable number of instances prove that for copper(II) compounds in the solid state we may observe the existence of different modifications, differing in their structures by different degrees of distortion from some

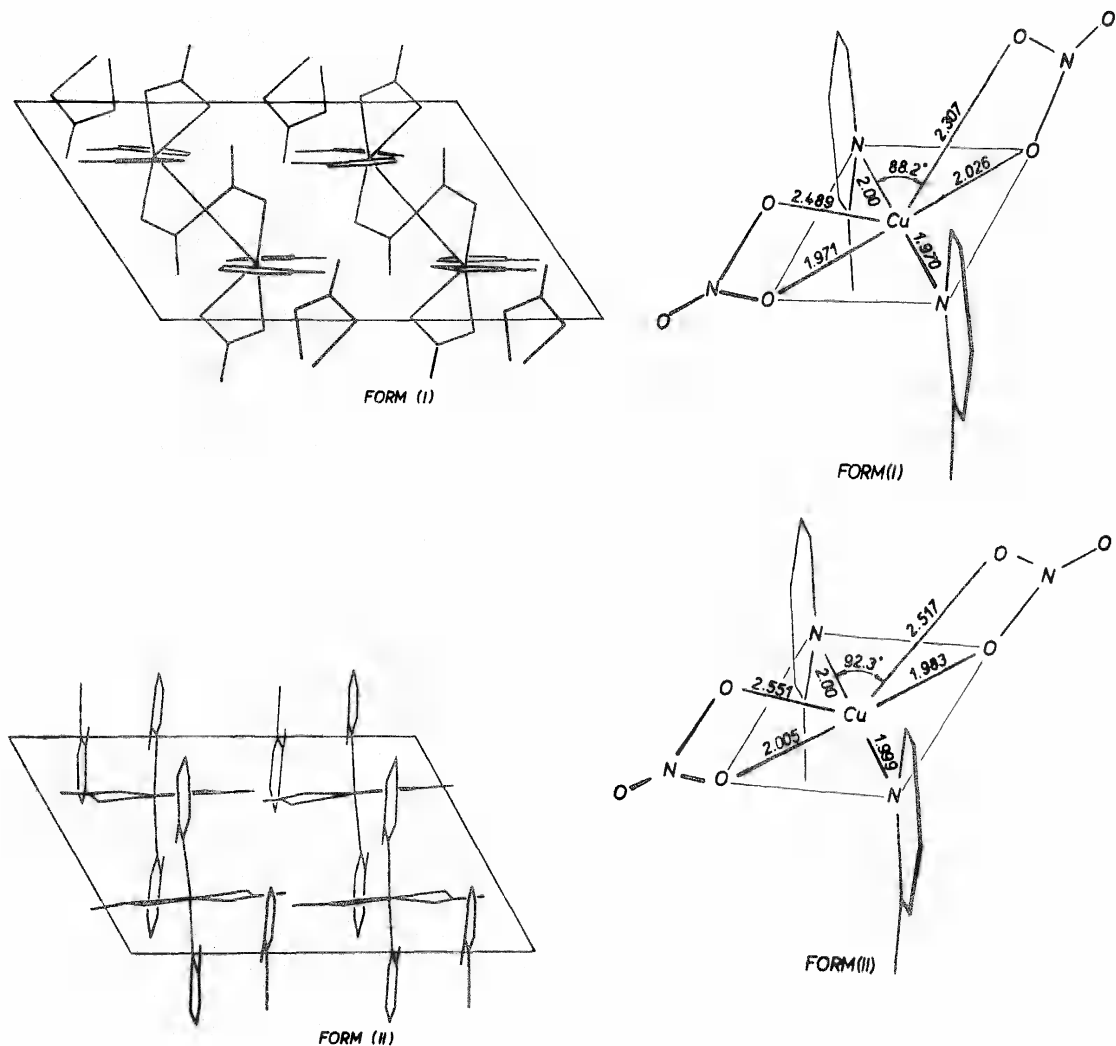


Figure 7. Schematic representation of the coordination sphere around Cu^{II} and crystal structure of form (I) and form (II) of $\text{Cu}(2\text{-pic})_2(\text{NO}_3)_2$. Data from ref. 31. (b) Form (II).

ideal coordination polyhedron. The modifications exhibit different properties being in direct connection with bonding interaction of the central atom with its ligands (electron spectra, i.r. spectra, magnetic properties as well as different chemical conditions of formation, differences in decomposition mechanisms and in chemical reactivity)^{13, 14, 26, 46-48}. In the case when the differences between the modifications of Cu^{II} compounds are due to the different distortion degree of the coordination polyhedron (which may cause still other effects, e.g. different degrees of polymerization), we call these differences distortion isomerism.

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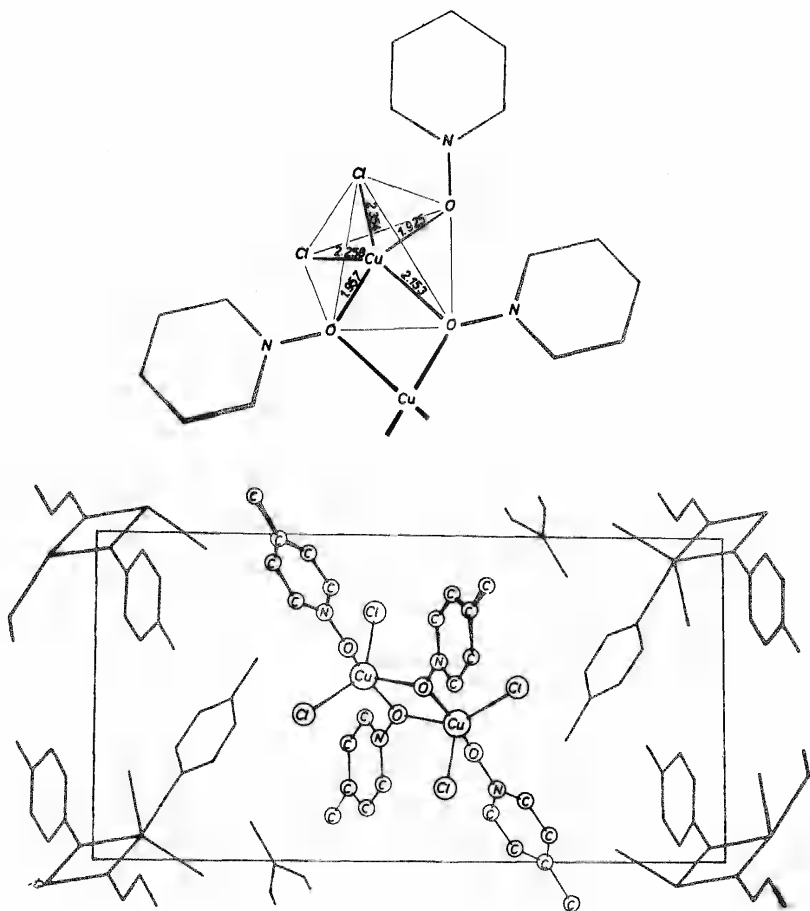


Figure 8a. Schematic representation of the coordination sphere around Cu(II) and crystal structure of yellow modification of dichlorobis(4-methyl-pyridine *N*-oxide) copper(II). Data from ref. 36.

Even though distortion isomerism of copper(II) compounds, in most cases, is connected with differences in axial positions, often may be found expressive differences also in the whole coordination sphere (interatomic distances and valence angles between the central atom and the ligand atoms to which it is directly coordinated) as well as in the conformation of ligands.

As in the changes of one isomer to the other no rearrangement of ligands is necessary but only by their partial shifts, the isomerization is realized by rather inconsiderable changes of conditions (temperature, pressure) and this is also to be observed in the reversible thermochromism of some of these compounds.

A peculiarity of distortion isomerism is the possibility of the existence of intermediates between two limited distortion states.

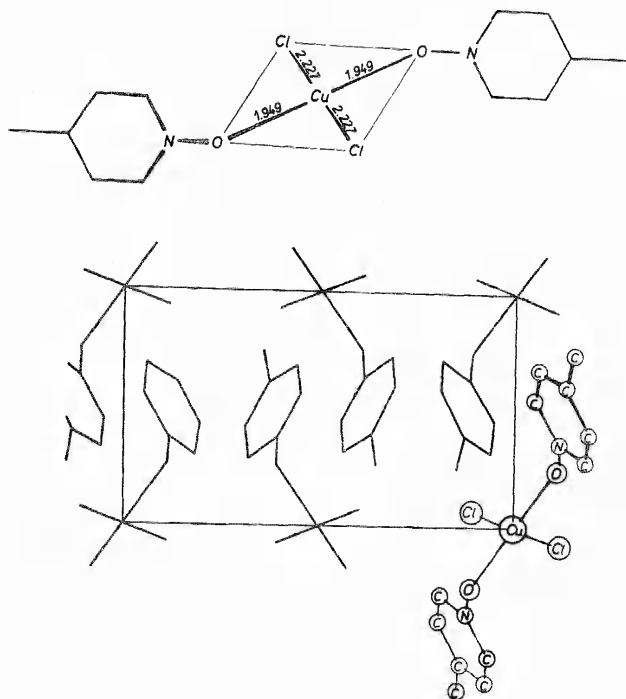


Figure 8b. Schematic representation of the coordination sphere around Cu^{II} and structure of green modification of dichlorobis(4-methylpyridine *N*-oxide)copper(II). Data from ref. 36.

Though we have deduced the concept of distortion isomerism on the basis of experimental knowledge of copper(II) compounds in the solid state, there are also experimental reasons to suspect this type of isomerism for Cu^{II} compounds also in solutions (dependence of preparing modification on the conditions in solutions)^{4, 6, 18}.

DISCUSSION: ASPECTS OF DISTORTION ISOMERISM

The existence of different modifications of some copper(II) compounds, differing only in the degree of distortion from some geometrically ideal coordination polyhedron, is, of course, not a sufficient factor to mark this phenomenon as 'distortion isomerism'. In this connection in order to understand the concept of isomerism itself, one must draw attention to the influence of the crystal structure as a whole on the isomerism and to the influence of the ligand properties on the rise of this phenomenon, and also to the question of the causes of different degrees of distortion of the

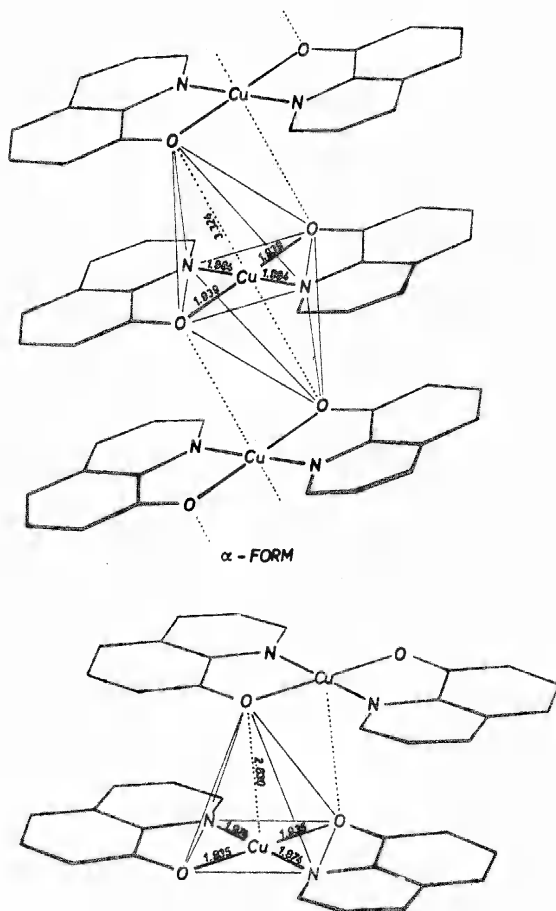


Figure 9. Schematic representation of the coordination sphere around Cu^{II} in structural fragment of α -copper 8-hydroxyquinolate and β -copper 8-hydroxyquinolate. Data from ref. 38.

coordination polyhedron in connection with properties of the central atom.

Though isomerism has become a classic concept of coordination chemistry, it appears necessary to restate the position with respect to theory as well as experimental research of the structure of coordination compounds. In connection with the dynamics of nuclei of coordination compounds obviously it is not sufficient to state that two isomers differ by the configuration of their atomic nuclei. We must agree with Bersuker⁴⁹ according to whom 'it is justified to state that these two configurations correspond to two

formations of the same composition (isomers, tautomers, etc.) only when those configurations correspond to two different minima of adiabatic potential, with the (least) depth of about twice as much as the oscillation quanta in the minimum'. With respect to experimental identification of such different configurations the relativity rule to the means of observation⁵⁰ plays an important part, expressing the possibility of recording the state corresponding to a certain minimum of the adiabatic potential in dependence on

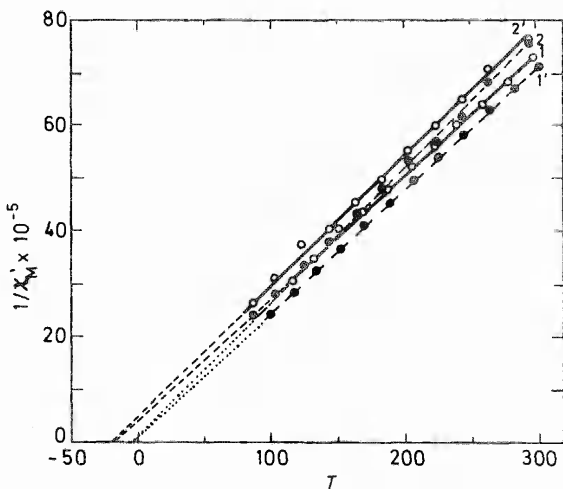


Figure 10. Dependence of $1/\chi_M'$ on T for the blue (1) and red isomers (1') of $\text{Cu}[\text{asym}(\text{C}_2\text{H}_5)_2\text{en}]_2(\text{NO}_3)_2$, as well as of α -(2) and β - $\text{Cu}(\text{cyclohexylamine})_2\text{Cl}_2$ (2'). Data from refs. 39 and 26.

the lifetime of this state and the duration of the experimental observation. In other words, if the observation is longer than the mutual change of states corresponding to different minima of the adiabatic potential, in observing we register the average state of the substance and not the different possibilities of atom configurations, corresponding to the minima on the curve of the adiabatic potential and vice versa. In this connection we see that in studying isomerism not only questions of the methods of observation used came to the fore, but also the temperature at which the observation was made. The longer the observation time and the higher the temperature, the smaller are the possibilities to register the states corresponding to the different minima on the curve of the adiabatic potential. This circumstance underlines the importance of investigating the distortion isomerism of copper(II) compounds at low temperatures and confirms the necessity of the kind of investigation that has already been applied^{39, 42}.

The experimental results that lead to the formulation of the concept of 'distortion isomerism' for copper(II) compounds prove that even using relatively long observations (as e.g. for x-ray analysis, magnetic moments, long-term study of 'isomerization') this phenomenon for Cu^{II} compounds

may be observed. This would indicate that between the states with different types of distortion of coordination polyhedron, there are sufficiently high energetic barriers, i.e. a relatively long time is necessary to overcome these barriers. The fact that for some compounds also so-called intermediates were observed at the room temperature^{11-13, 19, 20} indicates the possibility of the existence of several minima on the curve of the adiabatic potential, to which correspond the really ascertainably different configurations of atomic nuclei of the given copper(II) compounds. With respect to the latter statement the results of the study of temperature dependence of the tetragonal distortion for some copper(II) compounds with thermochromic properties are interesting³⁹.

Concluding the question, whether the observed phenomenon of the existence of copper(II) compounds in different forms differing by various degrees of distortion from some ideal coordination polyhedron may be denoted by the word isomerism, we must make the following remark: From a merely crystallographic standpoint it might be possible to interpret the experimentally observed facts also in connection with the term of polymorphism, or eventually denote some of the modification couples otherwise (e.g. coordination polymerism, since the polymerization degree of some coordination polyhedra is sometimes different). The fact that in all the cases, irrespective of the circumstance, whether we have considered molecular structures or cases of the same or of different polymerization degree of coordination polyhedra, the feature of the differences remains in the different degree of distortion of coordination polyhedra (which also arises in considering structure problems from the point of view of crystallographic polymorphism) and lets us suggest that the term isomerism of coordination polyhedron is in our cases justified. There actually exists a mutual conditionality between the polymorphism of crystals (as also coordination polymerism) and the ability of copper(II) compounds to exhibit different distortion degrees of their coordination polyhedra.

While for assigning the phenomenon observed for copper(II) compounds to the conception of isomerism it is sufficient to define the term isomerism and to confront it with the experimental observations, elucidation of the reasons causing the distortion isomerism of copper(II) compounds is a more pretentious task.

The above facts proved the occurrence of distortion isomerism in copper(II) compounds in the solid crystalline state. Such an isomerism in the solid state may be caused as much by specific properties of the compound as by effects concerning crystal structure as a whole.

It is not surprising that in this connection the question arises, whether the existence of distortion isomerism is not conditioned only by this last reason. This standpoint is also supported by the fact that the occurrence of different modifications may be explained by the geometry of the crystal structure and by the possibility of closest possible arrangement. Stackelberg⁵ applied this explanation of the existence of some modifications of copper(II) compounds, and starting from the method of symmetry of 'potential functions and overlapping trajectories' Zorkij, Valach and Poraj-Košic⁵¹ substantiate the possibility of the existence of different crystalline forms of the $\text{Cu}(\text{NH}_3)_2(\text{SCN})_2$. Information on the different physical properties of the

differing modifications of copper(II) compounds pointing out directly the bonding properties of the central atom prove on the other hand that there also must be differences between the distortion isomers from the chemical point of view. Also the fact that distortion isomerism appears for compounds of a certain central atom suggests the importance of the peculiarities of the electron shell of the central atom for the existence of distortion isomerism. In our opinion elucidation of the existence of distortion isomerism for copper(II) compounds with respect to the reasons caused by specific properties of the central atom on one side and to those connected with the laws of the solid state on the other side is not contradictory, but these two explanations complement each other.

An example of mutual conditionality of these two factors may be found just in the chemistry of those copper(II) compounds, where the Jahn–Teller effect is expected. In the case of copper(II) compounds with a homogeneous coordination sphere, where due to the Jahn–Teller effects three types of distorted octahedra may occur (along the three axes), we can understand that, influenced by the surroundings, a stationary tetragonal distortion of the coordination sphere may occur and this is why we find in some complexes ligand arrangements in the form of a tetragonal bipyramid (as e.g. in the ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$)⁵². Likewise it is understandable that in some cases (as e.g. in $\text{K}_2\text{PbCu}(\text{NO}_2)_6$)⁵³ a situation may occur, being seemingly conflicting with the conclusions following from the Jahn–Teller effect just because the lattice allows some dynamics between the different tetragonal distortions and such a case results in the average regular octahedral arrangement of ligands around copper(II). Starting from the knowledge of the symmetry of coordination polyhedra of copper(II) compounds with a homogeneous coordination sphere, we again must agree with the opinion⁵⁴ that for these compounds the distortion of the coordination polyhedron in the crystal is influenced by specific electron properties of the central atom as well as by the arrangement in the crystal structure fixing a certain type of tetragonal distortion.

In discussing the question of influences by effects arising from specific properties of the central atom Cu^{II} and from the laws of crystal structure on the occurrence of distortion isomerism of copper(II) compounds we must explain our opinion on the relationship between conformation of ligand and distortion isomerism. This is also stimulated by the fact that some copper(II) compounds exhibit quite unusual conformations of ligands⁵⁵, and that the distortion isomers of copper(II) compounds show differences in the geometry of ligands^{20, 29, 30}.

Also in discussing this question it appears logical to express the concept of mutual relationship between distortion isomerism and ligand conformation. This opinion is in full agreement with the present theories of the chemical structure of coordination compounds. The compounds are interpreted with respect to the problems of bonding of the particle as a whole, as well as with respect to the experimental results as consequences of mutual interaction of the indirectly bonded atoms in the compound (e.g. induction effects in organic compounds, *trans*-effect in Pt^{II} compounds⁵⁶, redox properties of Cu^{II} compounds and mutual influence of their ligands)⁵⁷. The fact that distortion isomerism of copper(II) compounds occurs even there, where no

conformation of ligands is observed (e.g. in isomers of $\text{Cu}(\text{NH}_3)_2\text{Br}_2$)^{9, 10}, or that unusual geometries of ligands are the accompaniments of distortion isomerism (e.g. deviations from linearity of the NCS^- groups in distortion isomers of $\text{Cu}(\text{NH}_3)_2(\text{NCS})_2$)²⁰ allow us again to suggest a primary influence of the properties of the central atom on the occurrence of distortion isomerism, one of the consequences of which is the changing conformation of the ligands. This does not exclude, of course, the reverse influence of the possibility of ligand conformation on the occurrence of distortion isomerism of copper(II) compounds.

An expressive mutual influencing of the geometry of coordination polyhedra of copper(II) compounds and of the surroundings has been clearly shown in ref. 58. This paper showed that in binuclear copper(II) compounds small stereochemical changes in the region of one central atom are able to cause great stereochemical effects in the region of the other Cu^{II} atom.

A great number of experiments today unambiguously prove that distortion (often tetragonal distortion) is a typical phenomenon also for copper(II) compounds with a heterogeneous coordination sphere⁵⁹. The question of the reasons causing the distortion of an ideal coordination polyhedron for copper(II) compounds with heterogeneous coordination spheres is not yet solved and is up to now an open question. Consequently the problem of the reasons causing the existence of distortion isomerism of copper(II) compounds with heterogeneous coordination spheres is on the whole not cleared up, though different steps were taken for its interpretation.

After the experimental evidence of the existence of two modifications of $\text{Cu}(\text{NH}_3)_2\text{Br}_2$ ^{9, 10} in the form of the different type of distorted tetragonal bipyramid, there appeared a paper⁶⁰, bringing this case into correlation with the Jahn-Teller effect and suggesting to call this kind of isomerism 'affinity isomerism'. Though there were objections⁶¹ to the simple interpretation of the fact found with respect to the Jahn-Teller effect, on the basis of calculations, Bersuker showed that in principle compounds of the composition MA_4X_2 may exhibit two types of tetragonal bipyramid, differing, however, only in their interatomic distances on the axis $\text{X}-\text{Cu}-\text{X}$. Though this conclusion could not be simply applied to the modifications of $\text{Cu}(\text{NH}_3)_2\text{Br}_2$ it is interesting for two reasons: as an example of theoretical explanation of distortion isomerism of copper(II) compounds with heterogeneous coordination sphere and today perhaps also as a certain possibility of elucidation of some cases of known distortion isomerism of copper(II) compounds.

The fact that from formal aspects the situation with respect to the distortion of an ideal coordination polyhedron for homogeneous and heterogeneous copper(II) compounds is analogous, leads some authors to explain also in heterogeneous copper(II) compounds the necessity of such distortion. This is made from the point of view that 'although the molecular symmetry is irregular, the "effective" electronic symmetry is regular and will require a distortion to remove the degeneracy'⁶².

Calculations have been made to explain for copper(II) compounds with chain structure (starting from the concept of Jahn-Teller type vibronic interactions leading to some instability effects) the existence of different

distortion forms of these compounds^{63†}.

The complication in solving the question of the reasons causing the existence of distortion isomerism with respect to the specific properties of copper(II) is also indicated by Miller *et al.*⁵². They showed that the data known so far of the seven Cu^{II} compounds which satisfy the requirements of donor site equivalence indicate a tetragonality ratio T ($T = R_S/R_L$, where R_S and R_L are the main equatorial and axial bond distances) not differing substantially from this ratio in Mg^{II} and Ni^{II} compounds, where the Jahn–Teller effect is not taken into consideration. The exception is the ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. This comparison led the authors⁵² to the conclusion that the static Jahn–Teller effect is either small, or not detectable; besides they point out the importance of finding this effect at low temperatures. Thus the basic question for the reasons causing distortion of ideal coordination polyhedra in copper(II) compounds with heterogeneous coordination spheres in their crystals is until now not explained satisfactorily. To fulfil this task certainly it will be necessary to have experimental data serving as criteria for theoretical elucidation. Our aim, which is to evaluate the knowledge obtained so far and to point out the existence of distortion isomerism for copper(II) compounds, has to be understood and correlated also in connection with this aspect.

Concluding the discussion on the problems of distortion isomerism for copper(II) compounds we would like to express opinions on two questions: that of exclusiveness of this type of isomerism to copper(II) and that of the topicality of the study of these problems.

The first question has two aspects: the experimental and the theoretical. From the experimental aspect we may expect that the application of modern methods of research will bring knowledge on the ability of compounds of other central atoms to appear in several forms differing from each other by the configuration of their atom nuclei formally being analogous to the distortion isomerism of Cu^{II} compounds. Such a case has been already found in the so-called configurational isomerism of nickel(II) compounds⁶⁴. The difference in the configurations, d^8 for the central atom of nickel(II) compounds and d^9 for that of copper(II) compounds, is with respect to the discussed aspect rather significant. The stereochemistry and therefore also the isomerism of d^8 compounds of Ni^{II} is characterized by alternation in spin multiplicity and for these compounds the Jahn–Teller effect is not taken into account. This probably means that it will not be possible to explain the reasons for different distorted tetragonal bipyramids of coordination polyhedra for copper(II) compounds on the one hand, and the existence of octahedral and square-planar nickel(II) compounds as isomers on the other,

† According to Bersuker⁶³ the identity of ligands and the defined degeneration are not necessary for the Jahn–Teller effect. This effect also appears for the case that neither the differences between the ligands nor the splitting of the degenerated term are too great. For such a case the discussed phenomenon obtained the name 'Jahn–Teller pseudoeffect'⁶³. According to Bersuker certain differences between the ligands even cause the stabilization of some minima on the curve of the adiabatic potential. This makes it possible to determine this state by x-ray analysis.

from the same starting points. This does not exclude, however, a certain analogy in the mentioned non-classical types of isomerism for Cu^{II} and Ni^{II} compounds (e.g. in similar space possibilities of their isomerization).

The vigorous development of experimental techniques for the structural study of complex compounds, its precision and the increasing rapidity of obtaining information due to automation allows the gathering of such information as interatomic distances, distortions of atom groups, the so-called valence angles, i.e. of the molecular geometry which were initially not taken into account either in the classic or in the modern theoretical conceptions. This not only makes it possible by experiment to detect the existence of substances in new forms, with nuances in their structure differences, but also stimulates the development of theoretical concepts of chemical structure of substances and provides presuppositions for their new qualitative development.

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† On the other hand there also exists the opinion⁶³ that an excited degenerated state near the ground state for Ni^{II} may lead to the Jahn-Teller pseudoeffect with distortions analogous to those observed for the polyhedra of Cu^{II} complexes. This concept would allow the elucidation of the distortion isomerism of copper(II) complexes and also the configuration isomerism of nickel(II) complexes from an analogous theoretical basis.

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