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PLASTICITY OF THE COORDINATION SPHERE OF COPPER(II) COMPLEXES, ITS MANIFESTATION AND CAUSES

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CONTENTS

A. INTRODUCTION

The ability of coordination polyhedra to undergo distortion has been known in chemistry for some time. These distortions are determined by internal tendencies in substances and are realized by external influences.

Present experimental methods permit us to determine comparatively very fine structural features in compounds and also to detect the existence of new types of modifications and isomers. Likewise the development of modern theory leads to the stage where certain particularities of the distortion of coordination polyhedra may be satisfactorily explained in connection with the electron configuration of their central atoms. These new possibilities given by

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experiment and theory allow us to present some new aspect of the stereochemistry of copper(II) complexes connected with the plasticity of their coordination sphere.

We are using the term "plasticity" to describe a special case of non-rigid complexes [1], caused by a feature of the central atom's electronic shell.

The aim of this paper is to discuss in more detail the following statements made on the basis of experimental results and quantum chemistry analysis.

1. The coordination sphere of Cu^{II} octahedral complexes, in contrast to most other central atoms, clearly demonstrates some pronounced properties of plasticity (non-rigidity) in the sense that it may have not one but several (or an infinite number of) stable configurations which differ in metal—ligand distances. These plasticity properties are shown to be due to the Jahn—Teller or pseudo-Jahn—Teller effect and hence they may occur with other metal complexes (as well as other molecular systems) with degenerate and pseudodegenerate electronic terms.
2. The so-called distortion isomers of Cu^{II} complexes [2], elaborated earlier, occur as a consequence of the plasticity properties of the Cu^{II} coordination sphere combined with the stabilization properties of the crystal lattice. The compromise between these two characteristic properties, local and crystal, leads in the case under consideration to several stable configurations with nearly equal energies which can be observed at the same (room) temperature.

B. STEREOCHEMISTRY OF COPPER(II) COMPLEXES IN THE SOLID STATE AND THE PLASTICITY OF THEIR COORDINATION SPHERE

As far as their structure is concerned, copper(II) compounds display a richness of shapes. This is due to a great number of various coordination polyhedra, related to the possibility of distortion of the coordination polyhedron around Cu^{II}. Structures of Cu^{II} compounds have been studied fairly extensively, several hundreds having been solved by single crystal X-ray analysis. Apart from this, intensive research into the structure of Cu^{II} compounds is being undertaken with the aid of indirect physicochemical and physical methods.

The coordination numbers of copper(II) vary from four to seven. The most usual are the four, five and six coordination numbers.

The schematic representation of the coordination polyhedra of copper(II) should be completed by further types shown in Fig. 1. In subsequent paragraphs we shall try to show how far the arrowheads in the scheme have just a formal character and how far they represent a successive and continuous transition from one type of coordination to another (we will not deal here with the case of square—tetrahedron transition though experimental evidence exists for this mutual transformation [3—5]).

In complexes of Cu^{II}, continuous transition from one type of coordination to another may be demonstrated using the example of distorted octahedral coordination. Here the bonding angles change very little and thus handling of experimental data is greatly facilitated. Since there are many factors which

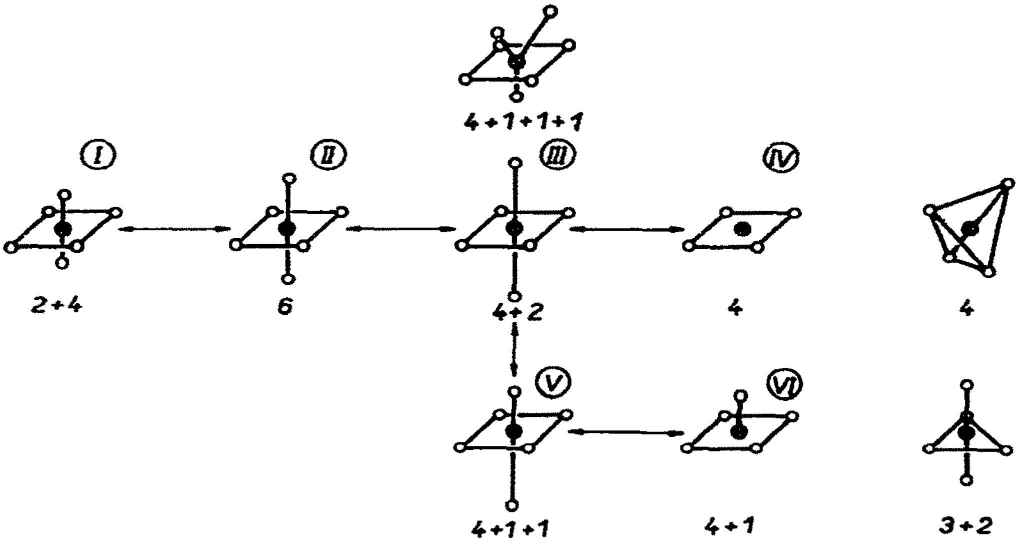

Fig. 1. Scheme of coordination polyhedra of copper(II) complexes

influence the structure of a crystal, (e.g. formation of hydrogen bonds, interaction of ligands, neighbouring atoms and molecules, lattice defects, etc.), useful correlations must be based on a great many structural results. A statistical elaboration of data is necessary in spite of the fact that they were obtained by various techniques and consequently their degree of accuracy and precision varies a great deal. With regard to these circumstances we concentrate chiefly on structures in which the coordination number of Cu^{II} is six. This is the most common coordination number and a great number of structures have been solved.

In this part of the paper we try to prove that there exists the possibility of dynamic transition between the coordination polyhedra as arrowed in Fig. 1. In this connection we determined and correlated the quantities R_S and R_L for the chromophores CuO_6, CuN_6 and CuN_4O_2. R_S is the average value of the four interatomic distances in the equatorial plane and R_L is the central atom—donor atom distance at the fifth and sixth coordination sites for coordination number 4 + 2 (tetragonally distorted octahedron).

We were also stimulated by Hathaway and Hodgson [6], who investigated the dependence of T (tetragonality) on the parameters R_S and R_L for some copper(II) complexes. Our investigation also followed work by Tomlinson et al. [7] who studied the dependence of R_S on R_L for compounds of the type $Cu(NH_3)_4X_2$, to find out how distorted the bond Cu—X has to be, in order to be considered a case of "semicoordination". Our correlation led to the conclusions presented here to demonstrate that the transitions shown in Fig. 1 are possible. These conclusions express at the same time certain special properties of the stereochemistry of the coordination polyhedron of Cu^{II}.

A correlation exists between the variation of axial and equatorial interatomic distances in Cu^{II} complexes. We shall prove this on the basis of crystallochemical data for some chromophores. The same conclusion may also be drawn from some structure studies of copper(II) complexes by indirect methods, as discussed, for example, in papers by Lever et al. [8,9]. For irregular deformed octahedral coordination (coordination number 4+1+1) the symbols R_L^6 and R_L^5 are introduced; these are chosen in such a way that the ratio R_L^6/R_L^5 should be greater than one (Fig. 2). The values R_S and R_L for the group of Cu^{II} compounds with a homogeneous and quasi-homogeneous coordination sphere * and with the coordination number 4+2 are given in Tables 1 and 2. For these compounds the pertinent correlations are shown in Figs. 3a and 3b.

The coefficients of order correlation and their critical values on the significance level of 0.01 with $\nu = n - 2$ degrees of freedom, where n denotes the number of experimental data of the respective set [84] are collected in Table 3 For both correlations the relation $|R| > R_{crit}$ holds, thus their coefficients of order correlation are statistically significant. Some experimental data in these diagrams diverge considerably from the statistical mean values, most probably being due to experimental error. These values were not taken into account in the calculation of correlation coefficients and in the diagrams these points are marked by full circles (Figs. 3a and 3b).

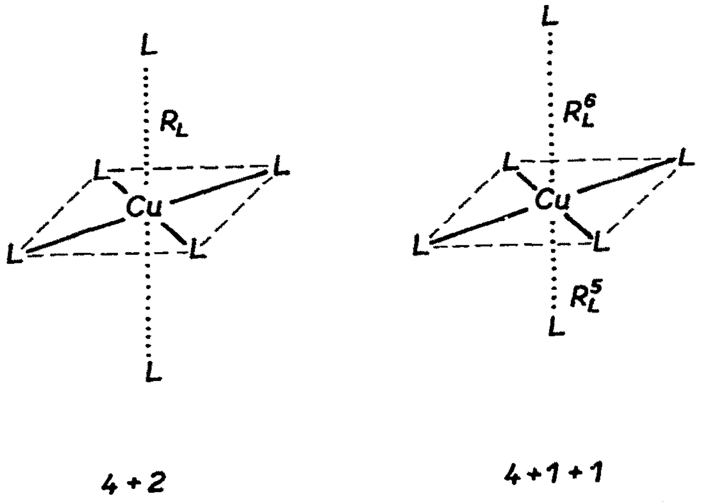

Fig. 2. Schematic representation of the values of R_L, R_L^6 and R_L^5 in coordination polyhedra.

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* With the expression "homogeneous coordination sphere" we understand the coordination sphere of those complexes which have not only identical atoms coordinated directly to the central atom, but those atoms belonging to the same ligands. The expression "quasi-homogeneous sphere" denotes cases, when the same atoms are coordinated to the central atom, as e.g. CuN_6 and CuO_6, but they are not, however, equivalent since they belong to different ligands.

TABLE 1

Values of R_S and R_L of some copper(II) compounds with the CuO_6 chromophore and coordination number 4+2

Compound	R_S [Å]	R_L [Å]	Ref.
$Cu(C_6H_4OHCOO)_2 \cdot 4H_2O$	1.88	3.00	10
$Cu(PCD)_2$	1.88	3.07	11
Cu(salicylaldehydate)$_2$	1.90	3.24	12
Cu(ethyl acac)$_2$	1.91	3.12	13
Cu(2,4-diphenyl acac)$_2$	1.91	3.14	14
Cu(3-methyl acac)$_2$	1.91	3.22	15
Cu(tropolone)$_2$	1.91	3.30	16
Cu(3-phenyl acac)$_2$	1.91	3.50	17
Cu(glycollate)$_2$	1.92	2.54	18
Cu(1-phenyl acac)$_2$	1.92	3.06	19
Cu(acac)$_2$	1.92	3.08	20
Cu(salicylaldehydate)$_2$	1.92	3.15	21
Cu(salicylaldehydate)$_2$	1.92	3.21	22
Cu(ω-nitroacetophenate)$_2$	1.93	2.60	23
$Na_2Cu(CO_3)_2$	1.93	2.77	24
$Cu(C_5H_5NO)_4(ClO_4)_2$	1.93	3.38	25
$Cu(C_6H_5COO)_2 \cdot 3H_2O$	1.94	2.51	26
$Na_2Cu(PO_3)_4$	1.94	2.52	27
Cu(*meso*-tartrate) · 3 H_2O	1.94	2.54	28
$Cu(OMPA)_2(ClO_4)_2$	1.94	2.55	29
Cu(phthalate)$_2$ · H_2O	1.94	2.58	30
$Cu(OH)_2$	1.94	2.63	31
CuB_2O_4	1.94	3.07	32
$CuSO_4$	1.95	2.37	33
$Cu_2P_4O_{12}$	1.95	2.38	34
Cu(*d*-tartrate) · 3 H_2O	1.95	2.40	28
Cu(*meso*-tartrate) · 3 H_2O	1.95	2.48	28
Cu(2-hydroxy-2-methyl-propionate)$_2$ · 2 H_2O	1.95	2.56	18
$CuUO_4$	1.95	2.56	35
$Cu(C_8H_5O_4)_2 \cdot 2H_2O$	1.95	2.68	36
Cu(H-maleate)$_2$ · 4 H_2O	1.95	2.68	37
CuO	1.95	2.78	38
$CuSO_4 \cdot 3H_2O$	1.96	2.42	39
$Ca(Cu,Zn)_4(OH)_6(SO_4)_2 \cdot 3H_2O$	1.96	2.43	40
Cu(phthalate)$_2$ · H_2O	1.96	2.46	30
Cu(phenoxyacetate)$_2$ · 2 H_2O	1.96	2.50	18
$Ca(Cu,Zn)_4(OH)_6(SO_4)_2 \cdot \cdot 3H_2O$	1.96	2.52	40
$PbCuSO_4(OH)_2$	1.96	2.53	41
$CuSO_4 \cdot 5H_2O$	1.97	2.41	42
$Cu(NaSO_4)_2 \cdot 2H_2O$	1.97	2.41	43
$Cu_2O(SO_4)$	1.97	2.52	44
β-$Cu_2P_2O_7$	1.97	2.58	45
$Cu_2(OH)_2CO_3$	1.97	2.58	46
$Cu_6(Si_6O_{19}) \cdot 6H_2O$	1.97	2.68	47

TABLE 1 (continued)

Compound	R_S [Å]	R_L [Å]	Ref.
$Cu(C_2H_5OCH_2COO)_2 \cdot 2H_2O$	1.98	2.38	48
$CuWO_4$	1.98	2.40	49
$CuIO_3(OH)$	1.98	2.59	50
$Cu_5(PO)_2(OH)_4$	1.98	2.69	51
Cu(cronotate)$_2 \cdot 2H_2O$	1.99	2.33	52
$Tl_2[Cu(SO_3)_2]$	1.99	2.44	53
$Ba_2Cu(HCOO)_6 \cdot 4H_2O$	2.00	2.18	54
$Cu(HCOO)_2 \cdot 2H_2O$	2.00	2.30	55
$Cu(CH_3C_6H_4SO_2) \cdot 4H_2O$	2.00	2.34	56
$Cu_2(OH)_2CO_3$	2.00	2.36	46
$Cu(HCOO)_2 \cdot 4H_2O$	2.01	2.36	57
$Cu(HCOO)_2 \cdot 2H_2O$	2.01	2.37	55
$[C_{14}H_{19}N_2]Cu(hfacac)_3$	2.02	2.18	58
$Cu(CH_3OCH_2COO)_2 \cdot 2H_2O$	2.03	2.13	18
$CdCu_3(OH)_6(NO_3)_2 \cdot H_2O$	2.03	2.43	59
$K_2BaCu(NO_2)_6$	2.04	2.29	60
$Cu_2(OH)AsO_4$	2.04	2.34	61
$Cu_4(NO_3)_2(OH)_6$	2.04	2.34	62
$CuCrO_4$	2.05	2.15	63
$Cu_4(NO_3)_2(OH)_6$	2.05	2.23	62
$(NH_4)_2Cu(C_2O_4)_2 \cdot 2H_2O$	2.05	2.49	64
$(NH_4)_2Cu(C_2O_4)_2 \cdot 2H_2O$	2.05	2.74	64
$Ca(Cu,Zn)_4(OH)_6(SO_4)_2 \cdot 3H_2O$	2.06	2.23	40
$Cu(OMPA)_3(ClO_4)_2$	2.07	2.07	65
$Cu(H_2O)_6SiF_6$	2.07	2.07	66
$Cu(IPCP)_3(ClO_4)_2$	2.07	2.11	67
$Cu_2(OH)PO_4$	2.07	2.28	68
$Cu(NO_3)_2HgO \cdot 3H_2O$	2.10	2.10	69
$Ca(Cu,Zn)_4(OH)_6(SO_4)_2 \cdot 3H_2O$	2.11	2.11	40
$Cu(ClO_4)_2 \cdot 6H_2O$	2.13	2.28	70
$Cu(H_2O)_8(UO_2)_4(AsO_2)_2$	2.14	2.58	71
$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$	2.15	1.97	72

Abbreviations: PCD, *N*-phenyl-2-carbamoyl-5,5′-dimethylcyclohexane-1,3-dienate; acac, acetylacetonate; OMPA, octamethylpyrophosphoramide; hfacac, hexafluoroacetylacetonate; IPCP, tetraisopropylmethylenediphosphonate.

From the plots in Figs. 3a and 3b the following conclusions may be drawn for coordination number 4+2:

1. The coordination sphere in the CuO_6 and CuN_6 species may be described as a symmetrically axially distorted octahedron (tetragonal bipyramid). There are four structures of copper(II) complexes with a chromophore CuO_6 and two structures with a chromophore CuN_6 which are exceptions in that the

TABLE 2

Values of R_S and R_L of some copper(II) compounds with the CuN_6 chromophore and coordination number of 4+2

Compound	R_S [Å]	R_L [Å]	Ref.
β-Cu(phthalocyanine)$_2$	1.94	3.28	73
Cu(ethylenebidiguanide)$Cl_2 \cdot H_2O$	1.96	3.17	74
$Cu(C_4H_7N_5O)_2(ClO_4)_2$	1.97	3.14	75
$Cu(NH_3)_4(NO_2)_2$	1.99	2.65	76
$Cu(NH_3)_2(N_3)_2$	2.01	2.62	77
$Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2 \cdot NH_3$	2.01	2.88	78
Cu(phen)$_3(ClO_4)_2$	2.05	2.33	79
Cu(N,N′-$(CH_3)_2$en)$_2$(NCS)$_2$	2.06	2.52	80
[Cuen$_2$]Hg(SCN)$_4$	2.08	2.58	81
$K_2PbCu(NO_2)_6$	2.11	2.11	82
Cuen$_3SO_4$	2.15	2.15	83

Abbreviations: phen, o-phenanthroline; en, ethylenediamine.

central atom has a regular octahedral configuration. The dashed lines in Figs. 3a and 3b represent the regular octahedron.

2. The interatomic distances R_L in the axial direction of the tetragonal bipyramid depend unambiguously (within the limits of experimental error) on the average value of the interatomic distances in the equatorial plane R_S. The

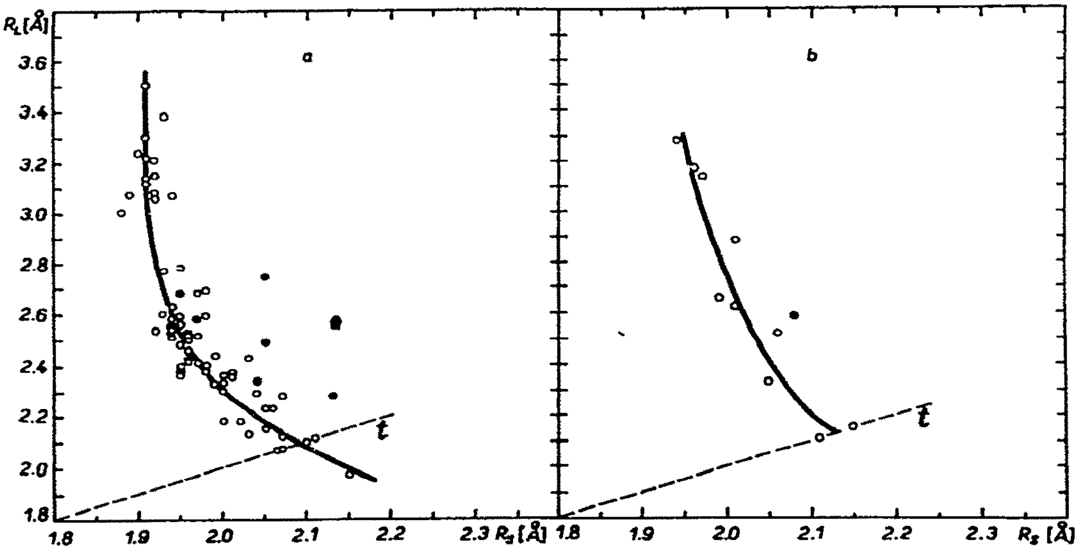


Fig. 3. Diagram R_S vs. R_L for copper(II) complexes with the coordination number 4+2, 6 and 2+4; a — chromophore CuO_6; b — chromophore CuN_6.
The data in Fig. 3a are tabulated in Table 1; the data in Fig. 3b are tabulated in Table 2.

TABLE 3

Values of the coefficients of order correlations

Chromophore	Correlation	R	$\nu = n - 2$	R_{crit} [a]
CuO_6	R_S vs. R_L	−0.851	71	0.302
CuN_6	R_S vs. R_L	−0.949	8	0.765
CuN_6, CuN_4O_2	R_S vs. R_L or R_L(c)	−0.664	37	0.418

[a] Critical value of coefficient of order correlation.

tetragonal bipyramidal coordination of the Cu^{II} atom in these compounds represents a unit in which an increase of the interatomic distances in the plane leads to a strengthening of the chemical bonds, and consequently, to shortening of interatomic distances in the axial direction. In the middle part of the curves (Fig. 3) the sum of all the interatomic distances Cu—L is constant and is approximately 12.6 Å for the chromophore CuO_6. An analogous sum for the chromophore CuN_6 is approximately 14.3 Å.

3. In the diagrams R_S vs. R_L for the chromophore CuO_6 there is lying under the line t only one point which refers to a molecule with a flattened tetragonal bipyramid. This is a rather unusual type of coordination for Cu^{II}. At the lower end the curve has to stop at such a value of the axial distance R_L, which is for steric reasons, still possible. The value of the minimal R_L is approximately 1.9 Å for the chromophore CuO_6, and 2.1 Å for CuN_6, respectively.

4. For the chromophore CuO_6 the curve $R_L = f(R_S)$ lies under the analogous curve for CuN_6.

5. The correlation R_S vs. R_L approaches the Y axis asymptotically. In the range where R_L is greater than 3.1 Å for the chromophore CuO_6 and 3.3 Å for CuN_6, R_S is relatively insensitive towards further increase of the value of R_L. For this reason the plots in Figs. 3a and 3b answer the question "how long may the distance Cu—X (where X is the oxygen or nitrogen atom) be and still be considered as a chemical interaction?" Evidently, it is that interatomic distance R_L at which no further decrease of the value R_S takes place. At such an interatomic distance the ligands in the plane approach the central atom at a minimal distance R_S^O(min), which for the chromophore CuO_6 is 1.92 Å. Comparing the above with paragraph 3 we see that this is approximately the same distance as the least possible distance R_L^O(min) in flattened tetragonal pyramidal coordination. By analogy, for the chromophore CuN_6, R_S^N(min) equals 1.95 Å, when the interatomic distance R_L is about 3.3 Å, and there is practically no chemical interaction between Cu^{II} and the nitrogen from the ligand in the axial position. The value of R_S^N(min) is smaller than that of R_L^N(min), which is most probably caused by the fact that the points in the lowest part of the curve of the CuN_6 chromophore (Fig. 3b) are not the lowest possible values of R_L, (it is possible that the parameter R_L may have a value lower than the minimum value R_L^N(min) $\approx$2.1 Å found to date).

6. *From the distribution of points in Figs. 3a and 3b it may be concluded that* transition between the various types of coordination for copper(II) compounds, represented by schemes I—II—III—IV in Fig. 1, is practically continuous in the range where R_L = 1.9—3.5 Å and R_S = 1.9—2.15 Å for the chromophore CuO_6; and for the chromophore CuN_6 where R_L = 2.1—3.3 Å and R_S = 1.9—2.15 Å. Hence, it is evident that in this range of interatomic distances we meet various types of distortion of the coordination polyhedron, the changes in the axial and equatorial positions being interdependent. It is a manifestation of the plasticity of the coordination sphere of Cu^{II} in that a flattening of the coordination polyhedron in one direction brings about elongation in the other direction, and vice versa. It is also a manifestation of the consequence of the mutual influence of ligands in copper(II) complexes on their stereochemistry.

It is also possible to show that some complexes of Cu^{II} with different ligands comply with the R_S vs. R_L relationship under certain circumstances. We examined data on complexes with the chromophore CuN_4O_2 which is frequently discussed in the literature. The oxygen atoms are always on the longer coordinate.

We designate experimental data for the interatomic distances Cu—O in the chromophore CuN_4O_2 by the symbol R_L^O. Then from the data for the square-planar complexes $R_S^O(\min)$ and $R_S^N(\min)$ (chromophores CuO_6 and CuN_6, i.e. cases where the axial interaction of the central atom with the ligand is excluded) we calculate with the aid of eq. (1)

$$\frac{R_L^O(c)}{R_L^O} = \frac{R_S^N(\min)}{R_S^O(\min)} \qquad (1)$$

the value of $R_L^O(c)$ (R_L^O corrected), which we take for the Cu—O interatomic distance in a hypothetical chromophore CuN_4O_2 in which the Cu—O distance in axial positions is calculated from this eq. (1).

As may be seen from Fig. 4, after using the above equation for the mixed ligand complexes with the CuN_4O_2 chromophore (Table 4) these complexes may also be included into the set of data for the CuN_6 chromophore (Fig. 3b). From Fig. 4 it follows that the values of $R_L^O(c)$, calculated with the aid of eq. (1), (in Fig. 4 marked by squares) agree with the data obtained from the coordination sphere for the CuN_6 chromophore. We did not succeed, however, in finding cases in which the value of $R_L^O(c)$ would be less than 2.5 Å. Also this diagram has a statistically significant coefficient of order correlation, (Table 4; data corresponding to the full squares in Fig. 4 have not been included in the calculation), and consequently, the existence of a mutual dependence between R_S and R_L or $R_L^O(c)$ can be confirmed.

In Figs. 5a and 5b the values of R_S vs. R_L^6/R_L^5 for copper(II) compounds with chromophores CuO_6 and CuN_6 or CuN_4O_2 (Tables 5 and 6) with coordination number 4+1+1 are plotted.

Considering the data for the coordination polyhedra with coordination number 4+1+1 we stress the following conclusions:

1. From Figs. 5a and 5b, it follows that there is, for the chromophores

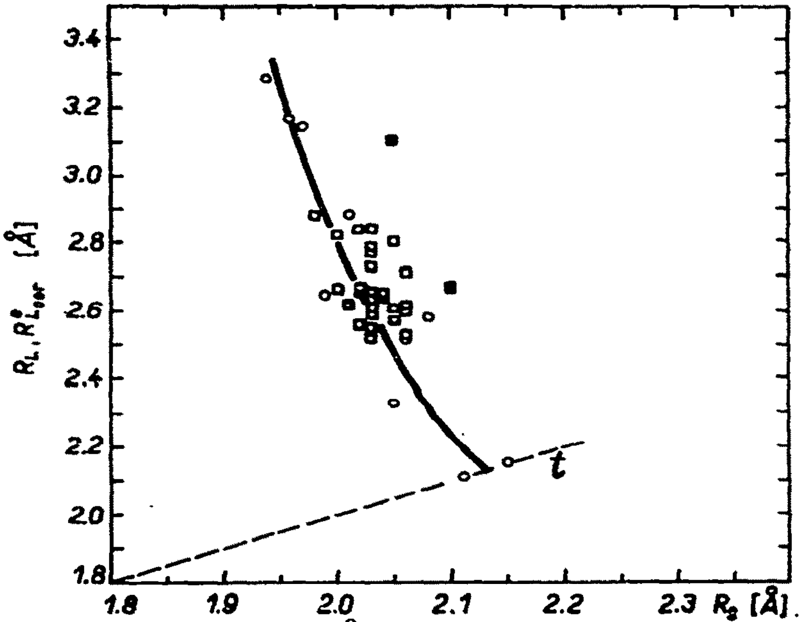


Fig. 4. Diagram R_S vs. R_L, R^0_L(c) for copper(II) complexes with the coordination number 4+2, 6; ○ — chromophore CuN_6; □ — chromophore CuN_4O_2.
The data in Fig. 4 for the chromophore CuN_6 are tabulated in Table 2; and for the chromophore CuN_4O_2 in Table 4.

CuO_6 and CuN_6 or CuN_4O_2, a continuous transition between the coordination expressed in Fig. 1 by schemes III—V and V—VI, as well as by II—III; the data for the latter correspond to $R^6_L/R^5_L = 1.0$.

2. The four shorter Cu—L distances are very sensitive to changes in the R^6_L/R^5_L ratio only when deviations from the symmetrically distorted octahedron are small, ($R^6_L/R^5_L \sim 1.05$). With increase of the ratio R^6_L/R^5_L, no substantial changes in the values of R_S were observed.

3. In the range where R_S is fairly insensitive to variation of R^6_L/R^5_L, the average value of the R_S parameter for the chromophore CuO_6 is smaller (1.97 Å) than the analogous value for the chromophore CuN_6 or CuN_4O_2 (2.03 Å). This is in agreement with conclusions from paragraphs 5 and 6 for the coordination number 4+2 where the value R^O_S(min) was also smaller than R^N_S(min). Whereas the latter values correspond to the square-planar arrangement around the Cu^{II} in the chromophores CuN_6 and CuO_6, the distances R_S from Figs. 5a and 5b correspond to the tetragonal pyramidal coordination of Cu^{II}. Increase of the coordination number causes an increase of the interatomic distances in the equatorial plane of the coordination polyhedron, which agrees with conclusions from paragraph 2 for the coordination number 4+2.

The above data show that the structure data for the coordination polyhedra of various selected groups of Cu^{II} complexes, do reveal an interdepen-

TABLE 4

Values of R_S and $R_L^0(c)$ of some copper(II) compounds with the CuN_4O_2 chromophore and coordination number of 4+2

Compound	R_S [Å]	$R_L^0(c)$ [Å]	Ref.
$Cu(CH_3OCH_2COO)_4$(imidazole)	1.98	2.88	85
$K_2Cu(H_2NCH_2CONCH_2COO)_2 \cdot 6\,H_2O$	2.00	2.82	86
$Cuen_2Cl_2 \cdot H_2O$	2.00	2.66	87
Cu(imidazole)$_4$SO$_4$	2.01	2.62	88
Cu(histamine)$_2$(ClO$_4$)$_2$	2.02	2.67	89
Cu(*N*,*N*-(CH$_3$)$_2$en)$_2$(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)	2.02	2.84	90
Cu(1,2-PDA)$_2$(ClO$_4$)$_2$	2.02	2.66	91
$Cu(NH_3)_4(CuCl_2)_2 \cdot H_2O$	2.03	2.78	92
Cu(1,3-BDA)$_2$(ClO$_4$)$_2$ — blue	2.03	2.63	93
Cu(1,3-BDA)$_2$(ClO$_4$)$_2$ — violet	2.03	2.73	93
Cu(*N*-(CH$_3$)en)$_2$(C$_2$O$_4$) · 2 H$_2$O	2.03	2.55	94
Cu(*N*-(CH$_3$)en)$_2$(ClO$_4$)$_2$	2.03	2.57	95
$Cuen_2(NO_3)_2$	2.03	2.64	96
$[Cuen_2]_4Si_8O_{20} \cdot 38\,H_2O$	2.03	2.65	97
Cu(*N*-(CH$_3$)en)$_2$(NO$_3$)$_2$	2.03	2.59	98
Cu(*N*,*N*-(CH$_3$)en)$_2$(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)	2.03	2.84	90
$Cuen_2(SCN)(ClO_4)$	2.03	2.77	99
Cu[*N*-(2-hydroxyethyl)en]$_2$(ClO$_4$)$_2$	2.03	2.52	100
$Cuen_2(ClO_4)_2$	2.04	2.65	101
Cu(*N*,*N′*-(CH$_3$)$_2$en)$_2$SO$_4$ · 4 H$_2$O	2.05	2.60	102
Cu(*N*,*N′*-(CH$_3$)$_2$en)$_2$(NO$_3$)$_2$	2.05	2.57	103
$[Cuen_2]_4Si_8O_{20} \cdot 38\,H_2O$	2.05	2.80	97
	2.05	3.10	
Cu(1,3-PDA)$_2$(C$_6$H$_5$COO)$_2$	2.06	2.53	104
Cu(1,3-PDA)$_2$(NO$_3$)$_2$	2.06	2.60	105
$[Cuen_2]_4Si_8O_{20} \cdot 38\,H_2O$	2.06	2.71	97
Cu(1,2-PDA)$_2$(NO$_3$)$_2$	2.06	2.62	106
Cu(1,2-PDA)$_2$Cr$_2$O$_7$	2.10	2.67	107

Abbreviations: PDA, propanediamine; BDA, butanediamine.

dence between the Cu—L distances in the axial direction and those in the equatorial plane of the coordination polyhedron, and further indicate the plasticity of the coordination sphere of Cu^{II}.

In studying the plasticity of coordination polyhedra of Cu^{II} complexes the question arose, "to what extent do Cu^{II} complexes differ in this property from complexes of other central atoms?" The theory would predict similar properties for complexes of some other central atoms (see section E). On the other hand the experimental data indicate that other central atoms generally exhibit much less plasticity than copper. This may be seen in comparing differences in the interatomic central atom—ligand distances for complexes

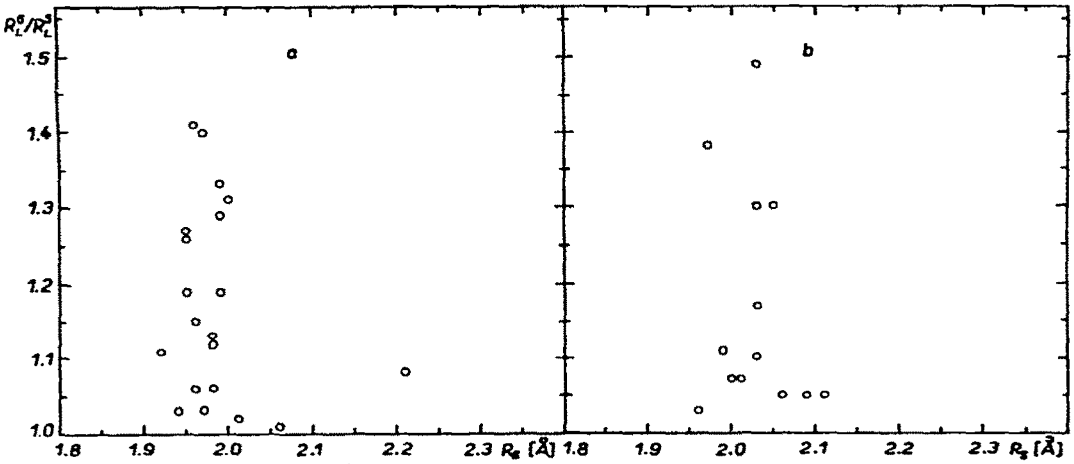


Fig. 5. Diagram R_S vs. R_L^6/R_L^5 for copper(II) complexes with the coordination number 4+1+1;
The data in Fig. 5a are tabulated in Table 5; and in Table 6 for Fig. 5b.

TABLE 5

Values of R_S and R_L^6/R_L^5 of some copper(II) compounds with the CuO_6 chromophore and coordination number of 4+1+1

Compound	R_S [Å]	R_L^6/R_L^5 [Å]	Ref.
Cu(acac)$(H_2O)_2$picrate	1.92	1.11	108
Cu(*d*-tartrate)$(H_2O)_3$	1.94	1.03	28
α-$Cu_2P_2O_7$	1.95	1.27	109
$Cu(NO_3)_2CH_3NO_2$	1.95	1.19	110
Cu(*dl*-lactate)$_2$ · H_2O	1.95	1.26	18
$CuSeO_3 \cdot 2\,H_2O$	1.96	1.41	111
$Cu(C_6H_5NO)_2(NO_3)_2$	1.96	1.15	112
$Cu_5(PO_4)_2(OH)_4$	1.96	1.06	113
$CuTeO_3$	1.97	1.40	113
Cu(phenoxyacetate)$_2$ · 2 H_2O	1.97	1.03	18
$Cu_3Mo_2O_9$	1.98	1.06	114
$Cu(NO_3)_2 \cdot 2.5\,H_2O$	1.98	1.12	115
$Cu_5(PO_4)_2(OH)_4$	1.98	1.13	51
α-$Cu(NO_3)_2$	1.98	1.06	116
$Cu_3(OH)_2(CO_3)_2$	1.99	1.19	117
Cu(maleate)$_2$ · H_2O	1.99	1.33	37
$CuHPO_3 \cdot 2\,H_2O$	1.99	1.29	118
Cu(phenoxyacetate)$_2$ · 3 H_2O	2.00	1.31	119
Cu(hfacac)$_3$	2.01	1.02	120
Cu(PCP)$_3$$(ClO_4)_2$	2.06	1.01	121
$Cu_3Mo_2O_9$	2.21	1.08	114

Abbreviations: acac, acetylacetonate; hfacac, hexafluoroacetylacetonate.

TABLE 6

Values of R_S and R_L^6/R_L^5 of some copper(II) compounds with the CuN_6 and CuN_4O_2 chromophore and coordination number 4+1+1

Compound	R_S [Å]	R_L^6/R_L^5 [Å]	Ref.
$[Cu(C_4H_{12}N_6)(C_2H_4N_4)]SO_4 \cdot H_2O$	1.96	1.03	122
$Cu(IBO)_2Cl_2$	1.98	1.38	123
$Cu(bipy)_2(ClO_4)_2$	1.99	1.11	124
$Cu(N_3)_2$	2.00	1.07	125
$Cu(NH_3)_4SeO_4$	2.01	1.07	126
$Cu(1,3\text{-}PDA)_2SO_4 \cdot H_2O$	2.03	1.30	127
$Cu(NH_3)_4SO_4 \cdot H_2O$	2.03	1.49	126
$Cu(bipy)_3(ClO_4)_2$	2.03	1.10	128
$Cu(N\text{-}(CH_3)en)_2(malonate) \cdot 2\,H_2O$	2.03	1.17	129
$Cu(NH_3)_4SO_4 \cdot H_2O$	2.05	1.30	130
$Cutren\text{-}py_3$	2.09	1.05	131
$Cu(dien)_2(NO_3)_2$	2.11	1.05	132

Abbreviations: IBO, 2,2′-iminobis(acetamidoxime); bipy, bipyridine; PDA, propanediamine; en, ethylenediamine; tren-py$_3$, tris(4-(2-pyridyl)-3-aza-3-butenyl)amine; dien, diethylenetriamine.

with analogous chromophores e.g. $Cu^{II}O_6$ and $Co^{III}O_6$ [133]. Where divalent cobalt, nickel and di- or trivalent iron are coordinated by ligands with formation of a more or less regular octahedron, the copper(II) compounds usually possess a less symmetric coordination polyhedron resulting from deformation of the coordination polyhedron around Cu^{II}. Thus, e.g., in compounds MX_2, where X is a halogen, with Co^{II}, Ni^{II}, Fe^{III}, Fe^{II} the coordination of the metal approaches an octahedron, with Cu^{II}, however, a deformed octahedral coordination is present.

Compounds of the type $M_2P_2O_7$ (where M = Zn^{II}, Cu^{II}, Ni^{II}, Co^{II}, Mn^{II} and Mg^{II}) exhibit a crystal structure of the thortveitite type [45,109]. With the exception of $Mn_2P_2O_7$, there exist two modifications — the high-temperature (β) and the low-temperature (α) modifications. The high-temperature modification shows the bonding angle P—O—P = 180°, while for the low-temperature form this angle is smaller than 180° (Fig. 6).

The difference in the bond lengths $R_L - R_S$ in the coordination polyhedra of the high-temperature modifications for the central atoms studied decreases in the sequence

$Cu^{II} > Co^{II} > Ni^{II} > Zn^{II} > Mn^{II} > Mg^{II}$ (Table 7).

This order also reflects the difference in the degree of distortion of the coordination polyhedron of the central atoms.

From the data in Table 7 it is apparent that Cu^{II} also keeps in its low-temperature modification, the coordination number 6, while the other central atoms in their low-temperature form generally decrease their coordination

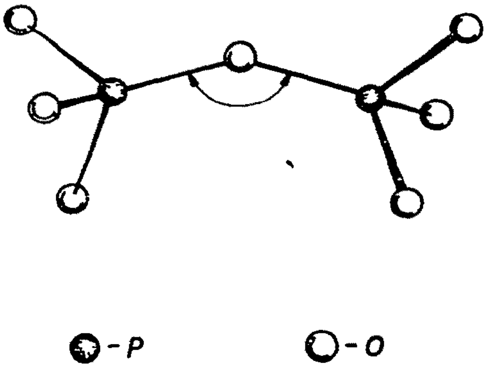


Fig. 6. Schematic representation of the bond angle P—O—P in the crystal structures of α-$M_2P_2O_7$ (M = Cu, Ni, Co, Mn, Mg and Zn).

number. Half of the central atoms in the low-temperature modifications of $Co_2P_2O_7$, $Ni_2P_2O_7$ and $Mg_2P_2O_7$ keep their coordination number 6 while the other half decrease to 5. In $Zn_2P_2O_7$ only one third of the central atoms in the low-temperature form retain their original coordination number of 6, while two thirds decrease to 5. These circumstances indicate that in the low-temperature form of all the pyrophosphates mentioned, the central atom Cu^{II} adapts best to the new conditions (owing to the greatest plasticity of its coordination polyhedron).

$Cu_2P_2O_7$ also suffers the smallest variation in the bonding P—O—P angles between the high-temperature and the low-temperature modifications compared with the other compounds; this also indicates that copper(II) is the "softest" metal of the group and therefore has the least influence on the change in structure of the pyrophosphate anion in the transition from the high-temperature modification of $Cu_2P_2O_7$ to the low-temperature form.

The case of the $M_2P_2O_7$ compounds and others [133] prove that Cu^{II} complexes exhibit some peculiarities which require comment and consideration.

The data presented above, knowledge from the next section on distortion isomerism of Cu^{II} complexes, and also the currently generally accepted understanding that copper(II) complexes are characterized by a high-degree of distortion of their coordination polyhedra, made us search for a better understanding of the reasons for these properties. In section E we elucidate the plasticity of the coordination polyhedra and the existence of distortion isomers of Cu^{II} complexes, using the theory of vibronic interactions in electronically degenerate states, a special case of which is the effect and the pseudo-effect of Jahn—Teller. This section shows why the d^9 electron configuration of the central Cu^{II} atom has such a significant effect on certain properties of the stereochemistry of complexes of this central atom. This section also indicates for which further complexes the phenomena may be expected.

TABLE 7

Structure data for diphosphate modifications with the thortveitite structure

Compound	Coord. poly-hed.	Interatomic distances Me—O [Å]	R_S [Å]	R_L [Å]	$R_L - R_S$	Bond angle P—O—P (°)	Change of angle P—O—P (°)	Ref.
α-$Zn_2P_2O_7$	DO DP 1 : 2	2.0[illegible], 2.060; 2.024; 1.956; 2.060; 2.056; 2.032; 2.057; 2.092; 1.929 2.083; 2.051; 2.102; 2.032; 2.177; 2.097				148 139	32	134
β-$Zn_2P_2O_7$	DO	2.061; 2.001; 2.275	2.03	2.275	0.245	180	41	135
α-$Cu_2P_2O_7$	DO	1.990; 1.968; 1.907; 1.935; 2.322; 2.947	1.94	2.63	0.69	157		109
β-$Cu_2P_2O_7$	DO	2.003; 1.937; 2.574	1.97	2.57	0.60	180	23	45
α-$Ni_2P_2O_7$	DO DP 1 : 1	1.989; 2.054; 2.065; 1.990; 1.935 2.110; 2.003; 2.141; 2.001; 2.097; 2.111				137		136
β-$Ni_2P_2O_7$	DO	2.021; 2.007; 2.319	2.01	2.32	0.31	180	43	137
α-$Co_2P_2O_7$	DO DP 1 : 1	2.072; 2.067; 2.040; 1.957; 2.110 2.126; 2.099; 2.085; 2.183; 2.062; 2.139				143		138
β-$Co_2P_2O_7$	DO	2.067; 2.056; 2.394	2.06	2.39	0.33	180	37	
$Mn_2P_2O_7$	DO	2.08; 2.08; 2.21	2.08	2.21	0.13	180		139
α-$Mg_2P_2O_7$	DO DP 1 : 1	2.037; 2.054; 2.120; 1.985; 2.024 2.073; 2.084; 2.135; 2.137; 2.142; 2.059				144	36	140
β-$Mg_2P_2O_7$	DO	2.05; 2.02; 2.15	2.035	2.15	0.115	180		141

DO, Deformed octahedron; DP, Deformed pyramid.

C. ISOMERS OF COPPER(II) COMPLEXES ARISING FROM THE PLASTICITY OF THE COORDINATION SPHERE, AND SOME OF THEIR PHYSICAL PROPERTIES

(i) General survey

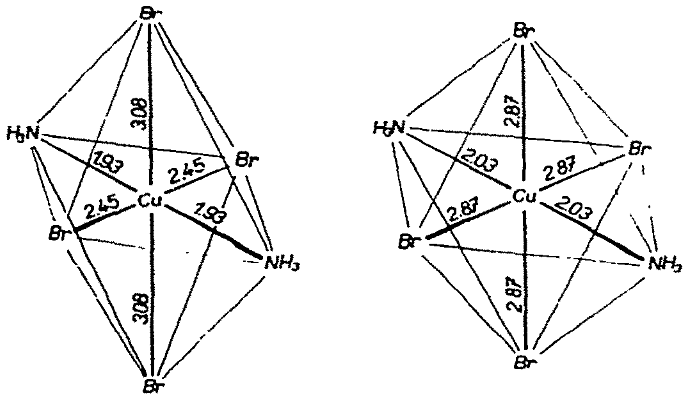
The plasticity of the coordination sphere of copper(II) complexes is most evident in a phenomenon we called distortion isomerism [2].

We collect here the results of X-ray analysis together with those indicating the existence of a relationship between the changes in distortion of the coordination polyhedra of Cu^{II} complexes and their physical properties.

In studying the analogy between the mutual influence of ligands for Cu^{II} and Pt^{II} compounds in 1959 we published [142] data on the preparation of α- and β-isomers of $Cu(NH_3)_2X_2$ (X = Cl, Br). The compounds prepared were subjected to X-ray analysis [143—145].

Figure 7 shows that the two complexes, α- and β-$Cu(NH_3)_2Br_2$, may be considered to reflect different types of distortion of the octahedral arrangement of the coordination polyhedron. Some experimental data can be also explained by the existence of so-called intermediates: compounds occurring between the two limiting states of distortion of the octahedral ligand configuration [146]. We also present information on the spontaneous interconversion of the different isomers of $Cu(NH_3)_2X_2$ and on the influence of pressure and temperature on these transformations (see below).

With regard to the above differences in structure, it is possible to predict how the relative *d*-orbital energies will vary, and hence predict how the spectrum of one will compare with that of another. The experimental results [147] are in agreement with these predictions. Magnetic measurements indicate [148] the presence of a relatively strong antiferromagnetic inter-



α-$Cu(NH_3)_2Br_2$ β-$Cu(NH_3)_2Br_2$

Fig. 7. Schematic representation of the coordination sphere around Cu^{II} of α- and β-$Cu(NH_3)_2Br_2$. Data from refs. 143—144.

action which is different for the α- and β-isomers of $Cu(NH_3)_2Br_2$.

Using analogous methods as in the preparation of α- and β-$Cu(NH_3)_2Br_2$ (applying the so-called Peyron—Jørgensen rules [149,150] for the preparation of *cis—trans* isomers of PtA_2X_2), we succeeded in preparing different isomers of $Cu(NH_3)_2(NCS)_2$ [151]. Also for these compounds intermediate structures were found [152]. X-ray analysis [153] showed that the differences between the isomers are caused by deviations from linearity in the NCS groups and in some central atom—ligand interatomic distances. Both isomers have a distorted octahedral ligand arrangement with the sulphur atoms in *trans*-positions in the more distant axial places (Fig. 8). The isomers differ though not greatly in several physical properties. The electronic spectra show [154] that the *d—d* band of the β-isomer has a higher energy than the α-isomer, indicating that the β-isomer is somewhat more distorted than the α-isomer. This is in agreement with the values of the magnetic moments, which are practically, in the whole temperature region measured, an average of 0.04 B.M. lower for the β-isomer [154], owing to the increased tetragonal distortion.

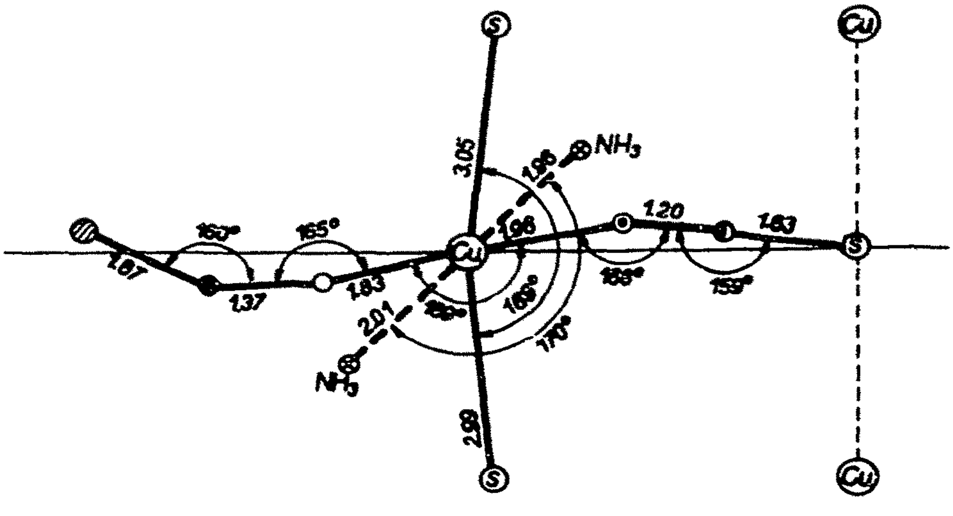
There is a marked difference in the EPR spectra, the spectrum of the β-form being axial and that of the α-form orthorhombic. This implies the presence of distortion in the equatorial plane in the α-isomer [154].

The possibility that these phenomena for complexes of the composition $Cu(NH_3)_2X_2$ could occur more commonly and could represent an example of a new type of isomerism for copper(II) compounds [155] stimulated us to devote appropriate attention to this problem. We presented results [2] which showed unambiguously that in substances of the type CuA_2X_2 isomerism of the above type is often found. In the following paragraphs we present those cases which have been studied in some detail.

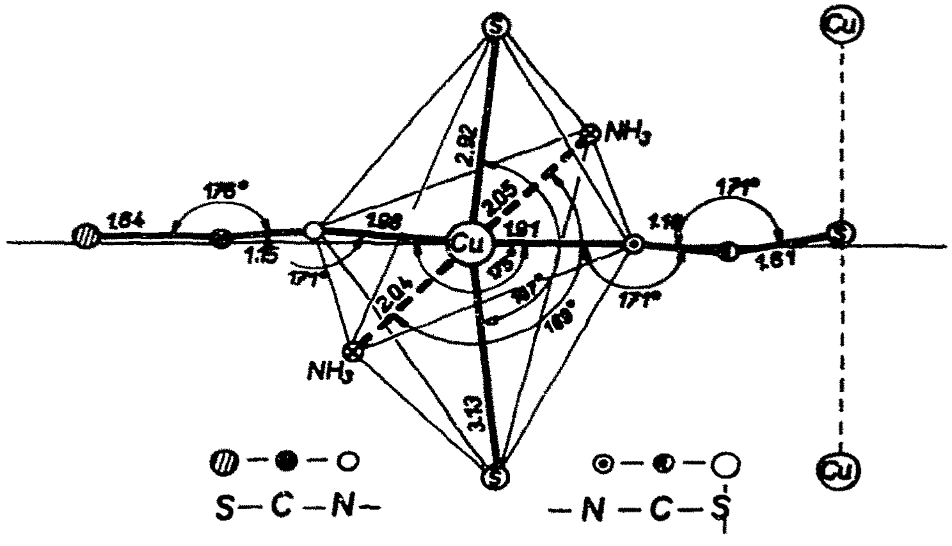
Investigation of two forms of bis(salicylaldehydato) copper(II) compounds [21,22] showed that they differ in different axial contact with the π-bonding system of the adjacent molecule. Figure 9 shows these differences and stimulates a more profound analysis of π-bonding interactions with the central atom.

The two isomers of bis(1,3-diaminobutane)copper(II) perchlorate exhibit very similar structures [93]. 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 rather differing angles. The greatest differences in the interatomic distances have been observed in the Cu—O bonds to the oxygen atoms of the perchlorate group in the axial positions. This distance is 2.579(6) Å for the blue-violet form and 2.676(10) Å for the red (Fig. 10). There is little interaction between neighbouring molecules in this structure.

In both forms of $Cu(NH_2NHCONH_2)Cl_2$, semicarbazide is bonded to Cu^{II} as a chelate [156]. Besides the differences in the mutual positions of the semicarbazide ligands in adjacent octahedra, there are differences in the interatomic distances between the central atom Cu^{II} and the Cl atom in axial positions of the distorted octahedron (see Fig. 11).



α-Cu(NH$_3$)$_2$(SCN)$_2$



β-Cu(NH$_3$)$_2$(SCN)$_2$

Fig. 8. Schematic representation of the coordination sphere around Cu^{II} of α- and β-Cu(NH$_3$)$_2$(SCN)$_2$. Data from ref. 153.

In the crystal structures of α- and β-$Cu_2P_2O_7$ the copper atoms are coordinated by six oxygen atoms which are placed at the apices of a distorted octahedron [45,109]. The equatorial plane is formed by four oxygen atoms

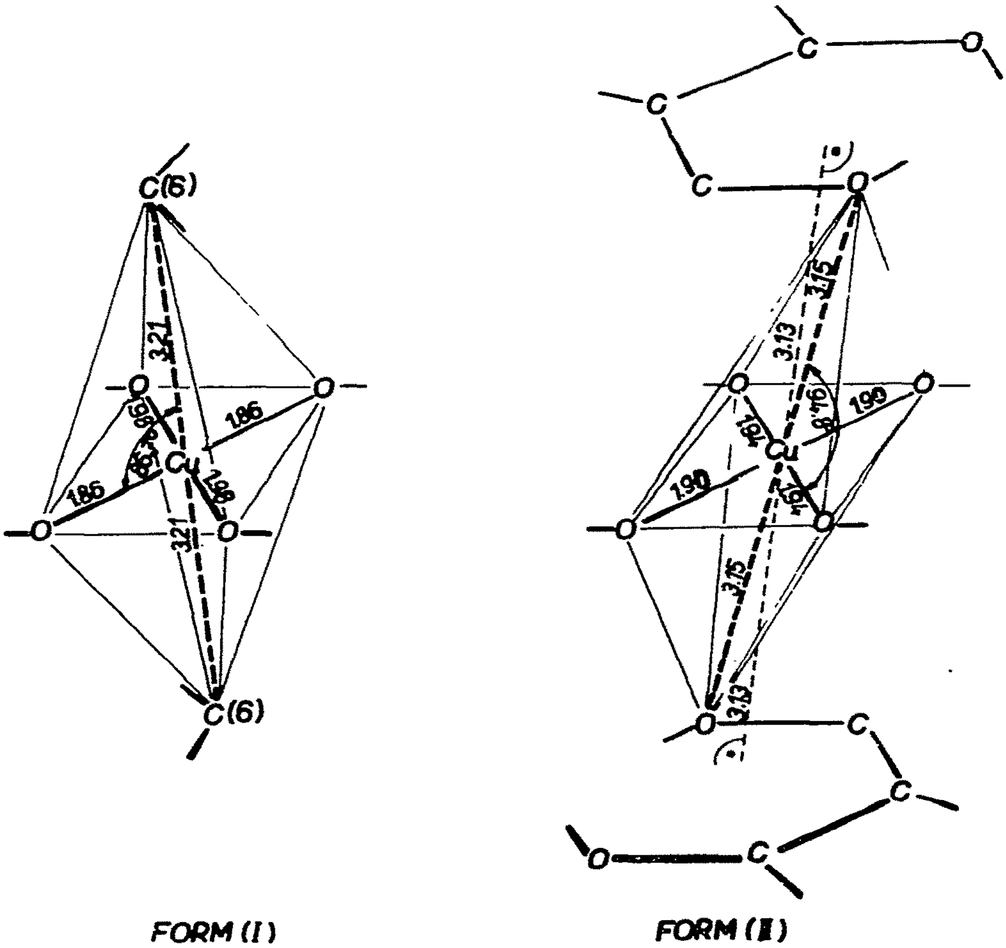


Fig. 9. Schematic representation of the coordination sphere around Cu^{II} of form (I) and form (II) of Cu(salicylaldehydate)$_2$. Data from refs. 21,22.

from three pyrophosphate anions. The isomers differ mostly in their Cu—O bond lengths on the long coordinates. The α-isomer has terminal oxygen atoms on the axis, with Cu—O distances of 2.32 and 2.94 Å, the β-isomer is symmetrical with interatomic distances of 2.58 Å (Fig. 12).

Kidd et al. [157] prepared three pairs of isomers CuL_2Cl_2, where L = 3-picoline-*N*-oxide, 4-picoline-*N*-oxide, or 2.6-lutidine-*N*-oxide. In each, one form is green and the other is yellow. X-ray analysis of the isomers with L = 4-picoline-*N*-oxide showed [158] that the yellow form consists of a highly distorted tetragonal pyramid with chlorine atoms in apical positions, while the green form has a square structure with chlorine atoms in the *trans* position (Fig. 13). The yellow isomer is dimeric, whereas the green is monomeric

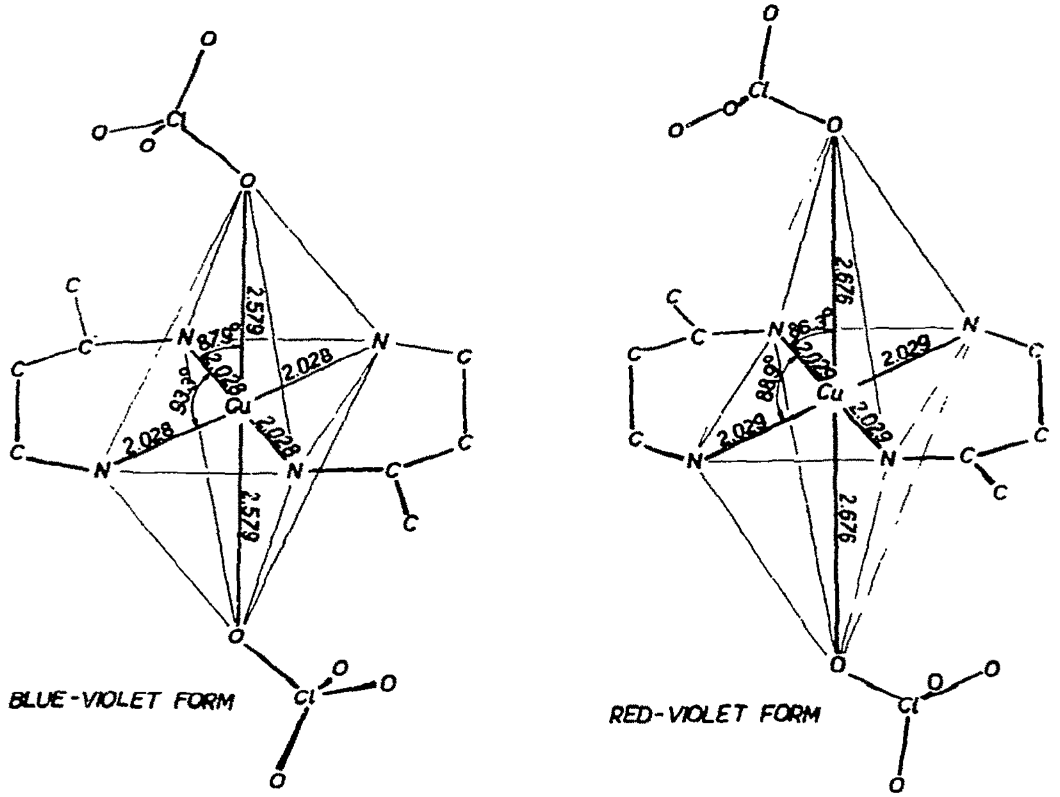


Fig. 10. Schematic representation of the coordination sphere around Cu^{II} of the blue-violet and red-violet form of bis(1,3-diaminobutane) copper(II) perchlorate. Data from ref. 93.

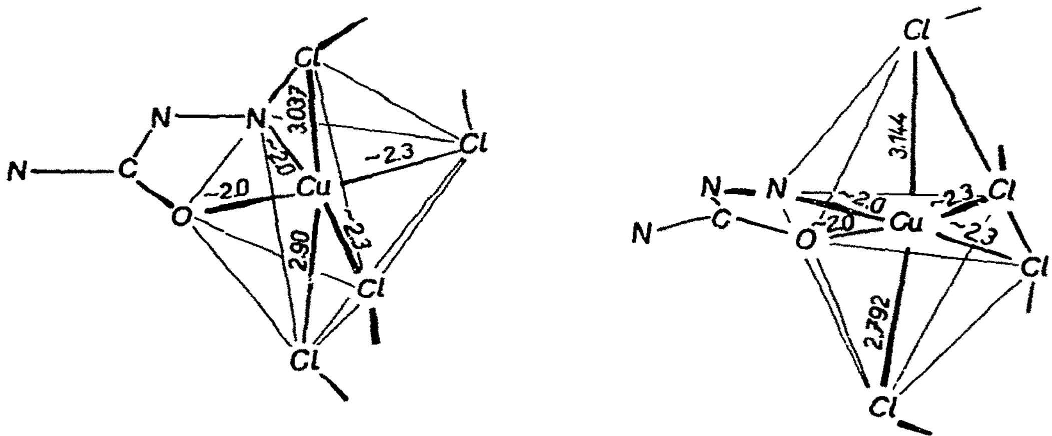
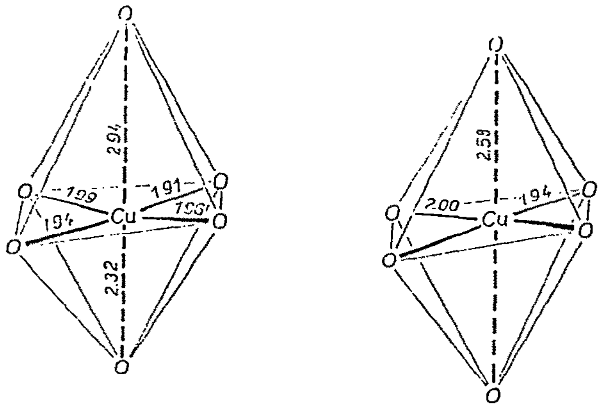


Fig. 11. Schematic representation of the coordination sphere around Cu^{II} of the orthorhombic and monoclinic isomer of $Cu(NH_2NHCONH_2)Cl_2$. Data from ref. 156.



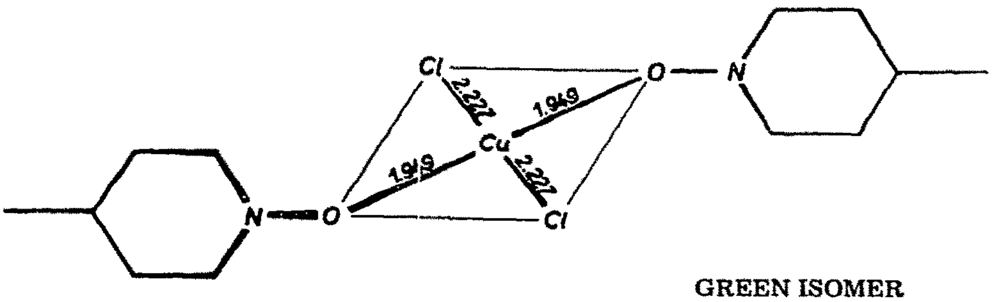
α-$Cu_2P_2O_7$ β-$Cu_2P_2O_7$

Fig. 12. Schematic representation of the coordination sphere around Cu^{II} of α- and β-Cu_2·P_2O_7. Data from refs. 45, 109.

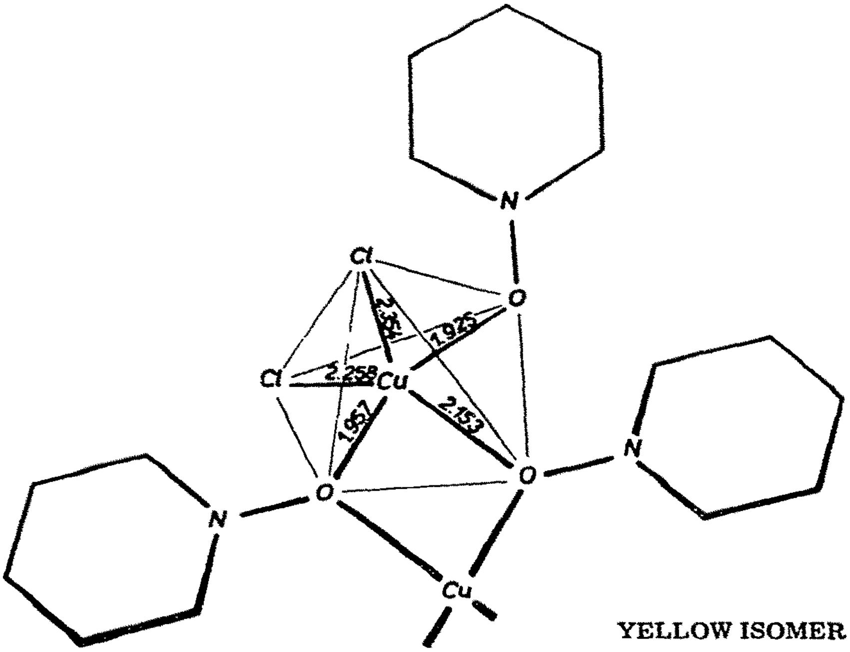
in agreement with its magnetic moment of 1.96 B.M. For the isomers with L = 3-picoline-*N*-oxide the value of μ_{eff} (1.97 B.M.) is only known for the green isomer, being practically identical with that of the green isomer with L = 4-picoline-*N*-oxide; consequently, a similar structure may be assumed. The yellow form is thermally less stable and at 100—110° C changes to the green form. The structure of the yellow isomer with L = 2,6-lutidine-*N*-oxide may be regarded, according to the X-ray analysis [159], as an intermediate between a *cis*-square and tetrahedral structure. Its μ_{eff} value is 2.09 B.M. at 273 K and with decreasing temperature drops to 1.85 B.M. at 77 K, evidently caused by a weak antiferromagnetic interaction. The green isomer of the same composition displays interesting magnetic behaviour; at 273 K, μ_{eff} equals 1.50 B.M., with decreasing temperature it rises to 1.73 B.M. at 77 K. It seems that in this isomer ferromagnetic as well as antiferromagnetic interactions take place, with the former dominating at lower temperature.

Two isomers of $Cu(8\text{-hydroxyquinolate})_2$ [160,161], α and β, differ in their structures. The less stable α-isomer has a pseudo-octahedral environment for Cu^{II} in a polymer chain structure, whereas the more stable β-isomer consists of dimers and the environment of the Cu^{II} atom has the shape of a tetragonal pyramid with an oxygen atom at the apex. While the equatorial bond lengths are approximately identical in both isomers, there is a considerable difference in axial bond lengths. Their magnetic properties are practically identical and their μ_{eff} values are constant with temperature. A marked decrease of these values may be observed at temperatures below 7 K. The EPR spectrum of the α-isomer is axial, that of the β-isomer is orthorhombic.

The different isomers of $Cu(2\text{-pic})_2(NO_3)_2$ possess [162] an almost unique case of polymorphism, since both forms have the same space group and almost the same unit cell, but, different crystal packing. Both isomers have a mono-



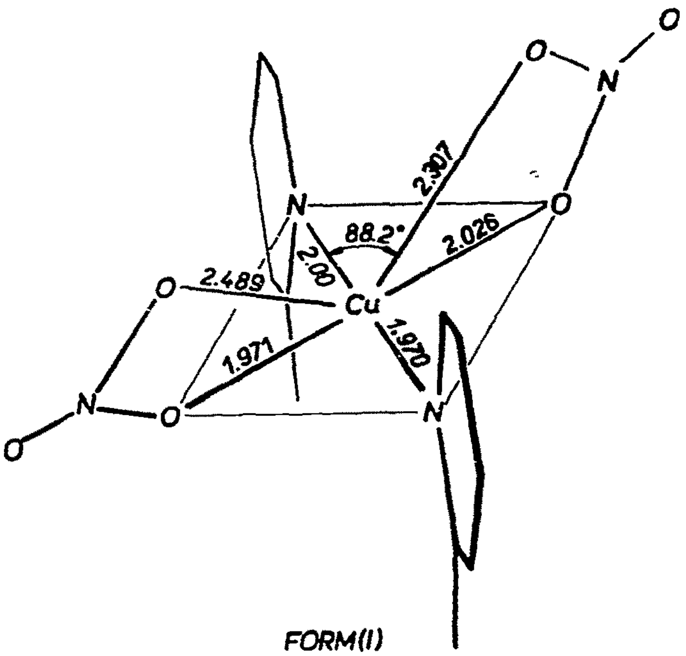
GREEN ISOMER



YELLOW ISOMER

Fig. 13. Schematic representation of the coordination sphere around Cu^{II} of the yellow and green isomer of $Cu(4\text{-picoline } N\text{-oxide})_2Cl_2$. Data from ref. 158.

meric structure. Above the basic square-planar arrangement, approximately in the middle of which the Cu^{II} atom is sited, there are two longer distance oxygen atoms of the nitrate group mutually in *cis*-positions. The most significant differences are in the $Cu—O_1$ (oxygen atom of the nitrate group) distances (see Fig. 14). There are also significant differences in the polarized single crystal spectra [163] of these isomers and in the *g*-values. (g_1 = 2.0563; g_2 = 2.0742 and g_3 = 2.2740 — form I.; and g_1 = 2.0619; g_2 = 2.0642 and g_3 = 2.2830 — form II., single crystal data).



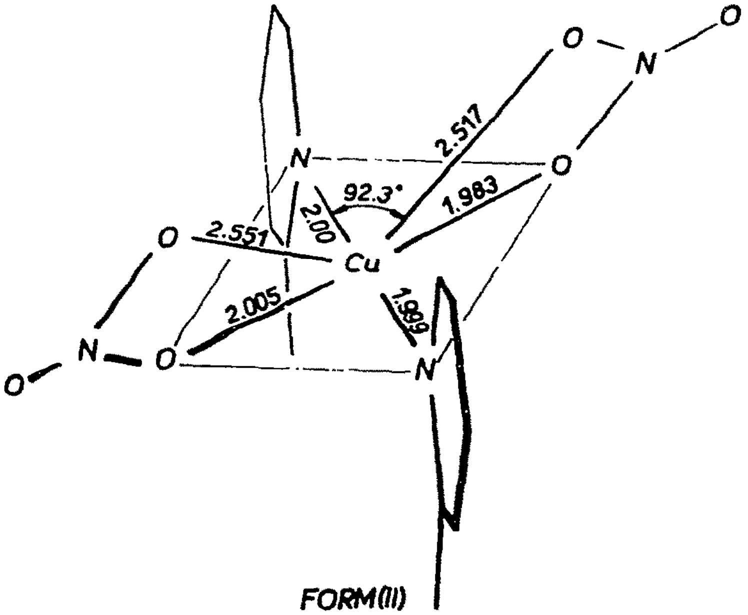


Fig. 14. Schematic representation of the coordination sphere around Cu^{II} of form (I) and form (II) of $Cu(2\text{-picoline})_2(NO_3)_2$. Data from ref. 162.

In the isomers of the monoclinic [164] and orthorhombic [165] Cu(*N*-ethylsalicylaldiminate)$_2$, the copper atoms are coordinated by two nitrogen atoms and two oxygen atoms from two chelate rings of *N*-ethylsalicylaldiminate. The two isomers differ in the degree of tetrahedral distortion of the square planar coordination of the central atom.

Stackelberg [166] studied three isomeric forms of Cu(*N*-methylsalicylaldimine)$_2$ (α, β, γ), described their unit cells and determined the space groups. X-ray analysis of the α-isomer [167] showed a perfect planar arrangement with the Cu^{II} atoms forming chains with the distance Cu—Cu = 3.33 Å. According to X-ray analysis [168], the γ-isomer contains dimeric five-coordinated molecules with the Cu—Cu distance somewhat greater than in the chains of the α-isomer. The EPR spectra [169] of both the above isomers are isotropic with g_{av} equal to 2.034 and 2.064 for the α- and γ-isomers, respectively.

The largest number of isomeric Cu^{II} complexes are those with composition Cu{1,7-bis(2′-pyridyl)-2,6-diazaheptane}(NCS)$_2$; Gibson and McKenzie [170] prepared seven products designated as α, γ, δ, ϵ, η, θ and κ. Among these, β and ξ have different stoichiometric composition and consequently are not isomers. The structures of the α and γ isomers have been solved by X-ray analysis [171] and consist of complex cations which form distorted trigonal-bipyramidal structure in which only one NCS anion is coordinated to the Cu^{II} by one nitrogen atom. These two isomers differ in the conformation of organic ligands and in the Cu—N bond lengths. The greatest differences occur in the Cu—NCS bonds. The two isomers above, as well as others from this group were also examined with the aid of powder diffraction patterns [170] which showed that there are significant differences between the individual isomers. The electronic and IR spectra [170] were recorded for the α, γ and θ isomers. It is interesting that the *d*—*d* band energy is identical for both the α and θ isomers (15.0 kK), and different for the γ isomer (13.4 kK), while on the other hand the vibrational frequencies NH, and those of the pyridyl ring and of NCS are identical in the γ and θ-isomers and different in the α-isomer. Decreased energy of the *d*—*d* band in the γ-isomer, compared with that of the α-isomer, is in agreement with the somewhat longer Cu—N distances and consequently with the weaker ligand field. Gibson and McKenzie [170] prepared another pair of isomers, α- and β-Cu{1,6-bis(2′-pyridyl)-2,5-diazahexane} · Cl$_2$ · 0.5 H$_2$O. X-ray diffraction diagrams of these isomers differ, their electronic and IR spectra, however, show only small differences.

Two isomers of the complex Cu(*N*-*t*-butylpyrrole-2-carbaldimine)$_2$ are known, one triclinic and the other tetragonal. They have, according to X-ray analysis [172], a distorted tetrahedral configuration, with different Cu—N bond lengths and different dihedral angles, which, in the triclinic isomer are somewhat greater than in the tetragonal. The magnetic and spectral data have been published [173] only for the triclinic isomer, the μ_{eff} of which equals 1.98 B.M. at room temperature; in chloroform solution μ_{eff} = 1.95 B.M. and the absorption bands of the electronic spectrum lie at 15.50 and 23.53 kK. These data are in agreement with the structure which was found to be intermediate between a plane and a tetrahedron.

The compound $Na_2[Cu(cyanoureate)_4]$ exists in two modifications [174]; the purple-violet α- and the steel-blue β-form. The crystallographic data obtained from the X-ray diffraction diagrams show that both forms possess the same space group ($Pmm2_1$); they differ in the number of formula units in the unit cell and in the dimensions of this unit cell. The electronic spectra of both α- and β-modifications display broad bands in the range 16.7—20.0 kK and 33.4—35.7 kK, and in the range 12.5—15.4 kK and 33.4—45.5 kK respectively. The EPR spectrum of the α-modification is axial with $g_\perp = 2.0149$ and $g_\parallel = 2.092$; the β-modification has a pseudo-isotropic EPR spectrum with $g_{av} = 2.0149$. Nutiu et al. [174] believe that the α-modification exists in a monomeric and the β-modification in an associated form. The spectroscopic data agree with this assumption since the *d—d* band energies indicate for the α-modification a planar and for the β-modification a pseudo-octahedral configuration. The pseudo-isotropic EPR spectrum of the latter modification depends most probably on the exchange interaction which occurs as a consequence of the association.

Three isomeric forms [175] of $Cu(2,4\text{-lutidine})_2(NCO)_2$ were prepared, two violet α-, and β-, and one blue γ-form. According to X-ray powder patterns the crystal structures of the α- and β-forms are closely similar, whereas the γ-form has a quite different structure. For the α- and β-isomers the electronic spectra indicate a tetragonal structure which is slightly more distorted in the β-isomer; the γ-isomer possesses a pseudo-octahedral structure. The IR spectra infer that in the γ-isomer the NCO groups are N-bridging, this proposal being supported by the ferromagnetic interaction. In this isomer axial ligation of $Cu(2,4\text{-lutidine})_2(NCO)_2$ takes place through nitrogen atoms of the NCO groups. These results show that the α- and β-$Cu(2,4\text{-lutidine})_2(NCO)_2$ are distortion isomers and that the diminished distortion of γ-$Cu(2,4\text{-lutidine})_2$-$(NCO)_2$ is related to linkage isomerism.

The blue [176] and dark blue isomers [177] of Cu(*N*,*N'*-dibenzylethylenediamine)$_2$Br$_2$ prepared from aqueous or ethanol solutions display differences in their electronic spectra attributed to the existence of a five-coordinated configuration for the blue form, and of tetragonal coordination for the dark blue isomer. The EPR spectrum of the five-coordinated isomer indicates a distorted trigonal-bipyramidal environment for the Cu^{II} atom with the ground state d_{z^2}.

The brown and yellow-orange isomers [178] of Cu(*N*-methylsalicylideneimine)Cl were found to possess distinctly different magnetic properties. It is evident that a very strong antiferromagnetic interaction takes place in both but is much stronger in the yellow-orange isomer. Significant differences were also found in the *d—d* band energies. Both isomers are supposed to possess a binuclear structure with a pseudo-octahedral environment in the brown and a distorted trigonal-bipyramidal environment of the Cu^{II} atom in the yellow-orange isomer, respectively.

The electronic spectra of the red and orange isomers [179] of Cu(diantipyrrylmethane)$_2$(ClO$_4$)$_2$ with *d—d* bands at 11.85 and 12.30 kK, respectively, are typical for pseudo-tetrahedral geometry and indicate greater planar distortion for the orange isomer.

(ii) Effect of temperature or pressure

Because of the plasticity of the coordination sphere of Cu^{II} complexes, distortion of the polyhedra of these complexes should be influenced by temperature or pressure. It is some time since Pfeiffer and Glaser showed [180] that Cu(asym-(C$_2$H$_5$)$_2$ethylenediamine)$_2$(ClO$_4$)$_2$ which is red at room temperature, becomes blue at 40° C. Similarly, orange [(C$_2$H$_5$)$_3$NH]$_2$CuCl$_4$ changes to a green form [181] with decreasing temperature. On the basis of the present state of understanding of the structure of Cu^{II} complexes the above changes may be attributed to changes in the distortion of the respective coordination polyhedra.

Interconversion of some isomers of Cu^{II} may also be brought about by the action of pressure [151]. Increasing pressure of α-Cu(NH$_3$)$_2$Br$_2$ is transformed to a certain degree into the β-form. On the other hand, with increasing the temperature, the transition of the β-isomer to the α-form, which occurs slowly even at room temperature, is accelerated [182].

Two isomeric forms of the complex Cu(bis(2-pyridyl)-disulphide)Cl$_2$ have been prepared [8], the yellow-green and the dark blue. The electronic and IR spectra recorded at room temperature and at low temperature indicate a pseudo-octahedral and a *cis*-planar structure for the yellow-green and for the dark blue isomer, respectively. The yellow-green isomeric form is transformed by the action of heat or pressure to the dark blue form which has the greater axial distortion.

Lever et al. [9] measured the electronic and IR spectra and magnetic moments of the complexes Cu(asym-(C$_2$H$_5$)$_2$ethylenediamine)$_2$X$_2$ (where X = NO$_3$, BF$_4$ and ClO$_4$), at various temperatures. The complex with X = NO$_3$ was studied in two isomeric forms, the blue and the red. The blue isomer was assigned a pseudo-octahedral and the red a planar coordination of the Cu^{II} atom; in all complexes under investigation changing temperature resulted not only in pronounced changes in colour, but also in significant changes in the measured physical properties. All these changes were interpreted as due to distortion of the coordination polyhedra brought about by the changing interaction of the axial anionic ligands with the CuN$_4$ chromophore. With decreasing temperature a contraction of the planar Cu—N bonds and consequently a weakening of the above mentioned axial interaction take place. In this context it is interesting to point out the magnetic behaviour of the blue and red isomers with X = NO$_3$; their magnetic moments at room temperature are very similar, at decreasing temperature, however, differences in the μ_{eff} values increase. Other isomeric pairs e.g. Cu(cyclohexylamine)$_2$Cl$_2$ [183], Cu(NH$_3$)$_2$(SCN)$_2$ [154]

and $Cu(NH_3)_2Br_2$ [148] were observed to have similar magnetic behaviour.

The complexes Cs_2CuCl_4 and Cs_2CuBr_4 which have a distorted tetrahedral structure (symmetry D_{2d}) are converted to planar structures by the action of high pressure [3].

We found, in many cases, interconversion of distorted isomers will occur spontaneously when these species are allowed to stand under normal conditions. Thus, for example, as mentioned earlier β-$Cu(NH_3)_2Br_2$ changes to the α-isomer [148] and α- and β-$Cu(NH_3)_2(NCS)_2$ change in the course of time to form a species whose structure is something between the structures of the α- and β-isomers [184]. The yellow-green isomer of dichloro-(bis(2-pyridyl)-disulfide)copper(II) changes spontaneously in the course of several weeks to form the blue isomer [8], etc.

All these facts indicate that the thermodynamic stability of the distortion isomers is different and that the energetic barriers of transition from one state to the other are not always great.

The data indicate that the differences in properties of the distortion isomers of Cu^{II} complexes are rather small, but are reproducible and become more pronounced with decreasing temperature.

Naturally, causes other than the plasticity of their coordination sphere may be responsible for differences in physical properties of Cu^{II} complexes. In addition to the isomers above less commonly, *cis*-, *trans*- and linkage isomers of Cu^{II} complexes are also known [185—193].

D. DIFFERENCES IN THE CHEMICAL PROPERTIES OF THE DISTORTION ISOMERS OF COPPER(II) COMPLEXES

In this section we discuss the chemical behaviour of the distortion isomers of Cu^{II} complexes.

(i) Preparation of distortion isomers of Cu^{II} complexes

All factors affecting chemical equilibrium (total solution concentration, pH, solvent, temperature, molar ratio of the components, pressure etc.) play an important role in the preparation of distortion isomers. This is regardless of whether the reactions are carried out in a homogeneous or heterogeneous system. The above factors are important because they exhibit great influence upon the composition and structure of the coordination sphere of the initial reactants.

The so-called Peyrone and Jörgensen rules [149,150], were applied to the preparation of isomers of CuA_2X_2 [142]. The synthesis did not produce *cis—trans* isomers, but just the distortion isomers of $Cu(NH_3)_2X_2$ (where X = Cl, Br, NCS). It was also observed that different Cu^{II} : NH_3 molar ratios and different crystallization temperatures [194] influence the preparation of α- and β-$Cu(NH_3)_2(SCN)_2$. Similar dependence was also observed when preparing isomers of $CuCl_2$(semicarbazide) [156], Cu(8-hydroxyquinolinate)$_2 \cdot 2\,H_2O$ [195] and Cu(8-hydroxyquinolinate)$_2$ [160]. Changing the composition of the coordination sphere of the initial Cu^{II} reactant has been used to prepare the distortion isomers of $Cu(py)_2(NCS)_2$ [196] and the isomers of Cu(salicylaldehydemethylamine)$_2$ [180,197].

The preparation of distortion isomers using various different solvents can also be connected with a change in the starting state of the coordination sphere of the central Cu^{II} atom, e.g. in the preparation of the isomers Cu(2-hydroxy-*N*-methyl-1-naphthaldimine)$_2$, or Cu(*N,N'*-disalicylidenepropane-1,2-diamine)$_2$ [22]. Similarly the isomers of Cu(salicylaldehydate)$_2$ [21,22], $Cu(C_6H_4OHCOO)_2(C_5H_5N)_2$ [198] and $Cu(C_6H_4OHCOO)_2 \cdot 4\,H_2O$ [199,200] have been prepared. Naturally in the preparation of isomers different solubility can sometimes play a role; e.g. γ-Cu(salicylaldehydemethylimine)$_2$ crystallizes from the mother liquor after the α-isomer [166].

We can demonstrate that the composition of the coordination sphere also plays an important role in the preparation of distortion isomers from complexes in solid state. By thermal decomposition of $Cu(NH_3)_6Br_2$, β-$Cu(NH_3)_2Br_2$ is formed [142], but by decomposition of $Cu(NH_3)_5Br_2$, α-$Cu(NH_3)_2Br_2$ is formed [201]. A similar situation prevails with the anhydrous $Cu(HCOO)_2$ isomers [202].

The effect of temperature on the preparation of distortion isomers can be demonstrated with a whole series of compounds, e.g. with α- and β-$Cu(NH_3)_2(NCS)_2$ [194], α- and β-Cu(8-hydroxyquinolinate)$_2$ [195], α- and β-$Cu(NO_3)_2$(2-pic)$_2$ [162], Cu(asym-$(C_2H_5)_2$en)$_2X_2$ [9], etc. Temperature plays an important role with reactions in heterogeneous systems as well. For example, when $Cu(C_6H_4OHCOO)_2 \cdot 4\,H_2O$ and $Cu(C_6H_5COO)_2 \cdot 3\,H_2O$ were dehydrated, two forms of $Cu(C_6H_4OHCOO)_2$ and three forms of $Cu(C_6H_5COO)_2$ were prepared [203] respectively. Prolonged heating of α-$Cu(CHA)_2Cl_2$ * in the solid state in a closed ampoule yields the β-isomer [204]. As examples of the preparation of distortion isomers at various temperatures and pressures, the preparation of α- and β-$Cu(NO_3)_2$ [116] and α- and β-Na_2[Cu(cyanoureate)$_4$] [174] could be also pointed out. In this connection papers [9,205] dealing with the influence of temperature on the tetragonal distortion of Cu^{II} complexes are interesting.

When preparing distortion isomers of Cu(salicylaldehydate)$_2$ [21,22], Cu(2-hydroxy-1-naphthaldehydate)$_2$ [180], Cu(*N,N'*-2-hydroxy-1-naphthylidenepropane-1,2-diamine)$_2$ [197] and Cu(*N*-methylsalicylaldiminate)$_2$ [180] the effects of solvent and temperature are mutually intermingled.

(ii) Decomposition reactions

Relatively small structural differences between distortion isomers often result in significantly different chemical reactions. The decomposition temperature of β-$Cu(NH_3)_2Br_2$ is about 30°C higher than that of the α-isomer [205].

When observing the thermal decomposition of α- and β-$Cu(NH_3)_2(NCS)_2$,

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* CHA = cyclohexylamine.

or their so-called intermediates [152] their DTA curves differ in the temperature range for the destruction of the thiocyanate group [206].

The thermal decomposition of some pairs of isomers (e.g. α- and β-Cu(Py)$_2$-(SCN)$_2$ [196]) also differs in stoichiometry. Isomers of Cu(2,6-lutidine)$_2$Cl$_2$ also have a different behaviour on heating [157]. When analysing the kinetics of the thermal decomposition of two isomers of Cu(HCOO)$_2$, it was found [207] that both isomers are decomposed at a different rate. The isomers of the oxalate—diammine copper(II) complex differ in enthalpy, kinetic parameters and stoichiometry of thermal decomposition [208].

More or less significant differences in the behaviour of distortion isomers were also observed with other types of reaction. Thus, α- or β-Cu(NH$_3$)$_2$Br$_2$ give differently coloured solutions in methanol or acetone [205]. The effect of structural differences between α-, β- and γ-Cu(NH$_3$)$_2$C$_2$O$_4$ on the course of hydrolysis of these complexes has been discovered [209]. Qualitatively the same results have been obtained in the reactions of isomers of the oxalate—diammine copper(II) complex with liquid and gaseous ammonia [209,210]. Different reactivity towards ammonia was also observed with the Cu(CHA)$_2$Cl$_2$ isomers [204].

On the basis of differences in stoichiometry, rate and mechanism in the chemical reactions of distortion isomers one can presume that they are different substances from the chemical view point, despite the fact that they may differ very little in structure.

E. THE JAHN—TELLER AND PSEUDO-JAHN—TELLER ORIGIN OF THE PLASTICITY OF THE Cu^{II} COORDINATION SPHERE AND DISTORTION ISOMERISM

The first papers dealing with distortion isomerism evoked interest and lively theoretical reverberations. The fact that such isomers were observed in Cu^{II} compounds which, in an octahedral configuration, have a doubly degenerate electronic ground term led from the very beginning to the assumption of their Jahn—Teller origin. Initially Djatkina and Porai-Koshits [211] made the assumption that affinity (distortion) isomers are due to several possible types of deformation of the coordination sphere of copper in CuA$_2$X$_2$ compounds arising as a consequence of the Jahn—Teller effect. What, however, was not taken into consideration in this paper [211] is that the differences in ligands of the first coordination sphere, strictly considered, break up the degeneracy, in consequence of which, it is not possible to expect distortions of the Jahn—Teller type [212]. Liehr [213] in this connection, pointed out that in cases similar to the one under consideration, deformations of a pseudo-Jahn—Teller type are basically possible.

In principle, this conceptually correct approach to the problem could not at that time lead to a satisfactory solution since the theory of vibronic interactions in electronically degenerate states (which includes the Jahn—Teller and pseudo-Jahn—Teller effects, as special cases) was not sufficiently elaborated at that time. However, since then, this theory has reaped significant successes, which allows us to present here a more exact view on the origin of distortion isomerism and its broader aspect the plasticity of the coordination sphere of some transition metals. Our study will be based on a detailed paper of one of us [214] which deals with Jahn—Teller effects in crystal chemistry and spectroscopy.

Let us first describe some general conclusions from the paper [214], which are relevant for what follows. The basic electronic state of the Cu^{II} complex in a regular octahedral configuration is doubly degenerate and the adiabatic potential energy of the nucleus in agreement with the Jahn—Teller theorem has no minimum in this configuration, which fact is generally interpreted as its instability. In the space of normal displacements of the octahedral nuclei Q_θ and Q_ϵ (Fig. 15) the adiabatic potential surface in the linear vibronic approximation has the shape of the so-called "Mexican hat" shown in Fig. 16. The depth of the trough depends on the linear vibronic coupling constant A_1 (determined by the rate of change of the electronic states with change of the metal—ligand distance).

From this figure we can see that in the linear approximation under consideration, the octahedral Cu^{II} complex has a continuous series of configurations

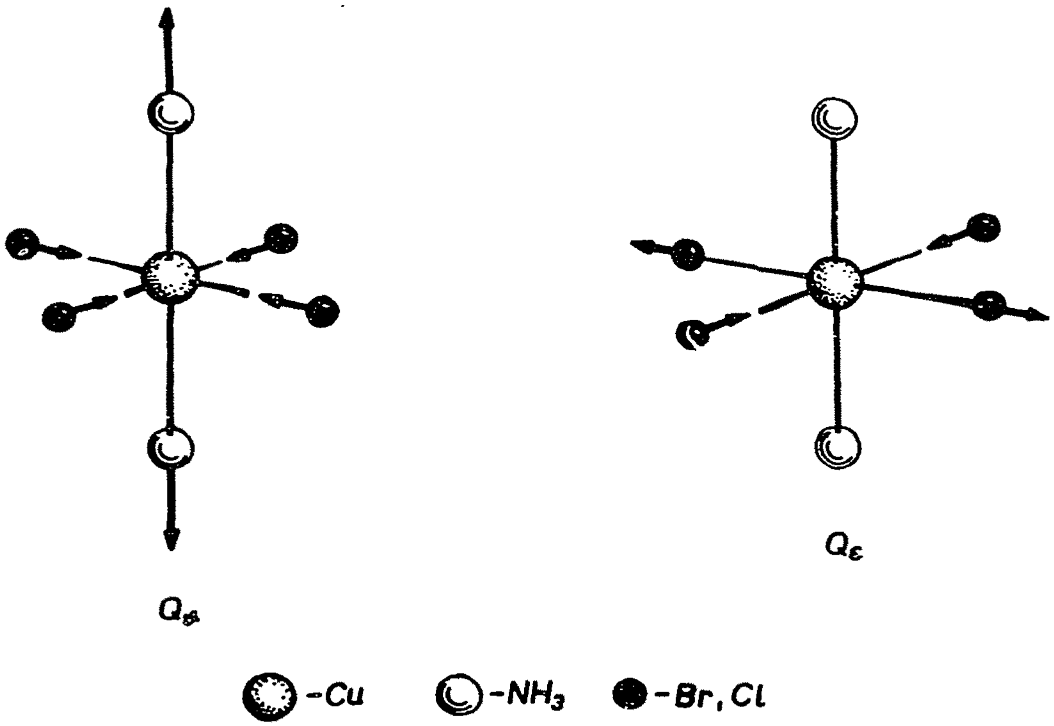

Fig. 15. The Q_θ and Q_ϵ normal coordinate displacements for an octahedral complex of O_h symmetry.

with equal energy, corresponding with the series of minima points along the circular trough. They change from tetragonal octahedron distorted along the O_z axis (Fig. 16a) to an equivalent tetragonally distorted octahedron — but now along the O_x axis (Fig. 16b) and to one along the O_y axis (Fig. 16c), through intermediate configurations where all three pairs of distances to the ligands are different (Fig. 16d). In the absence of any stabilizing factor (see below) the system performs uninterrupted circular motions along the trough, for which the (quantum—mechanically) averaged configuration is an undistorted octahedron [214,215].

It is just this continuous series of nuclear configurations with equal energy, determined by the "Mexican hat" type adiabatic potential (Fig. 16), which represents, in general, the basis of the plasticity of the Cu^{II} coordination sphere and leads to the diversity of distortion and other stereoisomers of its octahedral complexes. Indeed, as is easily seen from the illustration of the potential, any of the above mentioned configurations of minima points of the trough may be realized (with equal probability) in the stereochemistry of the complex, if only this configuration can be stabilized. In particular there may be conditions when stabilization of not one but several of these configurations

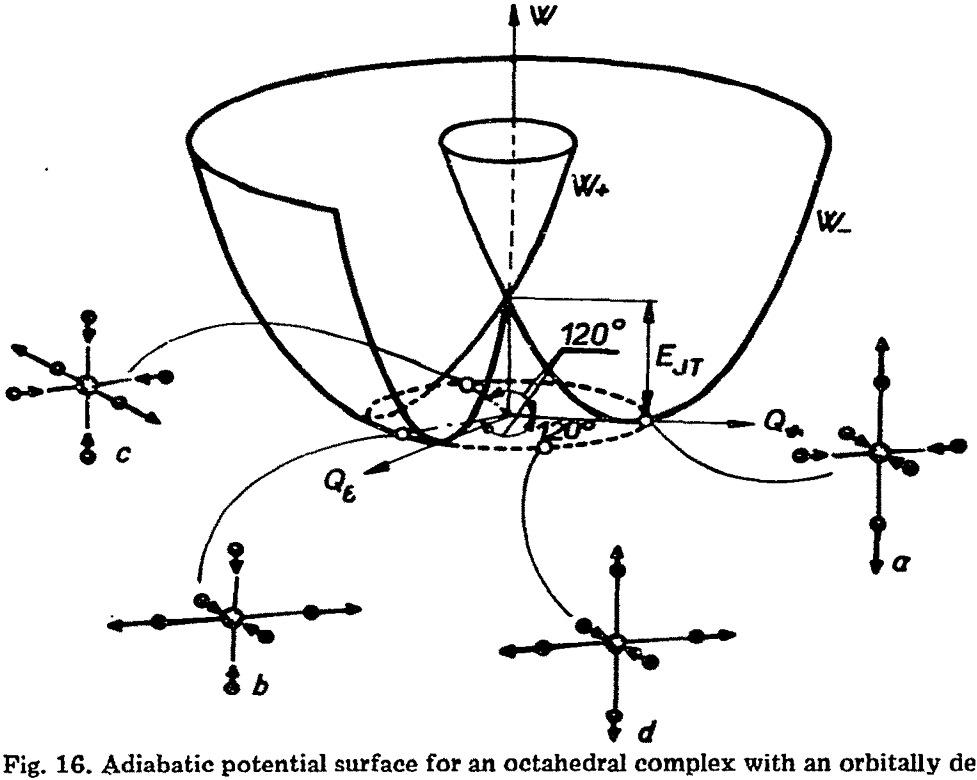

Fig. 16. Adiabatic potential surface for an octahedral complex with an orbitally degenerate E term as a function of the normal coordinates Q_θ and Q_ε shown in Fig. 15. The meaning of W is given in eqn. (6). E_{JT} is the value of the adiabatic potential for $Q = 0$, the Jahn—Teller stabilization energy.

is possible. In such a case we obtain distortion isomers which differ by the lengths of their metal—ligand bonds.

If, for the doubly degenerate E-term under consideration the second order (quadratic) vibronic interaction terms are also important, then their inclusion into the calculation leads to some warping of the "Mexican hat"; three additional minima occur along the trough, the respective distorted configurations corresponding with the three directions of tetragonal deformation of an octahedron (Fig. 16a, b, c). In this case the plasticity of the Cu^{II} coordination sphere is limited by these three directions. The importance of second order terms of the vibronic interaction is determined by the vibronic coupling constant A_2, which (similar to A_1) is dependent on the nature of the metal—ligand interaction, (see ref. 214). In some cases, the situation is possible when $A_2 << A_1$ (in comparable units) and then the quadratic terms are not essential.

Thus the general Jahn—Teller effect theory certainly predicts a plastic coordination sphere around Cu^{II}, in the sense that the electronic structure of Cu^{II} admits (even demands) an asymmetric spatial configuration of the six ligands, with the limitation that their coordinates must be placed in the trough of the "Mexican hat" a circle with normal coordinates $Q_\theta^2 + Q_\epsilon^2$ = constant, (or if quadratic terms are essential, into three minima of tetragonal type). There can be no doubt, at present, about this conclusion. The existence of this effect itself is testified to by its numerous direct as well as indirect experimental manifestations [214—216]. Only the magnitude of the effect remains, a priori, an unknown for concrete cases without detailed calculations. An example of a numerical estimate of the order of magnitude of the effect is given below (see p. 291). However, it is known that Cu^{II} (together with Mn^{III}, Cr^{II} and others) is one of the carriers of the strongest Jahn—Teller effect.

The manifestation of Jahn—Teller dynamics of the coordination sphere for complexes in electronically degenerate states, has been discussed in a number of papers (see ref. 214). Such dynamics of themselves can lead neither to absolute distorted configurations nor (the more) to isomers. The transformation of dynamic distortions to static ones can take place only under the influence of an additional stabilizing factor. Let us specify this last concept.

The external factor stabilizing a Jahn—Teller distorted configuration (one of many equivalent configurations) can be:

1. Any weak low symmetry perturbation, e.g. the influence of the next (subsequent) coordination sphere, intramolecular (Van der Waals) interactions, hydrogen bonds, etc.
2. Cooperative interactions of dynamically distorted complexes leading to a phase transition.

In the latter case, the effect of distortion of the neighbouring centres on a given centre, also represents a low symmetry perturbation, but unlike the former, it has dynamic character (at temperatures higher than the temperature of the phase transition). Low symmetry outside influences lead of themselves to the deformation of the complex, which in the case of weak perturbations is very small, but in the presence of the Jahn—Teller effect, these perturbations stabilize Jahn—Teller distortions, which can be much greater. The result is as though the weak outside influences were reinforced (amplified) by vibronic interactions [214,217]. The magnitude of the distortion in this case is determined, above all, by the magnitude of the Jahn—Teller effect, while the character and direction of the deformation depends on the outside stabilizing factor. The plasticity of the coordination sphere of copper(II) is, therefore, caused by the electronic and vibronic structure of the complex, but its manifestation depends on the character and nature of the stabilizing exterior factor (just as the plasticity of clay depends on itself, but the sculpture obtained from it is determined by the work of the sculptor).

These theoretical conclusions are qualitatively fully confirmed by the experimental data given above. The deformation statistics of octahedral CuO_6 and CuN_6 species, which are given in part B (Figs. 3a and 3b) testify with certainty that the tetragonally distorted (elongated) octahedron (corresponding to one of the three minima of the adiabatic potential taking into account the quadratic vibronic interaction terms) is stabilized in the crystal state. In each of the individual cases presented there it is possible to determine qualitatively what the nature of the stabilizing factor is: the differences in the second coordination sphere (sometimes in the limits of the polyatomic ligand itself) or the phase transition, caused by the cooperative interactions of the distortions. In a few cases, when diffraction measurements show a regular octahedral structure for the copper(II) complex (as in the case of the $[Cu(H_2O)_6]^{2+}$ octahedron in a crystal of $CuSiF_6 \cdot 6\,H_2O$ [66]) the Jahn—Teller dynamics of the Cu^{II} coordination sphere is preserved in the crystal, which fact is also proven by physical methods, especially by EPR spectra [214,218]. Such preservation of the dynamics at room temperature can be observed in all cases when the complex has cubic symmetry and when the interaction between the complexes in the crystal state is small (in these cases a phase transition with the stabilization of a definite distortion on each centre can, in principle, take place at lower temperatures).

Special consideration is needed for distortion isomers, whose formation is conditioned by the stabilization of not one, but two or several distorted configurations. The isomer cases discussed above seem to be due to such a compromise of the plasticity properties of the Cu^{II} coordination sphere and the stabilizing properties of the crystal lattice, that the various configurations so-formed have nearly equal energies and therefore the isomers exist simultaneously at the same (room) temperature.

It is necessary to emphasize that the requirement of very close energy values for the isomers, which is essential for the possibility of their observation at the same (or approximately the same) temperature, narrows very much the number of possible observations of distortion isomerism. In fact the number of such isomers is no doubt greater than those described above, but since the differences in their energies are great, they can be discovered only by investigation on a broader temperature scale.

Now consider the crystals $Cu(NH_3)_2X_2$ (X = Cl, Br) as an example to demonstrate how formation of the experimentally observed distortion isomers are caused by combination of the known electronic (more precisely — vibronic) properties of the central atom with the stabilization properties of the crystal as a whole [219]. First we take into account the fact that the crystal is made up of mutually parallel chains each of which is arranged as illustrated in Fig. 17, where all the X atoms occupy equivalent bridge positions [143—145]. Inside the chain there is a strong interaction between copper(II) centres through bridge atoms, while the chains between them are bonded by weak Van der Waals (and/or hydrogen) bonds. Each copper atom is surrounded by four X atoms in the plane of the square and two A atoms in positions 5 and 6. As a consequence of the difference between the X and A atoms the degeneracy of the basic Cu^{II} state in the octahedron is lifted, the ^2E_g term splits into $^2A_{1g}$ and $^2B_{1g}$. Let this splitting be 2Δ (Fig. 18). For the sake of simplicity we shall assume that the term $^2A_{1g}$ is lower (all further considerations are valid and remain the same in the opposite case too).

If we assume that the X atoms in the plane form a regular square, then the polyhedron CuX_4A_2 is a tetragonally deformed octahedron with D_{4h} symmetry. Let us examine the pseudo-Jahn—Teller effect on the orbital states $^2A_{1g}$ and $^2B_{1g}$ of such a complex (see refs. 214 and 219). Their wave functions $\psi_{A_{1g}}$ and $\psi_{B_{1g}}$ in the crystal field theory limit are identical with the atomic functions d_{z^2} or $d_{x^2-y^2}$ (for a d-hole). The normal vibration Q which mixes the investigated states transforms as $A_{1g} \times B_{1g} = B_{1g}$. The atomic displacement corresponding with this vibration is shown in Fig. 19. Let the vibronic coupling constant for the pseudo-Jahn—Teller effect be denoted by a,

$$a = \langle \psi_{B_{1g}} \left(\frac{\partial V}{\partial Q}\right) \psi_{A_{1g}} \rangle \tag{3}$$

where V is the electron—vibrational (vibronic) interaction operator.

Then the secular equation for the electronic state perturbed by the nuclear

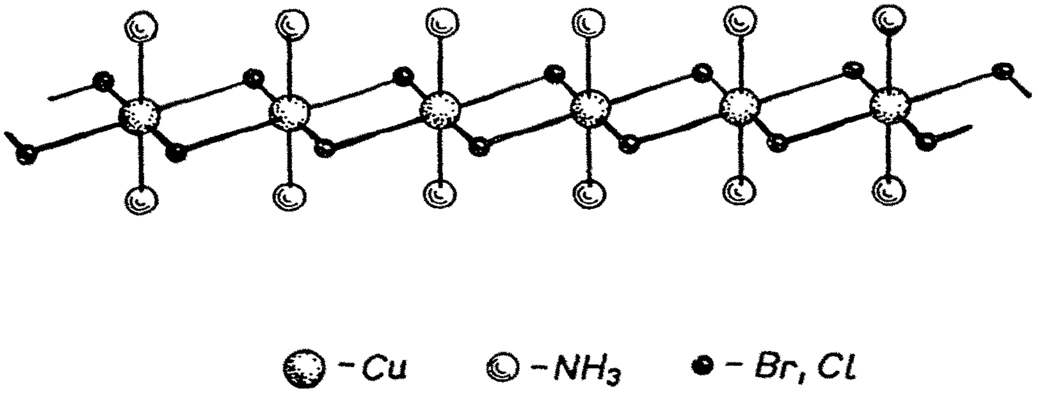

Fig. 17. Structure of parallel chains in the crystal CuA_2X_2.

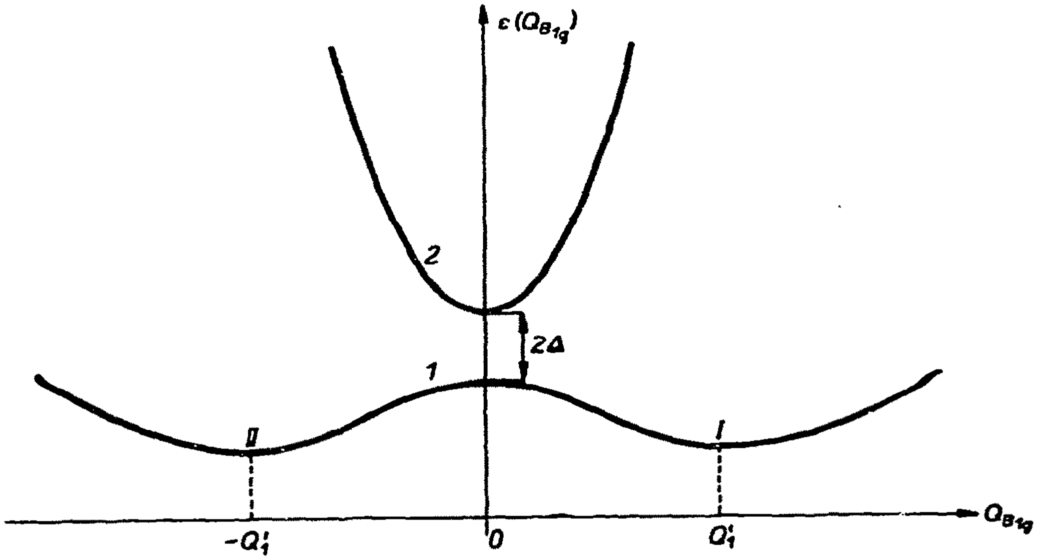

Fig. 18. Adiabatic energy of the ground (1) and the first excited state (2) of a bipyramidal $\mathrm{Cu^{II}}$ complex with D_{4h} symmetry as a function of normal displacements $Q_{B_{1g}}$.

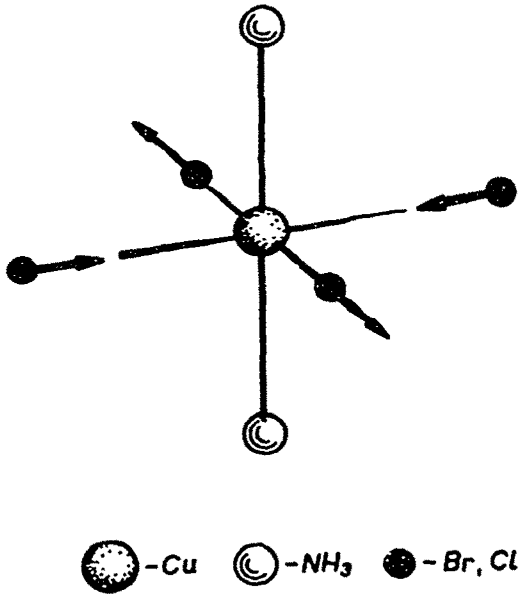

Fig. 19. The B_{1g} type nuclear displacements for a dipyramidal complex of D_{4h} symmetry.

movement has the form

$$\begin{vmatrix} -\Delta - \epsilon & a \,.\, Q \\ a \,.\, Q & \Delta - \epsilon \end{vmatrix} = 0 \qquad (4)$$

its roots being

$$\epsilon_{1,2} = \pm \sqrt{\Delta^2 + a^2 Q^2} \qquad (5)$$

Adding to these expressions for the electronic energy the core interaction (elasticity) terms $\frac{1}{2} KQ^2$, where $K = M\omega^2$ is the force constant of the normal displacement Q (M is the reduced mass, ω is the B_{1g} vibration frequency), we obtain the expression for the adiabatic potential

$$W_{\pm}(Q) = \frac{1}{2} KQ^2 \pm \sqrt{\Delta^2 + a^2 Q^2} \qquad (6)$$

The shape of the curves $W_{\pm}(Q)$ is essentially dependent on the relationship between the parameters a, Δ and K. If $\Delta > (a^2/K)$, then both curves are parabolas. The case of reversed inequality,

$$\Delta < a^2/K \qquad (7)$$

is of interest for us. In this case the curves $W_{\pm}(Q)$ have the form illustrated in Fig. 18. We see that in the lower curve the adiabatic potential for the ground state has its maximum at the point $Q = 0$, which corresponds to a regular bipyramid D_{4h}, and two equivalent (symmetrical with respect to point $Q = 0$) minima at the points

$$Q'_{1,2} = \pm \sqrt{\frac{a^2}{K^2} - \frac{\Delta^2}{a^2}} \qquad (8)$$

In this way, the vibronic interaction (the pseudo-Jahn—Teller effect) on each center causes a deformation of the tetragonal bipyramid so that the basic square with X atoms in its apex changes to a rhombus with a great diagonal along the O_x axis (minimum I in Fig. 18) or along the O_y axis (minimum II).

As a result of strong interaction between the deformations on the neighbouring centres in the chain (through the common X atoms) the last one easily passes into the ordered state in which the center distortions are correlated, and remains in this correlated state up to high temperatures [214]. Here the vibronic distortions are being fixed by the second of the stabilizing factors mentioned above — phase transition. Taking this into consideration, we can assume that an individual chain has, at room temperature, two stable states, I and II (Fig. 20), which correspond to two minima for each centre (I and II in Fig. 18). Thus we come to a conclusion about the possible existence of two stable equivalent structures of the chain CuA_2X_2, caused by the pseudo-Jahn—Teller effect on each bipyramidal centre CuX_4A_2, and the ordering of the distortions in the chain as a result of strong interaction between the centres.

There still remains one important crystalline factor to investigate — the

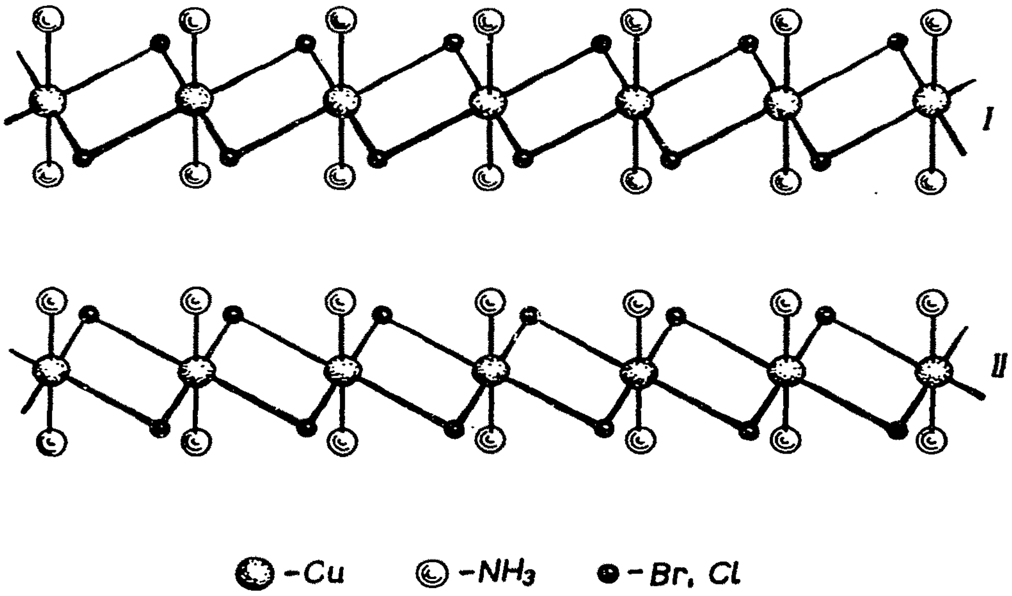

Fig. 20. Two equivalent motives in the ordered chains of the CuA_2X_2 crystal corresponding to the minima I and II in Fig. 18.

interaction between chains. Analysing the structure of the crystal CuA_2X_2 composed of parallel chains, one can see that the interaction between them will be optimal for the undistorted structure of each chain when the crystal as a whole is cubic. Indeed, in such a crystal, the corresponding distances between the atoms in different chains are minimal, and they increase with distortion of the chains towards the structures I or II. The magnitude of the energy differences for the interacting chains in a cubic crystal and in a crystal with chains of type I or II is not known (although in principle it could be estimated semiempirically). We can, however, imagine the situation qualitatively illustrated in Fig. 21a, where it is shown that the interaction energy of the chains in the crystal under consideration has its minimum when $Q = 0$, where Q is the coordinate of deformation of the chains, corresponding to the B_{1g}-type coordinate given above (Fig. 19) for each centre. By adding the adiabatic energy of the chain (taken from Fig. 18) to the energy of interaction between the chains as a function of Q (Fig. 21b), we obtain the resulting total energy of the crystal (Fig. 21c). This latter as evident from the figure has, under the accepted assumptions, three minima: in addition to the two minima I and II for the energy of the chains (corresponding with the pseudo-Jahn—Teller distorted configurations), there is a shallow minimum for the undistorted cubic configuration when $Q = 0$.

Complementary minima in this scheme can be obtained for crystals in which a part of the chains is in minimum I and another part in minimum II.

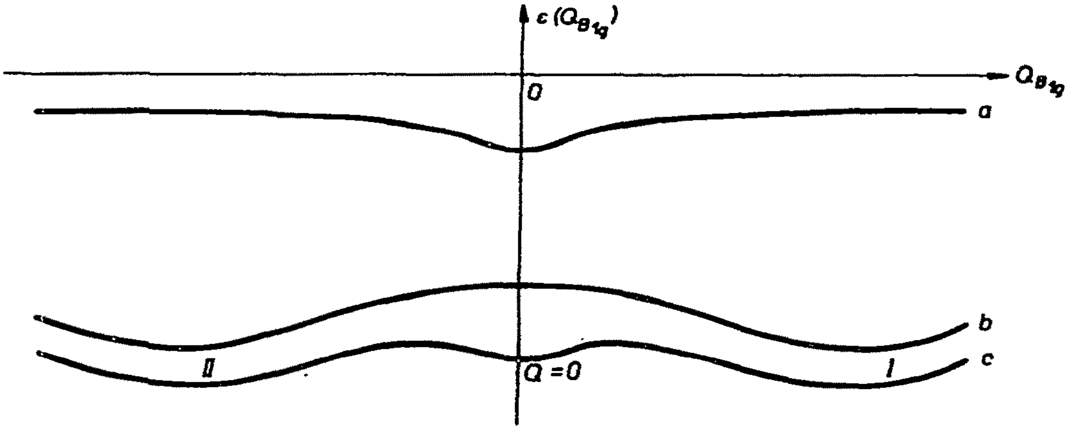

Fig. 21. Energies of intermolecular interaction between the chains (a), vibronic interactions in the chains (b) and their sum (c) as a function of ordered displacements consistent with the normal coordinates $Q_{B_{1g}}$ on each Cu^{II} center.

For these crystals, the interaction between the chains (for the same reasons as mentioned above) is even smaller than when all of them are mutually correlated (ordered) and are found in the same type of minima (either I or II), and therefore, the complementary minima will be shallower (less deep) than minima I and II for fully correlated crystals (but deeper than the minimum for a cubic crystal when $Q = 0$; it is assumed that the vibronic energy inside the chains prevails over the intramolecular energy).

It can be easily shown that the scheme described above qualitatively elucidates all the basic facts which are observed in the distortion isomerism of compounds CuA_2X_2. Indeed, the states of the deepest minima I or II (Fig. 21) correspond to the observed α-isomers with structure given in Fig. 20. The relative minimum, at $Q = 0$, corresponds to the unstable β-isomer which has a cubic structure with a regular bipyramid in each centre. The additional relative minima (for crystals with mutually uncorrelated distorted chains) correspond to the intermediate structures described in refs. 2, 146. Such an interpretation is in agreement with all the features (peculiarities) of these isomers, with the way they behave under the influence of temperature and pressure, with the methods of their preparation, the spectral properties, the conditions of their interconversion, ect. (see chapters C. and D.).

Good crystals are obtained only in the case of the β-isomer [2,143—145], i.e. in the case, when in agreement with the theory, the intramolecular interaction, leading to the formation of the crystal, is just a maximum. On the other hand, the α-isomer and intermediate structures, in agreement with the weak interaction between their chains, are not obtained in the form of crystals. In this connection it may also be relevant that especially in the case of the β-isomer (and only in this case) the crystal $Cu(NH_3)_2X_2$, (X = Cl, Br) contains a great admixture of the compound NH_4X [143], which itself grows in a cubic crystal isomorphic with the crystal of the β-isomer $Cu(NH_3)_2X_2$, these two compounds easily forming mixed cubic crystals [143]. It is quite possible that the cubic structures of the $Cu(NH_3)_2X_2$ chains, being unstable due to the pseudo-Jahn—Teller effect on each center, are stabilised not only by intramolecular interactions between chains, but also by the presence of many NH_4X molecules, which alternate in the chain with the $Cu(NH_3)_2X_2$ molecules (in the ratio ~1 : 1). A theoretical solution to the problem of what is the basic cause of cubic crystal structure stabilization — the presence of additional molecules in the chains or interaction between chains, will be possible only by evaluation of the chain interaction energy as a function of the distortion in the chains.

The results obtained are based essentially on the assumption that the non-equality [7], the criterion of the pseudo-Jahn—Teller effect, is fulfilled. To confirm this statement the constants Δ, a and K for the Cu^{II} system under consideration must be obtained and compared. For this reason a numerical calculation of the electronic energies $\epsilon(Q)$ for the system $Cu(NH_3)_2Br_4$ in the ground A_{1g} and first excited B_{1g} states as a function of the $Q_{B_{1g}}$ distortion was undertaken [220]. The results give directly the 2Δ value equal to the difference between these energies at $Q = 0$, and the a value, easily obtained from eqn. (5). The magnitude of $K = M\omega^2$ may be obtained from the experimental value of the B_{1g} type vibration frequency ω. Since the latter has not yet been measured, a value of $\omega \approx 100$—$200\ cm^{-1}$ was taken by analogy with other infrared spectra data available for Cu^{II} compounds.

The calculations allow us both to check the pseudo-Jahn—Teller effect criterion [7] and to estimate the magnitude of distortion in the adiabatic potential minimum through eqn. (8). The results are [220]: $\Delta \approx 1.3 \times 10^3\ cm^{-1}$, $a \approx 14 \times 10^3\ cm^{-1}\ Å^{-1}$, and $Q' \approx 0.2 - 0.5$ Å (Q' varies with the magnitude of ω), the last value being in qualitative agreement with the experimental $Q' \approx 0.4$ Å (see the X-ray data for the α-isomer [143—145]). Thus, direct numerical calculation confirms the pseudo-Jahn—Teller origin of the coordination sphere distortion in the crystal under consideration.

F. CONCLUDING REMARKS

The main intention of this paper is to draw the attention of the reader to a new type of crystallochemical property belonging to coordination compounds with degenerate or pseudo-degenerate electronic terms (especially E terms), namely, the plasticity of the coordination sphere and distortion isomerism. These properties were analyzed and confirmed by a comprehensive study of available experimental data on Cu^{II} coordination compounds, and the proof of their Jahn—Teller and pseudo-Jahn—Teller origin is given on the basis of the latest progress in the theory of these effects.

Many crystallochemical data as well as data obtained by different methods of structure research allowed us to show that the coordination polyhedron of Cu^{II} complexes is relatively plastic. A concrete manifestation of its plasticity is distortion isomerism, demonstrated in this paper by a considerable number of examples. The present experimental knowledge presented here and its theoretical interpretation allows us to draw the conclusion, according to which plasticity and distortion isomerism are typical and general features of copper(II complexes. This structure—geometry behaviour becomes evident in many of their physical and chemical properties.

Calculations of the pseudo-Jahn—Teller distortion in the Cu^{II} coordination sphere of the $Cu(NH_3)_2Br_2$ crystal were carried out and together with the idea of the cooperative effect in the crystal chains and interchain interactions lead to an uncontradictory qualitative (and even semiquantitative) elucidation of the origin of the distortion isomerism in this crystal. Since the vibronic constants for coordination compounds depend mainly on the nature of the metal atom (the calculations [220] show a relatively weak dependence of the "a" constant on the ligand atoms) there is no doubt of the general validity of the effect in other Cu^{II} compounds. Moreover, similar properties as described above for Cu^{II} complexes may be expected for all coordination systems with a doubly degenerate E ground term (octahedral Mn^{III}, Cr^{II}, Ni^{III}, low spin Co^{II}, etc.). However, since their vibronic constants may be quite different from that of Cu^{II}, it is not known a priori in what compounds and under what conditions (especially, at what temperatures) the properties of plasticity and distortion isomerism can be observed for the complexes of these metal ions.

The results of this paper are interesting also in another aspect. The crystal chemistry of coordination compounds is developing now mainly on the ground of the idea of compact packing of atomic groups in crystals governed by minimum Van der Waals (or, more generally, electronic) interatomic and intermolecular interaction energy. The considerations given above lead to stress upon a new important factor, namely, that of vibronic structure of the coordination center, which may lead to new trends in crystal chemistry.

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REFERENCES

1 MTP International Review of Science, Vol. 9, Reaction Mechanisms in Inorganic Chemistry, M.L. Tobe (Ed.), Butterworths, London, 1972, p. 37; E.I. Muetterties, Inorg. Chem., 4 (1965) 769.
2 J. Gažo, Pure Appl. Chem., 38 (1974) 279.
3 P.J. Wang and H.G. Drickamer, J. Chem. Phys., 59 (1973) 559.
4 R.L. Harlow, W.J. Wels, G.W. Watt and S.H. Simonsen, Inorg. Chem., 13 (1974) 2106.
5 R.D. Willett, J.R. Ferraro and M. Choca, Inorg. Chem., 13 (1974) 2919.
6 B.J. Hathaway and P.G. Hodgson, J. Inorg. Nucl. Chem., 35 (1973) 4071.
7 A.A.G. Tomlinson, B.J. Hathaway, B.E. Billing and P. Nicholls, J. Chem. Soc. A, (1969) 65.

8 M. Keeton, A.B.P. Lever and B.S. Ramaswamy, Can. J. Chem., 48 (1970) 3185.
9 A.B.P. Lever, E. Montovani and J.C. Donini, Inorg. Chem., 10 (1971) 2424.
10 F. Hanic and J. Michalov, Acta Crystallogr., 13 (1960) 299.
11 P.C. Chieh, G.G. Mesmer and G.J. Palenik, Inorg. Chem., 10 (1971) 133.
12 J.A. Bevan, D.P. Graddon and J.F. McConnell, Nature (London), 199 (1963) 373.
13 G.A. Barday and A. Cooper, J. Chem. Soc., (1963) 3746.
14 M. Blackstone, J. van Thuyl and C. Romers, Rec. Trav. Chim. Pays-Bas, 85 (1966) 557.
15 I. Robertson and M.R. Truter, J. Chem. Soc. A, (1967) 309.
16 W.M. McIntyre, J.M. Robertson and R.F. Zahrobsky, Proc. Roy. Soc. Ser. A, 289 (1965) 161.
17 J.W. Carmichael, L.K. Steinrauf and R.L. Belford, J. Chem. Phys., 45 (1965) 3959.
18 C.K. Prout, R.A. Armstrong, J.R. Carruthers, J.G. Forrest, P. Murray-Rust and J.C.F. Rossotti, J. Chem. Soc. A, (1968) 2791.
19 P.K. Hon, C.E. Pfluger and R.L. Belford, Inorg. Chem., 5 (1966) 516.
20 L.H. Dalh, referred to in T.S. Piper and R.L. Belford, Mol. Phys., 5 (1962) 169.
21 D. Hall, A.J. McKinnon and T.N. Waters, J. Chem. Soc., (1965) 425.
22 A.J. McKinnon, T.N. Waters and T.N. Hall, J. Chem. Soc., (1964) 3290.
23 M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, J. Chem. Soc., Dalton Trans., (1972) 2477.
24 P.C. Healy and A.H. White, J. Chem. Soc., Dalton Trans., (1972) 1913.
25 J.D. Lee, D.S. Brown and B.G.A. Melson, Acta Crystallogr. Sect. B, 25 (1969) 1378.
26 H. Koizumi, H. Osati and T. Watanabe, J. Phys. Soc. Japan, 18 (1963) 117.
27 M. Laight, J. Tordiman, J.C. Gnitel and G. Boss, Acta Crystallogr. Sect. B, 28 (1972) 2721.
28 C.K. Prout, J.R. Carruthers and J.C.F. Rossotti, J. Chem. Soc. A, (1971) 3336.
29 M.S. Hussain, M.D. Joesten and L.P.G. Lenhert, Inorg. Chem., 9 (1970) 162.
30 C.K. Prout, J.R. Carruthers and F.J.C. Rossotti, J. Chem. Soc. A, (1971) 3350.
31 H. Jaggi and H.R. Oswald, Acta Crystallogr., 14 (1961) 1041.
32 M. Martinez-Ripoll and S. Martinez-Carrera, Acta Crystallogr. Sect. B, 27 (1970) 677.
33 B. Rama Rao, Acta Crystallogr., 14 (1961) 321.
34 M. Langt, J.C. Gnitel, J. Tordiman and G. Bassi, Acta Crystallogr. Sect. B, 28 (1972) 201.
35 S. Siegel and H.R. Hockstra, Acta Crystallogr. Sect. B, 24 (1968) 967.
36 M.B. Gingi, C. Guastini, A. Musatti and M. Nardelli, Acta Crystallogr. Sect. B, 25 (1969) 1833.
37 C.K. Prout, J.C. Carruthers and F.J.C. Rossotti, J. Chem. Soc. A, (1971) 3342.
38 S. Asbrink and L.J. Norrby, Acta Crystallogr. Sect. B, 26 (1970) 8.
39 R.F. Zahrobsky and W.H. Baur, Acta Crystallogr. Sect. B, 24 (1968) 508.
40 C. Sabelli and D.F. Zanazzi, Acta Crystallogr. Sect. B, 24 (1968) 1214.
41 H.G. Bachmann and J. Zemann, Acta Crystallogr., 14 (1961) 747.
42 G.E. Bacon and N.A. Curry, Proc. Roy. Soc. Ser. A, 266 (1962) 95.
43 B. Rama Rao, Acta Crystallogr., 14 (1961) 738.
44 L. Flügel-Kahler, Acta Crystallogr., 16 (1963) 1009.
45 B.E. Robertson and C. Calvo, Acta Crystallogr., 22 (1967) 665.
46 P. Süsse, Acta Crystallogr., 22 (1967) 146.
47 H.G. Heide, K. Boll-Dornberger, Acta Crystallogr., 8 (1955) 425.
48 C.K. Prout, J.R. Carruthers and F.J.C. Rossotti, J. Chem. Soc. A, (1971) 554.
49 L. Kihlborg and E. Gebert, Acta Crystallogr. Sect. B, 26 (1970) 1020.
50 S. Ghose, Acta Crystallogr., 15 (1962) 1105.
51 S. Ghose, Acta Crystallogr., 16 (1963) 124.
52 M.D. Glick, G.L. Downs and L.F. Dahl, Inorg. Chem., 3 (1964) 1712.
53 I. Hjerten and B. Nyberg, Acta Chem. Scand., 27 (1973) 345.
54 R.V.G. Sundara Rau, K. Sundaramma and R. Sirasankara, Z. Kristallogr., 110 (1958) 231.

55 M.J. Kay, I. Almodovar and S.F. Kaplan, Acta Crystallogr. Sect. B, 24 (1968) 1312.
56 D.A. Langs and C.R. Hare, Chem. Commun., (1967) 853.
57 R. Kiriyama, H. Ibamoto and K. Matsuo, Acta Crystallogr., 7 (1954) 482.
58 D.E. Fenton, M.R. Truter and B.L. Vickery, Chem. Commun., (1971) 93.
59 H.R. Oswald, Helv. Chim. Acta, 52 (1969) 2369.
60 J.A. Bertrand and D.A. Carpenter, Inorg. Chem., 5 (1966) 514.
61 H. Heritsch, Z. Kristallogr., 99 (1938) 466.
62 W. Nowacki and R. Scheidegger, Helv. Chim. Acta, 35 (1952) 375.
63 K. Brandt, Ark. Kemi. Min. Geol. A, 17 (1948) 13.
64 M.A. Kisvomitre, J. Chem. Phys., 37 (1962) 1408.
65 M.D. Joesten, M.S. Hussain, P.G. Lenhert and J.H. Venables, J. Amer. Chem. Soc., 90 (1968) 1623.
66 B.J. Temple, unpublished results.
67 P.T. Miller, P.G. Lenhert and M.D. Joesten, Inorg. Chem., 12 (1973) 218.
68 H. Heritsch, Z. Kristallogr., 102 (1939) 1.
69 M. Kamenar, Acta Crystallogr. Sect. B, 25 (1969) 800.
70 N.V. Mani and S. Ramaseshan, Z. Kristallogr., 115 (1961) 97.
71 F. Hanic, Czech. J. Phys. B, 10 (1960) 169.
72 G.B. Brown and R. Chidambaram, Acta Crystallogr. Sect. B, 25 (1969) 676.
73 C.J. Brown, J. Chem. Soc. A, (1968) 2488.
74 M. Matthew and N.R. Kunchur, Acta Crystallogr. Sect. B, 26 (1970) 2054.
75 C.D. Stout, M. Sundaralingam and G. Hung-Yin Lin, Acta Crystallogr. Sect. B, 28 (1972) 2136.
76 M. Bukowska and M.A. Porai-Koshits, Zh. Strukt. Khim., 7 (1961) 712.
77 I. Agrell, Acta Chem. Scand., 20 (1966) 1281.
78 B.J. Hathaway and F.S. Stephens, J. Chem. Soc. A, (1970) 884.
79 O.P. Anderson, J. Chem. Soc., Dalton Trans., (1973) 1237.
80 J. Korvenranta and A. Pajunen, Suom. Kemistilehti B, 43 (1970) 119.
81 Scoulondi, Acta Crystallogr., 6 (1953) 541.
82 N.W. Isaacs and C.H.L. Kennard, J. Chem. Soc. A, (1969) 386.
83 D.L. Cullen and E.C. Lingafelter, Inorg. Chem., 9 (1970) 386.
84 Sh. Zacks, "The Theory of Statistical Inference", 1971, Wiley, New York.
85 C.K. Prout, G.B. Allison and F.J.C. Rossotti, J. Chem. Soc. A, (1971) 3331.
86 A. Sugihara, T. Ashida, Y. Sasada and M. Katudo, Acta Crystallogr. Sect. B, 26 (1970) 1836.
87 R.D. Ball, D. Hall, C.E.F. Pickerd and T.N. Waters, J. Chem. Soc. A, (1967) 1435.
88 G. Fransson and B.K.S. Lundberg, Acta Chem. Scand., 26 (1972) 3969.
89 J.J. Bonnet and Y. Jeanin, Acta Crystallogr. Sect. B, 26 (1970) 318.
90 M.A. Bush and D.E. Fenton, J. Chem. Soc. A, (1971) 2446.
91 A. Pajunen and M. Lehtonen, Suom. Kemistilehti B, 45 (1972) 43.
92 A. Baglio, J. Chem. Soc. A, (1969) 65.
93 A. Pajunen, K. Smolander and I. Belinskij, Suom. Kemistilehti B, 45 (1972) 317.
94 R. Hämäläinen, Suom. Kemistilehti B, 46 (1973) 237.
95 E. Luukkonen, A. Pajunen and M. Lehtonen, Suom. Kemistilehti B, 43 (1970) 158.
96 Y. Komiyama and E.C. Lingafelter, Acta Crystallogr., 17 (1964) 1145.
97 J.I. Smolin, J.F. Šepelev and I.K. Butikova, Kristallografiya, 17 (1972) 15.
98 E. Luukkonen and A. Pajunen, Suom. Kemistilehti B, 42 (1969) 474.
99 M. Cannas, G. Carta and G. Marongiu, Chem. Commun., (1971) 1462.
100 R.V. Chastain, Jr., and Th.L. Dominick, Inorg. Chem., 12 (1973) 2621.
101 A. Pajunen, Suom. Kemistilehti B, 40 (1967) 32.
102 J. Korvenranta, Suom. Kemistilehti B, 46 (1973) 240.
103 A. Pajunen, Suom. Kemistilehti B, 42 (1969) 261.
104 R. Uggla and M. Klinga, Suom. Kemistilehti B, 45 (1972) 10.
105 A. Pajunen, Suom. Kemistilehti B, 42 (1969) 15.

106 R. Uggla, J. Visti, S. Lundell and M. Näsäkkälä, Suom. Kemistilehti B, 43 (1970) 124.
107 R. Uggla, J. Visti, M. Klinga and M. Näsäkkälä, Suom. Kemistilehti B, 43 (1970) 488.
108 R.D. Gillard, D. Rogers, R.D. Diamond and D.J. Williams, Acta Crystallogr., 16 (1963) 467.
109 B.E. Robertson and C. Calvo, Can. J. Chem., 46 (1968) 605.
110 B. Duffin and S.C. Wallwork, Acta Crystallogr. Sect. B, 20 (1965) 210.
111 G. Gattow, Acta Crystallogr., 11 (1958) 377.
112 S. Sčavničar and B. Malkovič, Acta Crystallogr. Sect. B, 25 (1969) 2046.
113 O. Lindquist, Acta Chem. Scand., 26 (1972) 1423.
114 L. Kihlborg, R. Norrestam and B. Olivecrona, Acta Crystallogr. Sect. B, 27 (1971) 2066.
115 B. Morosin, Acta Crystallogr. Sect. B, 26 (1970) 1203; J. Garaj, Acta Chem. Scand., 22 (1968) 1710.
116 S.C. Wallwork and W.E. Adisson, J. Chem. Soc., (1965) 2925.
117 G. Gattow and J. Zemann, Acta Crystallogr., 11 (1958) 866.
118 M. Handlovič, Acta Crystallogr. Sect. B, 25 (1969) 227.
119 C.V. Groebel and R.J. Doedens, Inorg. Chem., 10 (1971) 2607.
120 M.R. Truter and B.L. Vickery, J. Chem. Soc., Dalton Trans., (1972) 395.
121 P.T. Miller, P.G. Lenhert and M.D. Joesten, Inorg. Chem., 11 (1972) 2221.
122 L. Coghi, A. Mangia, M. Nardelli, G. Pelezzi and L. Sozzi, Chem. Commun., (1968) 1475.
123 D.L. Cullen and E.C. Lingafelter, Inorg. Chem., 9 (1970) 1865.
124 H. Nakai, Bull. Chem. Soc. Japan, 44 (1971) 2412.
125 R. Söderquist, Acta Crystallogr. Sect. B, 24 (1968) 450.
126 B. Morosin, Acta Crystallogr. Sect. B, 25 (1969) 19.
127 B. Morosin and J. Howatson, Acta Crystallogr. Sect. B, 26 (1970) 2062.
128 O.P. Anderson, J. Chem. Soc., Dalton Trans., (1972) 2597.
129 R. Hämäläinen and A. Pajunen, Suom. Kemistilehti B, 46 (1973) 285.
130 F. Mazzi, Acta Crystallogr., 8 (1955) 137.
131 E.C. Lingafelter, L.C. Andrews, R.M. Kirchner, N.J. Rose and L.J. Wilson, Coord. Chem. Rev., 8 (1972) 55.
132 F.S. Stephens, J. Chem. Soc. A, (1969) 883.
133 J. Garaj, F. Valach and J. Gažo, unpublished results.
134 B.E. Robertson and C. Calvo, J. Solid State Chem., 1 (1970) 120.
135 C. Calvo, Can. J. Chem., 43 (1965) 1147.
136 K. Lukaszziewicz, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 15 (1967) 47.
137 A. Pietraszko and K. Lukaszziewicz, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 16 (1968) 183.
138 N. Krishnamachari and C. Calvo, Acta Crystallogr. Sect. B, 28 (1972) 2883; C. Calvo, private communication.
139 K. Lukaszziewicz and R. Smajkiewicz, Rocz. Chem., 35 (1961) 741.
140 K. Lukaszziewicz, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 15 (1967) 53.
141 C. Calvo, Can. J. Chem., 43 (1965) 1139.
142 J. Gažo, K. Serátorová and M. Serátor, Chem. Zvesti, 13 (1959) 5.
143 I.A. Čakajdová and F. Hanic, Acta Crystallogr., 11 (1958) 610.
144 F. Hanic, Acta Crystallogr., 12 (1959) 739.
145 L. Zsoldos, Magy., Fiz. Folyórat, 10 (1962) 189.
146 M. Serátor and J. Gažo, Zbornik Chemickotechnologickej Fakulty, SVŠT, Bratislava, 1960, pp. 47—52.
147 B.J. Hathaway and A.A. Tomlinson, Coord. Chem. Rev., 5 (1970) 1.
148 J. Kohout and J. Gažo, Chem. Zvesti, 22 (1968) 905, and references therein.
149 M. Peyrone, Lieb. Ann., 51 (1844) 1.
150 S.M. Jörgensen, J. Prakt. Chem., 33 (1886) 489.
151 J. Garaj and J. Gažo, Chem. Zvesti, 19 (1965) 593.
152 H. Langfelderová, M. Kabešová, J. Garaj and J. Gažo, Z. Chem., 6 (1966) 32.
153 M. Kabešová, J. Garaj and J. Gažo, Collect. Czech. Chem. Commun., 37 (1972) 942.

154 M. Melnik, M. Kabešová, T. Obert and J. Gažo, Proc. IVth Conf. Coord. Chem., Bratislava—Smolenice, Czechoslovakia, December 13—18, 1973, pp. 52—59.
155 J. Gažo, Chem. Zvesti, 20 (1966) 212.
156 A.Ch. Villa, A.G. Manfredotti, M. Nardelli and G. Pelizzi, J. Cryst. Mol. Struct., 1 (1971) 245.
157 M.R. Kidd, R.S. Sager and W.H. Watson, Inorg. Chem., 6 (1967) 946.
158 D.R. Johnson and W.H. Watson, Inorg. Chem., 10 (1971) 1069, 1281.
159 R.S. Sager and W.H. Watson, Inorg. Chem., 8 (1969) 308.
160 M.J. Frazer, G.V. Robinson and F.B. Taylor, J.Chem. Soc. A, (1969) 2451.
161 G.W. Inman, F.W. Hatfield and R.F. Drake, Inorg. Chem., 11 (1972) 2425.
162 A.F. Cameron, D.W. Taylor and R.H. Nuttall, J. Chem. Soc., Dalton Trans., (1972) 58.
163 R.J. Dudley, R.J. Fereday, B.J. Hathaway, P.G. Hodgson and P.C. Power, J. Chem. Soc., Dalton Trans., (1973) 1044.
164 E.N. Baker, G.R. Clark, D. Hall and T.N. Waters, J. Chem. Soc. A, (1967) 251.
165 G.R. Clark, D. Hall and T.N. Waters, J. Chem. Soc. A, (1969) 2808.
166 M. Stackelberg, Z. Anorg. Allg. Chem., 253 (1947) 136.
167 E.C. Lingafelter, G.L. Simmons and B. Morosin, Acta Crystallogr., 14 (1961) 1222.
168 D. Hall, V.S. Sheat and T.N. Waters, J. Chem. Soc. A, (1968) 460.
169 N.V. Lohskin, A.K. Piskunov, L.A. Karitsyna and D.N. Shigorin, Dokl. Akad. Nauk SSSR, 143 (1962) 867.
170 J.G. Gibson and E.D. McKenzie, J. Chem. Soc. A, (1971) 1666.
171 N.A. Bailey, E.D. McKenzie and J.R. Mullins, Chem. Commun., (1970) 1103.
172 C.H. Wei, Inorg. Chem., 11 (1972) 2315.
173 R.H. Holm, A. Chakraworthy and L.J. Theriot, Inorg. Chem., 5 (1966) 625.
174 M. Nutiu, F. Marx and G. Ostrogovich, Rev. Roum. Chim., 17 (1972) 1545, and references therein.
175 M. Hvastijová, J. Kohout, J. Gažo and F. Valach, J. Inorg. Nucl. Chem., 38 (1976) 705.
176 L.F. Larkworthy and K.C. Patel, J. Inorg. Nucl. Chem., 32 (1970) 1263.
177 K.C. Patel and D.E. Goldberg, Inorg. Chem., 11 (1972) 759.
178 M. Kato, K. Imai, Y. Muto, T. Totti and H.B. Jonassen, J. Inorg. Nucl. Chem., 35 (1973) 109.
179 G.L. Seebach, D.K. Johnson, H.J. Stoklasa and J.R. Wasson, Inorg. Nucl. Chem. Lett., 9 (1973) 295.
180 P. Pfeiffer and H. Glaser, J. Prakt. Chem., 153 (1939) 265.
181 J. Lamotte-Brasseur, Bull. Soc. Roy. Sci. Liege, 41 (1972) 331.
182 J. Garaj and J. Gažo, Chem. Zvesti, 28 (1966) 485.
183 Ľ. Macášková, M. Melnik, M. Kabešová, G. Ondrejovič and J. Gažo, Suom. Kemistilehti B, 46 (1973) 106.
184 M. Kabešová J. Garaj and J. Gažo, Zbornik Chemickotechnologickej Fakulty, SVŠT, Bratislava, 1969—1970, pp. 17—29.
185 D. Attanasio, I. Collamati and C. Ercolani, J. Chem. Soc. A, (1971) 2516.
186 T. Yasui and Y. Shimura, Bull. Chem. Soc. Japan, 39 (1966) 604, and references therein.
187 M. Mackoviak and J. Dorosz, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 21 (1973) 685.
188 F.A. Walker and H. Sigel, Inorg. Chem., 11 (1972) 1162.
189 P. Thomas, D. Rehorek and H. Spindler, Z. Chem., 12 (1972) 426.
190 D. Rehorek, B. Kirmse and P. Thomas, Z. Anorg. Allg. Chem., 395 (1972) 103.
191 G.C. Kulasingam and W.R. McWhinnie, Chem. Ind. (London), (1966) 2200.
192 E. Lidner, J.P. Lorenz and D. Langner, Chem. Ber., 106 (1973) 404.
193 J.C. Lancaster and W.R. McWhinnie, Inorg. Chim. Acta, 5 (1971) 515.
194 M. Kabešová, H. Langfelderová, J. Garaj and J. Gažo, Chem. Zvesti, 21 (1967) 887.
195 E. Suito and E. Sebido, Proc. Jap. Acad., 39 (1957) 196.
196 Ľ. Macášková, M. Kabešová, J. Garaj and J. Gažo, Monatsch. Chem., 104 (1973) 1473.

197 T.N. Waters and D. Hall, J. Chem. Soc., (1959) 1200.
198 J. Garaj and J. Krätsmár-Šmogrovič, Chem. Zvesti, 20 (1960) 763.
199 M. Inoue, M. Kishita and M. Kubo, Acta Crystallogr., 16 (1963) 699.
200 M. Melnik, M. Kabešová, F. Valach and J. Gažo, Finn. Chem. Lett., (1974) 8.
201 M. Dunaj-Jurčo, H. Langfelderová and J. Gažo, Z. Chem., 11 (1971) 2681.
202 R.L. Martin and H. Waterman, J. Chem. Soc., (1959) 1359.
203 M. Inoue, M. Kishita and M. Kubo, Inorg. Chem., 3 (1964) 239.
204 G. Ondrejovič, Ľ. Macášková and J. Gažo, Z. Anorg. Allg. Chem., 393 (1972) 173.
205 J. Gažo, K. Serátorová and M. Serátor, unpublished results.
206 H. Langfelderová, M. Kabešová, J. Garaj and J. Gažo, Chem. Zvesti, 22 (1968) 42.
207 B.V. Erofejev and L.S. Kravčuk, Kinet. Katal., 10 (1969) 533.
208 H. Langfelderová, J. Mikovič, J. Garaj and J. Gažo, Thermochim. Acta, 5 (1973) 303.
209 H. Langfelderová, M. Serátor, J. Garaj and J. Gažo, Chem. Zvesti, 28 (1974) 180.
210 H. Langfelderová, J. Garaj and J. Gažo, Chem. Zvesti, 28 (1974) 748.
211 M.J. Djatkina and M.A. Porai-Koshits, Dokl. Akad. Nauk SSSR, 125 (1959) 1030.
212 I.B. Bersuker, Zh. Fiz. Khim., 35 (1961) 471.
213 A.D. Liehr, J. Phys. Chem., 67 (1963) 389, 471.
214 I.B. Bersuker, Coord. Chem. Rev., 14 (1975) 357.
215 I.B. Bersuker, Elektronnoe strojenie i svojstva koordinacijonnych sojedineij. Vvedenie v teoriu, Izd. "Chimia", Leningrad, 1976.
216 R. Englman, The Jahn—Teller Effect in Molecules and Crystals, Wiley, London, 1972.
217 I.B. Bersuker and B.G. Vechter, Proc. IVth Conf. Coord. Chem., Bratislava—Smolenice, Czechoslovakia, December 13—18, 1973, pp. 132—143.
218 P.S. Ham, in S. Geschmind (Ed.), Electron Paramagnetic Resonance, Plenum, New York, 1972, p. 1.
219 I.B. Bersuker, Zh. Strukt. Khim., 16 (1975) 935.
220 I.B. Bersuker, Plenary Lecture at the 6th Soviet Conference on Quantum Chemistry, 23—26 June, 1975, Kishinev, U.S.S.R.