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EQUATORIAL–AXIAL INTERACTIONS IN COMPLEXES AS A MANIFESTATION OF MUTUAL INFLUENCE OF LIGANDS

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CONTENTS

ABBREVIATIONS

aep	2-(2-aminoethyl)pyridine
(13)ane	1,4,8,11-tetra-aza-cyclotridecane
3-Brpy	3-brompyridine
4-Clpy	4-chlorpyridine
4-CNpy	4-cyanepyridine
cyclam	1,4,8,11-tetra-aza-cyclotetradecane
DIM	2,3-dimethyl-1,4,8,11-tetra-aza-cyclotetradeca-1,3-diene
en	ethylenediamine
en′	ethylenediamine and its derivatives
Et_2en	diethylenediamine
4-Etpy	4-ethylpyridine
im	imidazole
4-iPrpy	4-isopropylpyridine
LF	ligand field
LMCT	ligand-to-metal charge transfer
3,5-lut	3,5-dimethylpyridine
3,4-lut	3,4-dimethylpyridine
MAC	macrocycle as a ligand
Me_2en	*N*,*N*′-dimethylethylenediamine
4-NH_2py	4-aminopyridine
3,7 NHnd	3,7-diazanone-1,9-diamine
4-NO_2py	4-nitropyridine
3-pic	3-methylpyridine
4-pic	4-methylpyridine
py	pyridine
TIM	2,3,9,10-tetramethyl-1,4,8,11-tetra-aza-cyclotetra-deca-1,3,8,10-tetraene
tn	1,3-diaminopropane
tnol	1,3-diaminopropane-2-ol
TPP	tetraphenylporphyrin

A. INTRODUCTION

More than fifty years ago I.I. Tchernaev formulated the first empirical rule concerning the mutual influence of ligands in square-planar complexes of Pt(II), the so called *trans* effect [1]. Failures in the application of the *trans* effect in the complexes of some other central atoms as well as an understanding that the *trans* effect is only one of the possible consequences of the mutual influence of ligands through the central atom resulted in a more frequent use of the term "mutual influence of ligands" (MIL). (The term "mutual influence of ligands" was used in the authors' papers for the first time in 1959 [2]. It was due to the fact that the *trans* effect was not simply applicable to Cu(II) complexes, as well as due to the influence of the Russian term "mutual influence of atoms" ("vzaimnoe vliyanie atomov") used first by V.V. Markovnikov, a Russian organic chemist [3].) The most general meaning of the term MIL is that it expresses the mutual influence of ligands in complexes through the central atom. This meaning of MIL is considered also in ref. 4.

MIL may have consequences on so-called static (for instance, thermodynamic, stereochemical, spectral) and so-called dynamic (mostly kinetic) properties. The former interaction is mostly termed "influence" (e.g. *trans* influence) whereas the latter is marked "effect" (e.g. *trans* effect). *Trans* effect in substitution reactions is only a particular manifestation of MIL (there are, e.g. consequences of MIL on redox properties of complexes. photoreactions of complexes etc. [5–7]).

Experimental data on the properties of complexes of some central atoms, in which the ligands can be classified into ligands in equatorial and axial positions, as well as theoretical study of the interactions of ligands through the central atom in such complexes, result in a conclusion that the concept of equatorial–axial influence and equatorial–axial effect of ligands is meaningful (abbreviations "equ–ax" influence and "equ–ax" effect) [8–10]. These terms express the collective interaction of ligands (eventually of polydentate ligands) in equatorial plane versus axial positions through the central atom. This interaction is actually manifest in the static and dynamic properties of complexes. Such an integral approach within the MIL conception differs from the long investigated *trans* effect and *trans* influence in the sense that in the latter case interactions of ligands are investigated only in a strongly limited segment of the complex (in the given case in *trans* ordinate).

The aim of this paper is to present experimental data and theoretical suggestions about the "equ–ax" influence and "equ–ax" effect.

B. EXPERIMENTAL DATA FOR THE CONCEPT OF "EQU–AX" INTERACTIONS AS THE MANIFESTATION OF MIL

(i) Stereochemical correlations and dependences R_a versus R_e in Cu(II) complexes

In trying to understand the reasons for the great number of various shapes of coordination polyhedra of Cu(II) complexes and the existence of distortion isomerism [11], the authors studied, several years ago, the changes between the central atom–ligand distances in the equatorial plane and axial positions and their relationships [12]. This analysis was limited to octahedral and pseudo-octahedral complexes (including limit cases when both or one axial bond is weakened to such a degree that the complex becomes pyramidal or square-planar). Cu(II) complexes with different chromophores were studied in this way. The mean value of central atom–ligand distances in the equatorial plane was denoted by R_S and in the axial positions by R_L. These symbols (S, short; L, long) in case of Cu(II) complexes were usually not controversial with reality (polyhedra of these complexes have mostly shapes of an elongated tetragonal bipyramid). To eliminate subsequent discrepancies between the symbols and reality we have introduced other symbols: R_e and R_a (e, equatorial; a, axial). In the above-mentioned paper [12] certain correlations between the values of R_a and R_e were found individually for several chromophores. The greatest number of data was collected for chromophores [CuO_6] and [CuN_6]. Theoretical elucidation of the origin of distortion isomerism and plasticity of coordination polyhedra of Cu(II) complexes, as well as the R_a versus R_e correlations registered, stimulated us to consider these correlations as a special manifestation of MIL [7,12] directing thus our further reseach in this way.

It can be seen from analysis of the data on Cu(II) complexes with chromophores [CuO_6] and [CuN_4O_2] and with metallo-cycles in the equatorial plane [13] that the degree of axial distortion of the coordination polyhedron depends on both the type of the metallo-cycle and its electronic structure. Axial distortion of coordination polyhedra is most extensive in complexes which have double bonds and nearly planar metallo-cycles in the equatorial plane. On the contrary, relatively strong axial bonds have been found in complexes with five-member or non-planar six-member metallo-cycles (e.g. in chair conformations). These data agree with other papers [14,15] discussing the stereo-electronic approach to elucidation of the structure of Cu(II) complexes. In Fig. 1 the zone corresponding to planar metallo-cycles (with double bonds in the equatorial plane) is especially noted and it is limited by a dashed line. This observation highlights the dominant importance of electronic interactions of ligands through the central atom of Cu(II).

Analogous variations of R_a versus R_e can be found with chromophores other than [CuO_6] and [CuN_6] [12] and will be mentioned in this paper when demonstrating the importance of the central atom effect (abbr. "c.a. effect").

It has been suggested [16,17] that the thermochromism of some Cu(II) complexes are associated with changes in tetragonal distortion of the polyhedra; a shortening of the central atom–ligand distances in the equatorial plane results in elongation of the interatomic distances between the central atom and the axial ligands and vice versa. In spite of the new interpretation [17] which implies a new view of the problem under study, the paper [16] still remains stimulating for the studies developed by the authors. In this connection interesting results are presented in ref. 18. It seems that in the systems under investigation the connection between the variation of R_a versus R_e and changes in the conformations of equatorial ligands has to be taken into account [19,20].

α-isomers $Cu(NH_3)_2X_2$ for $X = Cl$ and Br are changed into β-isomers

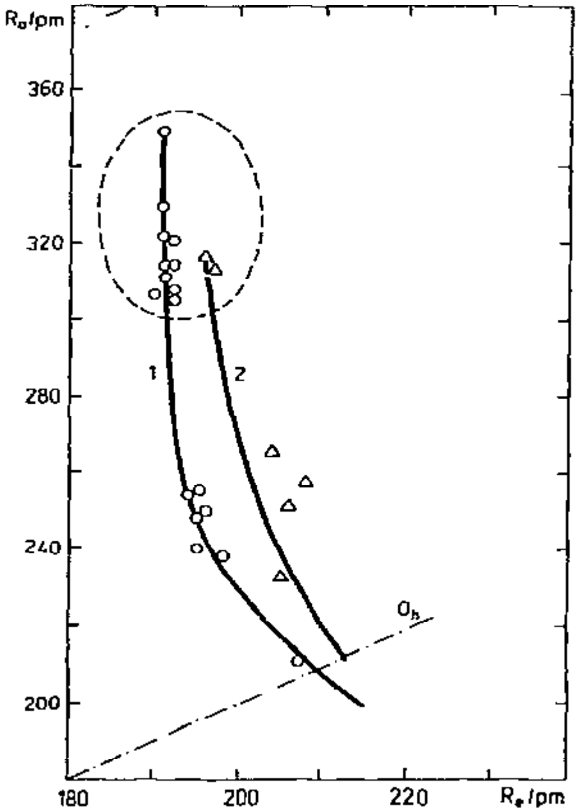


Fig. 1. R_a vs. R_e dependence for Cu(II) complexes of the chelate type with the coordination number 4+2 and 6; 1, chromophore [CuO_6]; 2, chromophore [CuN_6]. The corresponding data are taken from ref. 12.

under high pressure [21]. Rather a long time ago a spontaneous transformation of β-isomers of these complexes into α-isomers was reported [12,22–24]. In these cases an R_a versus R_e dependence is again suggested.

Even the mutual dependence of interatomic distances Cu–O in hydrated Cu(II) 2-substituted carboxylates, Chart I, is quite interesting [25–27]. These complexes are of the following type:

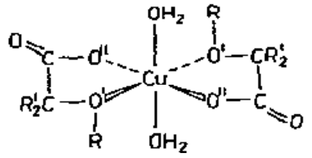


Chart I

They exhibit a well-defined equatorial plane while two water molecules are localized on the axial ordinate. Changes in the metal–ligand distances in the equatorial plane (i.e. $R_{Cu-O'}$ and $R_{Cu-O''}$), caused by the change in substituents on the ligand, give the reason for a change in the distance $R_a = R_{Cu-OH_2}$ in the axial direction. When using the mean value of $R_e = (2R_{Cu-O'} + 2R_{Cu-O''})/4$ it is possible to find a dependence R_a versus R_e along a smooth curve for known data on four compounds (Fig. 2).

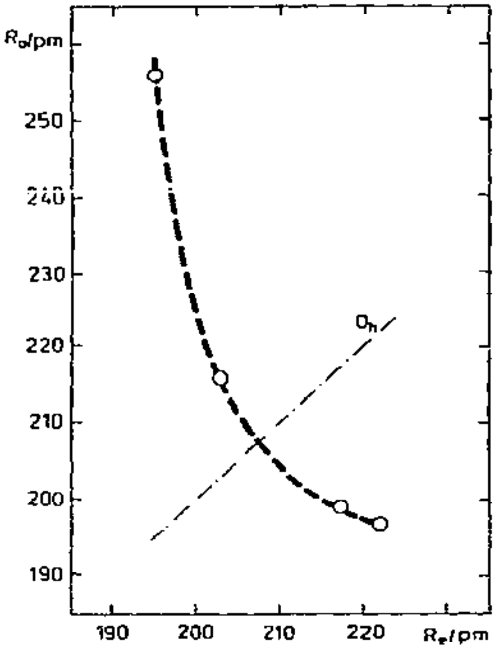


Fig. 2. R_a vs. R_e dependence in hydrated Cu(II) substituted carboxylates.

Further examples of the plasticity of Cu(II) complexes [12] are known. The fact that these are seen in complexes in the solid state complicate the situation from several aspects. Because of the latter reason a statistical processing of the data is preferred.

(ii) Comparison of the "equ–ax" influence on stereochemistry of complexes with plastic and rigid coordination polyhedron. Cu(II) and Ni(II) complexes

The complexes under present study contain $[MO_6]$, $[MN_6]$, and $[MN_4O_2]$ chromophores where the central atoms are M = Cu(II) and Ni(II). A set of such Cu(II) complexes is presented in ref. 12 and are re-investigated here by the procedure given below. The Ni(II) complexes being analysed are listed in Table 1 and in refs. 38 and 39. Only the compounds with octahedral or

TABLE 1

Values of R_e and R_a of some Ni(II) compounds with the $[NiO_6]$ chromophore (in picometres)

Compound	R_e	R_a	Ref.
$Ni(H_2O)_6SiF_6$	204.7	204.7	28
$Ni(H_2O)_6I_2$	206.4	206.4	29
$Ni_3(BO_3)_2$	207.9	207.1	30
	211.5	202.0	30
$Ni(H_2O)_6SeO_4$	204.5	208.0 [a]	31
$Ni(C_6H_4OCHO)_2 \cdot 2\ H_2O$	202.1	204.1 [a]	32
$Ni(UO_2)(VO_4)_2 \cdot 4\ H_2O$	203	201	33
$Ni(C_5H_7O_2) \cdot 2\ H_2O$	201.7	213.9	34
$(NH_4)_2Ni(SO_4)_2 \cdot 6\ H_2O$	208.4	203.6	35
$Ni(D_2O)_6SO_4$	208.5	202.0	36
$Ni(H_2O)_6(NO_3)_2$	207.8	203.3	37

[a] These values were not taken into account in the calculation of correlation coefficients.

square-bipyramidal configuration of the chromophores were taken into account, so that their coordination number was equal to 6, 4 + 2, and 2 + 4. The orthorhombic polyhedra of Cu(II) complexes (coordination number 2 + 2 + 2) were idealized to a square-bipyramidal form by means of averaging the central atom–ligand distances in the equatorial plane. The mean values of R_a and R_e were used as well as a statistical correlation between them. However, a more sophisticated treatment of such a correlation requires resolution of the following particular problems.

First, in order to select an appropriate set of complexes for the regression analysis some quantitative criteria of this selection are proposed. For this purpose the following formula

$$\Delta R_{ij} \leqslant 1.96\left[\sigma(R_i)^2 + \sigma(R_j)^2\right]^{1/2} \tag{1}$$

was accepted, derived from the Gauss law on error spreading, on the significance level equal to 0.05. In formula (1) $\Delta R_{i,j}$ is a difference between two central atom–ligand distances and $\sigma(R_i)$, $\sigma(R_j)$ are standard deviations of these two bonds lengths under X-ray experiments. If all combinations of the bond couples fulfil the relation (1), then these complexes become octahedral (corresponding bond angles are approaching 90 or 180°). For axially distorted complexes such compounds were selected for the regression analysis where two bonds in axial positions and simultaneously four bonds in the equatorial plane fulfil the relation (1) [38,39]. In addition, complexes were included into a set of the $[CuO_6]$ chromophore where, for differences in copper–oxygen distances, $\Delta R_{Cu-O} \leqslant 10$ pm. The limit of $|R_a - R_e| \leqslant 20$ pm was used for Ni(II) complexes as follows from Table 2.

Second, in order to form a common set of R_e and R_a values for the chromophores $[MN_6]$ and $[MN_4O_2]$ it was necessary to consider the differences in the central atom–ligand distances connected with coordination sphere heterogeneity. Correction on heterogeneity of the coordination sphere for the chromophore $[CuN_4O_2]$ was based on the following relation [12]

$$R_e^{\min}(\mathrm{Cu{-}N})/R_e^{\min}(\mathrm{Cu{-}O}) = R_a^{\mathrm{cor}}(\mathrm{Cu-O})/R_a(\mathrm{Cu{-}O}) \qquad (2)$$

where $R_e^{\min}$(Cu–N) and $R_e^{\min}$(Cu–O) were mean interatomic distances Cu–N and Cu–O in square-planar complexes $[CuN_4]$ and $[CuO_4]$ (read off the plot R_a versus R_e), R_a(Cu–O) were interatomic distances Cu–O in the complex with chromophore $[CuN_4O_2]$, and R_a^{cor}(Cu–O) were the corrected values.

In the case of Ni(II) complexes it is impossible to determine the $R_e^{\min}$(Ni–N) and $R_e^{\min}$(Ni–O) values from the plot R_a versus R_e and thus the relation (2) was modified.

The correction was based on the following relation:

$$\bar{R}(\mathrm{Ni{-}N})/\bar{R}(\mathrm{Ni{-}O}) = R_a^{\mathrm{cor}}(\mathrm{Ni{-}O})/R_a(\mathrm{Ni{-}O}) \qquad (3)$$

where $\bar{R}$(Ni–N) and $\bar{R}$(Ni–O) were the average nickel–ligand distances taken from octahedral complexes. The common set of R_a and R_e values and R_a^{cor}(Ni–O) for chromophores $[NiN_6]$ and $[NiN_4O_2]$ is listed in ref. 38. The plots R_a versus R_e for chromophores $[CuO_6]$, $[NiO_6]$, $[CuN_6]+[CuN_4O_2]$, and $[NiN_6]+[NiN_4O_2]$ are shown in Figs. 3 and 4.

On the basis of Figs. 3 and 4 as well as of the data from literature the following conclusions can be drawn:

TABLE 2

Some characteristics for the set of interatomic distances for chromophores with coordination numbers 4+2 and 2+4, respectively (in picometres)

Chromophore	R_e		R_a		$\lvert R_a - R_e \rvert$	
	Range	Difference	Range	Difference	Range	Difference
$[CuO'_4O''_2]$	191–215	24	202–328	126	6–145	139
$[NiO'_4O''_2]$	202–212	10	202–214	12	1–12	11
$[CuN'_4N''_2]$	194–208	14	233–328	95	28–134	106
$[NiN'_4N''_2]$	206–215	9	205–227	22	1–17	16
$[CuN_4O_2]$	198–210	12	256–315 [a]	59	51–110	59
$[NiN_4O_2]$	207–210	3	211–230 [a]	19	3–23	20

[a] Values of R_a^{cor}.

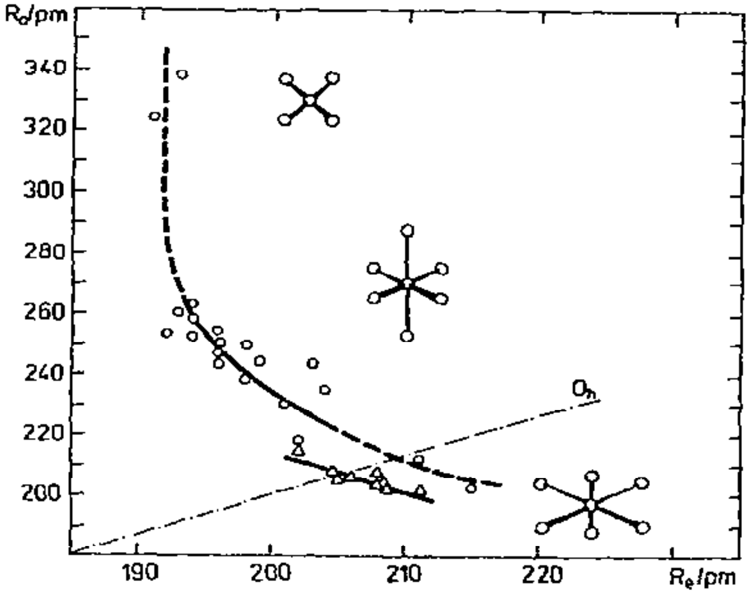


Fig. 3. Plot R_a vs. R_e for Cu(II) and Ni(II) complexes. ○, chromophore $[CuO_6]$; △, chromophore $[NiO_6]$.

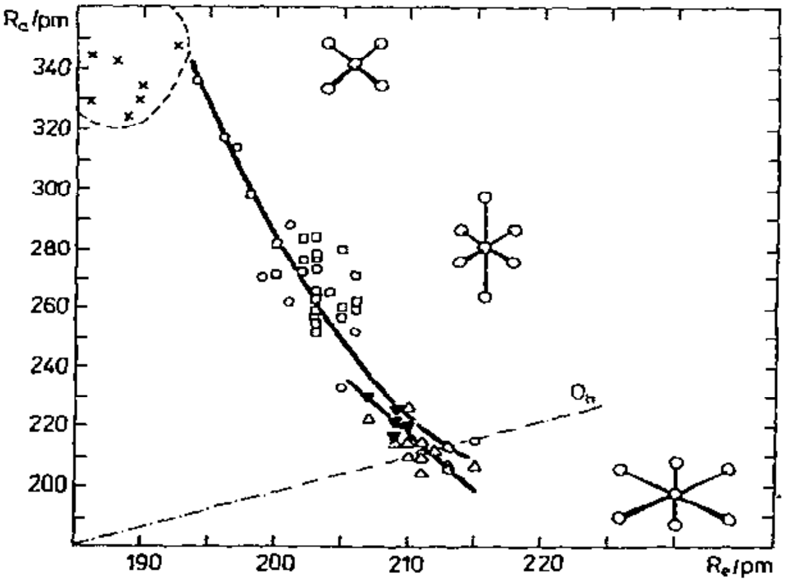


Fig. 4. Plot R_a vs. R_e for Cu(II) and Ni(II) complexes. ○, chromophore $[CuN_6]$; □, chromophore $[CuN_4O_2]$; △, chromophore $[NiN_6]$; ▼, chromophore $[NiN_4O_2]$; ×, chromophore $[NiN_4]$.

(1) A comparison of the compounds investigated with chromophores $[MO_4O_2]$, $[MN_4N_2]$, and $[MN_4O_2]$ shows that tetragonal distortion is considerably less important in Ni(II) complexes compared to those of Cu(II). This is in agreement with earlier knowledge on stereochemistry of Cu(II) and Ni(II) complexes [12,40,41]. It is evident from Table 2 that the length of the $|R_a - R_e|$ interval changes only slightly in the case of Ni(II), but it changes extensively for Cu(II) complexes. Clearly in the tetragonal distortion of coordination polyhedra due to "equ–ax" interactions the properties of the central atom play an important role.

(2) After a more detailed analysis of the experimental data, on the basis of the tests on the significance of the correlation coefficients at the level of significance 0.05 (Table 3), it is possible unambiguously to refuse the null hypothesis on mutual independence of the R_a and R_e parameters in the cases under study. The nearly linear correlation can be considered significant within the investigated interval for the chromophores $[NiO_6]$ and $[NiN_6]+[NiN_4O_2]$, and non-linear in case of the chromophores $[CuO_6]$ and $[CuN_6]+[CuN_4O_2]$. Thus, the central atom–axial ligand distances depend on the central atom–ligand distances in the equatorial plane at least in the series investigated. Increase in the central atom–ligand distances in the equatorial plane results in strengthening of axial bonds (shortening of R_a distances). The equ–ax influence within the MIL conception is thus demonstrated as an integral re-distribution of the bond strengths along three axes of the octahedron: weakening of the bonds on one axis causes strengthening of the bond on the remaining two axes and vice versa. Ni(II) complexes (Fig. 3) when comparing with $[CuO_6]$ are more rigid; this is probably due to the fact that this central atom (in contrast to Cu(II)) has no electronic degenerate or pseudodegenerate states (in O_h or D_{4h} symmetry) [42].

(3) As already mentioned the data for Cu(II) complexes [13] indicate that the axial distortion of octahedra is most extensive in complexes with practically planar metallo-cycles in which double bonds exist. On the other hand

TABLE 3

Values of the correlation coefficients

Chromophore	R	$\nu = n-2$	R_{crit}
$[CuO_6]$	-0.885 [a]	20	0.423
$[NiO_6]$	-0.860	7	0.602
$[CuN_6]+[CuN_4O_2]$	-0.664 [a]	37	0.325
$[NiN_6]+[NiN_4O_2]$	-0.730	18	0.444

[a] Values of the coefficients of order correlations.

this distortion is considerably smaller even in such a case when the metallo-cycle is nearly planar (that is, the sum of inner angles of a five-member metallo-cycle is 540° and that of six-member is 720°) but without π-electrons. With respect to this one can also expect, for Ni(II) complexes with a system of double bonds in the equatorial plane, a shortening of the bonds in the equatorial plane and simultaneously a weakening of the axial bonds, i.e. formation of square-planar complexes.

However, it has been found [38] that the interatomic distances Ni–N in the square-planar complexes with the $[NiN_4]$ chromophore are ranging within an interval of 180–196 pm regardless of the system of double bonds. Moreover, pseudooctahedral Ni(II) complexes (with bonding interactions in axial directions) exist in spite of a system of double bonds in the equatorial plane [43]. Therefore, this factor is not always dominant in the "equ–ax" interactions.

(4) When comparing non-rigidity of Ni(II) and Cu(II) complexes (Figs. 3 and 4) the average nickel–axial ligand distances span a much narrower interval. In the case of chromophores $[NiN_6]$ and $[NiN_4O_2]$ the tetragonal distortion does not change continously to a square-planar configuration; after reaching a certain value, $R_a \approx 230$ pm, square complexes are formed. Such a stereochemical change is especially marked in Fig. 4; the zone corresponding to square-planar Ni(II) complexes with weak axial bonds is limited here with a dashed line.

Figure 4 demonstrates a higher rigidity of Ni(II) complexes in comparison with Cu(II) ones, manifested by the stereochemical change octahedral to square-planar configuration and usually by a change in the spin state. The expressive non-rigidity of Cu(II) complexes, associated with electron degenerate or pseudodegenerate states of the central atom, has been termed "plasticity" [12].

(iii) Central atom effect and the "equ–ax" influence in complexes with homogeneous ligand sphere

Investigation of the "equ–ax" influence and effect within the MIL conception has some special characteristics. The mutual influence of ligands is often reported by studying the consequences of substitution of one ligand with another on various properties of the complex [4]. Not only complexes with different ligands in the equatorial plane and axial positions (heterogeneous complexes) are studied in this connection. Also complexes with ligands which are not identical but bonded to the central atom by the same donor atoms (quasi-homogeneous complexes) and complexes with all ligands identical (homogeneous complexes) are investigated. Such an approach to the investigation of the mutual influence of ligands is rather unusual.

However, when taking into consideration that the mutual influence of ligands is a phenomenon where a change in the interaction of the ligand (or of a group of ligands) is a result of a change in the interaction of another, even identical, ligand (or a group of ligands) via central atom, then this approach seems to be acceptable. Reasons for such an approach are also quite clear when studying the variation of R_a versus R_e in homogeneous and quasi-homogeneous complexes.

The fact that complexes with the chromophores $[CuO_6]$, $[NiO_6]$, $[CuN_6]$, $[CuN_4O_2]$, $[NiN_6]$, and $[NiN_4O_2]$ show significant distortions with respect to the octahedral arrangement of the donor atoms, is not surprising. In many cases identical donor atoms correspond to different ligands, which, of course, is reflected in the variability of the central atom–donor atom interatomic distances. One cannot exclude the possibility of changes of some interatomic distances as a consequence of a *cis* or *trans* influence. It was therefore necessary to perform a more detailed analysis of the structural data in the complexes with homogeneous coordination sphere of the type $^m[MX_6]^q$, where X are identical ligands and as simple as possible (m denotes the complex spin multiplicity).

This further stage of the study R_a versus R_e was started in ref. 44 with a series of hexafluoro complexes of the type $^m[MF_6]^q$; the central atom varied as follows: M = Cr, Mn, Fe, Co, Ni, Cu, and Zn at the oxidation state M(II) and M(III). As the fluoro-ligand has a weak ligand field, high-spin hexafluoro complexes are preferentially stabilized. The corresponding compounds are of the following types: MF_2, $A(I)MF_3$, $A_2(I)MF_4$, $A_2(II)MF_6$, MF_3, $A(I)MF_4$, $A_2(I)A'(I)MF_6$, and $A(I)A(II)MF_6$, where A(I), A'(I) = Li, Na, K, Rb, Cs, NH_4, and Tl, and A(II) = Ba. These compounds contain well defined octahedra, tetragonal bipyramids, or rhombohedra (coordination number 6, 4 + 2, 2 + 4, or 2 + 2 + 2) with single, double, or triple dimensional bridging. The geometry of the complexes with orthorhombic symmetry is described with three parameters: R_L (long), R_M (medium), and R_S (short) central atom–ligand distances. For coordination polyhedra with tetragonal symmetry the following relationships can be written: $R_L = R_M > R_S$ (compressed tetragonal bipyramid), or $R_L > R_M = R_S$ (elongated form). Four identical (or nearly equal) interatomic distances M–F define the equatorial plane of the complex and their mean value was termed R_e. The remaining two distances, after averaging in case of necessity, provide the axial value R_a. A complete list of the structures as well as of selected R_a, R_e data is given elsewhere [44]. Variation of R_a versus R_e is given in Fig. 5, individually for the oxidation numbers of the central atoms M(II) and M(III) and their formal d^n-electron configurations. This is the basis for the following conclusions.

(1) Provided there is a sufficient number of experimentally determined

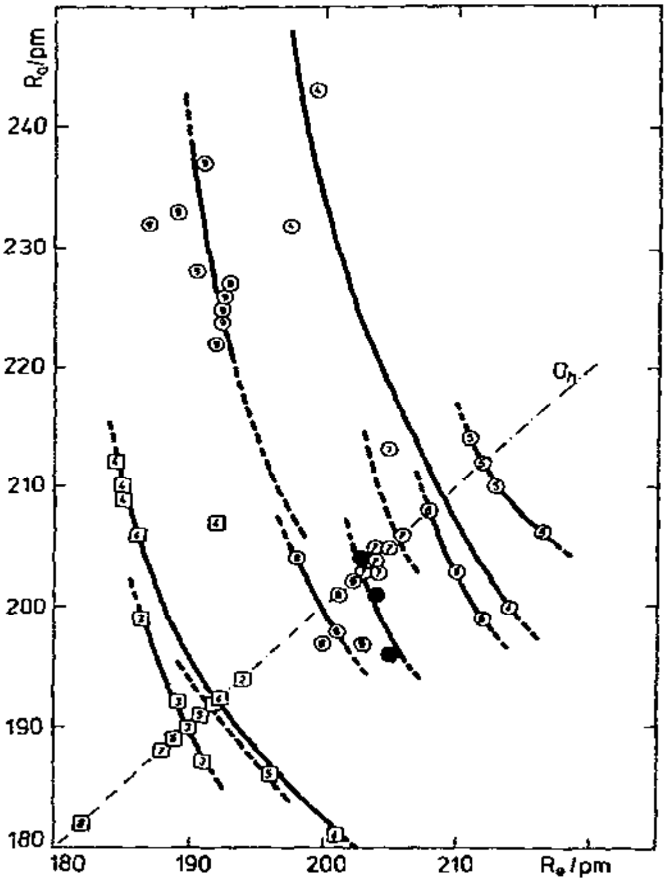


Fig. 5. R_a vs. R_e dependences in hexafluoro complexes. ⓝ, d^n system of M(II); ●, d^{10} system of Zn(II); [n], d^n system of M(III); dashed lines, expected dependences or extrapolations.

structures, then all R_a versus R_e curves show a similar shape. In the systems $[MF_6]^{3-}$ and $[MF_6]^{4-}$ a common intrinsic disposition to undergo distortions along the R_a versus R_e variation does exist. This is evidence of a more general validity of the situation found in $^2[CuF_6]^{4-}$ complexes [45].

(2) The cationic part of the crystal affects the general trend above: structures with large Cs^+ cations show a tendency to shift both R_a and R_e distances toward the higher values.

(3) The central atom–fluorine distances in the systems $[MF_6]^{3-}$ are considerably shorter in comparison with the systems $[MF_6]^{4-}$.

(4) Complexes ^{5}[Cr(II)], ^{5}[Mn(III)], and ^{2}[Cu(II)] show the highest deviations from the octahedral configuration within the R_a versus R_e depen-

dences. Their common feature lies in the fact that these systems have doubly degenerate electronic ground state E_g in the hypothetical octahedral configuration. Some of them, e.g. $[Cr(NH_3)_6]$ $[MnF_6]$, exhibit a regular octahedral configuration as a result of the dynamic Jahn–Teller effect [46,47].

(5) R_a versus R_e dependence was also found in the systems having non-degenerate electronic state A_{1g}, namely in hexafluoro complexes ^{4}[Cr(III)], ^{6}[Fe(III)], ^{6}[Mn(II)], ^{3}[Ni(II)], and ^{1}[Zn(II)].

(6) Systems having in their hypothetical octahedral configuration a triply degenerate electronic state T_{2g} (hexafluoro complexes ^{5}[Fe(II)], ^{4}[Co(II)], and ^{4}[Ni(III)] show distortions of approximately the same order as the systems at the A_{1g} state within the frame of R_a versus R_e.

It is important that the "c.a. effect" (an influence not only of the proton number of the central atom but also of its oxidation and the spin state) affects the observed dependence. As the above-mentioned complexes are considered in quantum-chemical calculations, this fact will be discussed in Section C in more detail.

In the variability of the stabilization of the actual shape of a coordination polyhedron the quality of the cationic part of the crystal bears primary responsibility; a secondary consequence is bridging of the polyhedra. For instance, in the K_2NiF_4 structure [48] the chromophore $NiF'_4F''_2$ contains four equivalent atoms F′ in the equatorial plane, which, due to bridging, exhibit a length $R_{Ni-F'} = R_e = 200$ pm, this being longer than could be expected in a free complex. Due to this, two axial lengths $R_{Ni-F''} = R_a = 197$ pm of non-linked ligands are shorter than could be expected by the R_a versus R_e dependence shape. This example demonstrates a situation where rather integral influence of the equatorial plane affects the shape of the coordination polyhedron. Simple considerations on the *cis* influence do not provide here an adequate image of the actual situation: to an individual bond Ni–F′ two different types of bonds in the *cis* position can be attributed, namely two other bonds Ni–F′ in the equatorial plane and different bonds Ni–F″ in the axial direction. Thus the concept of the *cis* effect results here in some confusion. The actual stereochemical situation is more truthfully described in terms of the equatorial–axial influence.

Next we deal with hexanitro complexes [49]. The systems studied are of the following type: $A_2(I)A(II)[M(II)(NO_2)_6]$, with metals A(I) = K, Rb, Cs, and Tl; A(II) = Ca, Sr, Ba, and Pb; and the central atoms M(II) = Co, Ni, and Cu. These compounds exhibit well-defined units $[M(II)(NO_2)_6]^{4-}$. As the NO_2^- ligands have a strong ligand field, then low spin complexes of ^{2}[Co(II)] are stabilized preferentially. It has been found in these compounds that phase transitions occur with decreasing temperature. Their structures are known for certain phases: α, β, β' and γ. A complete list of the structures as well as of selected parameters R_a, R_e is given elsewhere [49].

The R_a values were plotted versus R_e (Fig. 6) and the points belonging to individual compounds were connected with smooth curves. The following conclusions can be made:

(1) The dependence R_a versus R_e exhibits a similar course in various compounds. The cationic part of the crystal (A(I) = K, Rb, Cs) has influence on both R_a and R_e bond-lengths shifting them to higher values similar to the situation found in hexafluoro complexes.

(2) In individual compounds, let us say in $K_2Pb[Cu(NO_2)_6]$, a transition from elongated to compressed form of a tetragonal bipyramid (γ–β transition) was recorded with increasing temperature. The high-temperature α-phase, however, shows a regular octahedral structure under the conditions of X-ray or neutron-diffraction experiments. This is connected with the dynamic Jahn–Teller effect.

The principal result found in the case of hexanitro complexes is that the R_a versus R_e variations can be shown to occur within the same compound but in different phases. The individual phases differ only in the amount of the total energy. Therefore, a general intrinsic disposition of octahedral complexes to undergo distortions along the R_a and R_e vectors should exist

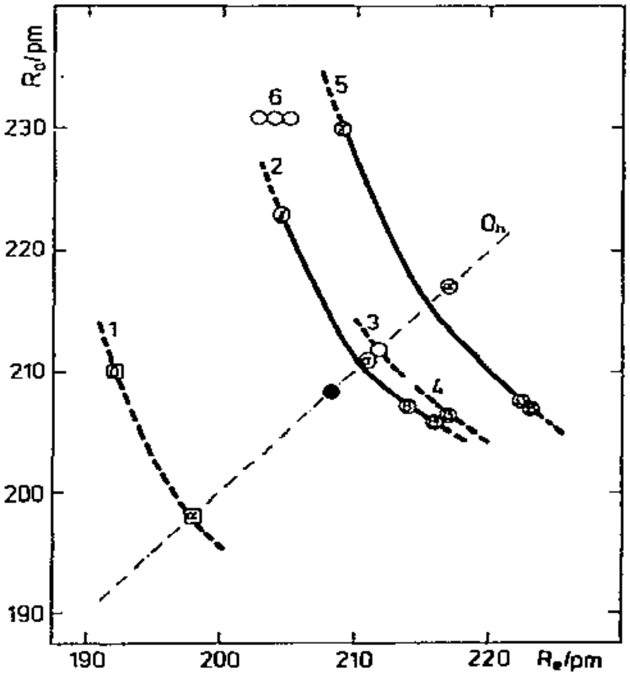


Fig. 6. R_a vs. R_e dependences in hexanitro complexes of $A_2(I)A(II)M(NO_2)_6$ type. ○, M=Cu(II); ●, M=Ni(II); □, M=Co(II); 1, $K_2PbCo(NO_2)_6$; 2, $K_2PbCu(NO_2)_6$; 3, $Tl_2PbCu(NO_2)_6$; 4, $Rb_2PbCu(NO_2)_6$; 5, $Cs_2PbCu(NO_2)_6$; 6, $K_2ECu(NO_2)_6$ for E=Ca, Sr, Ba. α, β, β', γ, individual phases; dashed lines, expected dependence or extrapolations.

here and be connected with energetic criteria. However, this may not always be manifested in the free complexes. In the solid state the tetragonal distortion of the coordination polyhedron can be stabilized as a result of external factors.

In connection with the investigation of the "equ–ax" influence and importance of the "c.a. effect" there is an interesting statement in ref. 50. A shortening of two axial bonds and elongation of all four bonds in the equatorial plane was reported in some Sn(IV) complexes. Therefore, the MIL in these d^{10} complexes is not manifested as a simple *trans-* or *cis*-influence: disproportionation of the bond strengths along all three axes of the octahedron occurs here.

(iv) "Equ–ax" influence and spectral properties of complexes

From the electronic spectra of tetragonally distorted complexes the quantities D_q^{xy} and D_q^z can be deduced. The D_q^{xy} parameter is considered a measure of the ligand field strength of equatorial ligands [51]. The second parameter D_q^z characterizes the axial ligand field [52]. The special interest in this parameter results from the fact that the parameter D_q^z usually depends on the parameter D_q^{xy}. By such dependence the "equ–ax" influence can be characterized for the Ni(II) and Co(II) complexes studied [51,53,54].

D_q^z decreases when the strength of the equatorial ligand field increase. This was explained on the basis of the inductive influence of ligands [53]. When the donor properties of different equatorial ligands increase (the formal charge of central atom is reduced), the axial Ni–Cl bonds weaken, which is evident from the reduced D_q^z values for Cl^-. In agreement with this approach it was shown [53] that the D_q^{xy} value for pyridine is higher in $Ni(py)_4(ClO_4)_2$ or $Ni(py)_4(BF_4)_2$ than in $Ni(py)_4Cl_2$ or $Ni(py)_4Br_2$. This can be expected considering the weaker donor properties of ClO_4^- and BF_4^- in comparison with those of Cl^- and Br^-. However, because of a low number of complexes under investigation these conclusions cannot be generalized.

The greatest changes in D_q^z are expected in the case of weakly coordinated ligands, such as ClO_4^- and BF_4^-. This was shown for a series: Ni(R-aniline)$_4$(ClO$_4$)$_2$, where $R = CH_3$, $O{-}CH_3$, $O{-}C_2H_5$, Cl, Br, and I [54]. These compounds belong to two groups: with a substituent in the position 3 or 4, and with a substituent in the position 2. Derivatives of aniline in the 2 position show steric hindrance which causes the perchlorate groups in the compounds with *o*-aniline and *o*-phenetidine to be uncoordinated. Hexacoordination of Ni(II) is then reached by two monodentate and two bidentate nitrogen-containing ligands. Spectral data for other compounds indicate a bipyramidal structure of the type Ni(R-aniline)$_4$(ClO$_4$)$_2$ with monodentate ClO_4^- groups on the axis. The dependence D_q^z versus D_q^{xy} is given in Fig. 7. The stronger the ligand field in the equatorial plane, the lower the axial ligand field produced by the perchlorate groups.

After exceeding a certain limited D_q^{xy} value distinct weakening of the axial bonds is often recorded as well as formation of diamagnetic (nearly planar) Ni(II) complexes. Such stereochemical changes accompanied by a change in spin state were observed in Ni(II) complexes with pyridine and its derivatives [55]. The position of a substituent in the pyridine ring also affects the coordination of axial ligands (Table 4). Table 4 [56] reveals that the shapes of the polyhedra of these NiL_4X_2 compounds are changed more regularly in solution compared to the solid state. In solution all halogen-containing complexes ($X = Cl^-$, Br^-, I^-) are nearly octahedral. However, for $X = ClO_4^-$ and BF_4^- the complexes are tetragonally distorted in the case of equatorial ligands with $pK_a < 5.5$ and square-planar in the case of equatorial ligands with $pK_a > 6.2$. Generally, with increasing basicity of the above nitrogen-containing equatorial ligands and with decreasing coordination ability of axial anionic ligands the probability of formation of square-planar complexes increases. In the solid state, however, some exceptions exist, associated with lattice effects.

The complexes $M(R\text{-}py)_4(ClO_4)_2$ for M = Ni(II) and Co(II) are compared in Table 5. In contrast to Ni(II) complexes all Co(II) compounds have tetragonally distorted structures. Changing the position of the substituents in the pyridine ring causes no major stereochemical consequences. However minor effects may become apparent when X-ray data are available.

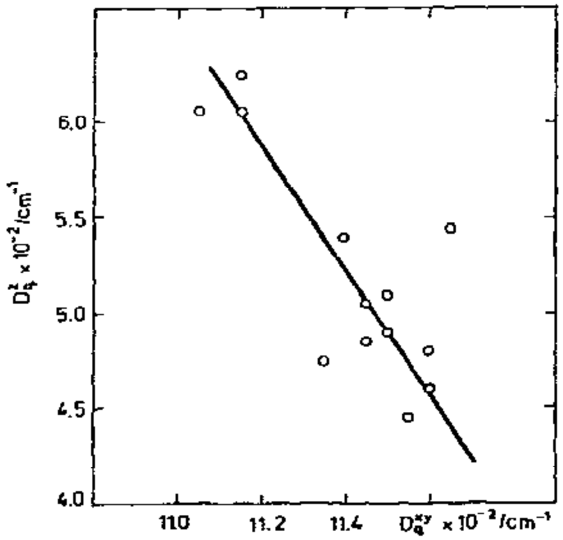


Fig. 7. Plot D_q^z vs. D_q^{xy} for complexes of the type $[NiA_4(ClO_4)_2]$. A, substituted anilines [54].

TABLE 4

Stereochemistry of NiL_4X_2 complexes [56]

L	pK_a	X									
		Cl		Br		I		ClO_4		BF_4	
		Solid	Liquid (solution)	Solid	Liquid (solution)	Solid	Liquid (solution)	Solid	Liguid (solution)	Solid	Liquid (solution)
py	5.17	o[a]	o	o	o	o	o	o	o	o	—
3-pic	5.68	o	o	o	o	o	o	o, sq	o, sq	o, sq	o, sq
4-pic	6.02	o	o	o	o	o	o	sq	o, sq	sq	o, sq
3,5-lut	6.15	o	o	o	o	o	o	o	sq	o	sq
3,4-lut	6.45	o	o	o	o	sq	o	sq	sq	sq	sq
4-NH_2py	9.17	o, sq	—	o, sq	—	sq	—	sq	—	sq	—

[a] o, octahedral; sq, square-planar configuration.

TABLE 5

Stereochemistry of complexes of the type M(II) $(Rpy)_4(ClO_4)_2$

Rpy	M(II) = Ni		M(II) = Co	
	Stereochemistry	Ref.	Stereochemistry	Ref.
py	o [a]	57	o	58,60
3-Brpy	o	57	o	58
3-pic	sq	57	o	58
3,5-lut	o	57	o	58
3,4-lut	sq	59	—	—
4-pic	sq	57	o	58,60
4-Etpy	o	57	o	58
4-iPrpy	o	57	o	58
$4\text{-}NH_2py$	sq	57	—	—

[a] o, octahedral; sq, square planar configuration.

Tetragonally distorted Cu(II) complexes usually show only one band in the visible region electronic spectra [61]. Therefore, the D_q^{xy} and D_q^z quantities cannot be determined from this band. The increase in the ligand field strength in the equatorial plane (resulting from strengthening the bonds) will be reflected in vibrational properties of the system, namely in the valence vibrations of Cu–L (more precisely in the force constants). The band energy in the visible region reflects the ligand field strength in the plane as well as ΔD_q (difference between the ligand field strength in the equatorial plane and axial positions) and can be associated with vibrational characteristics in the plane. Such a dependence was found for $Cu(en')_2X_2$ complexes where en′ is ethylenediamine and some of its derivatives. The dependence $[\tilde{\nu}(Cu\text{–}N)]^2$ versus the electronic transition energy (Fig. 8) shows a linear course [62].

There are several Ni(II) complexes with 14- to 16-member tetraaza saturated macrocycle in the equatorial plane. They are the strong σ-donors and do not form a dative π-bond with the central atom. In the case when the axial ligand X is constant and the macrocyclic ligand is varying D_q^z decreases with increase of D_q^{xy} [51]. The D_q^z value is strongly dependent on the ligand field in the equatorial plane. This "equ–ax" influence is illustrated in Fig. 9. Complexes with X = NCS were chosen as there are most data available. The slope of the line reflects sensitivity of the parameter D_q^z towards change of the ligand field strength in the equatorial plane.

"Equ–ax" influence is manifested in the same way when varying the axial ligand field by a fixed macrocycle in the equatorial plane. Although only data for four axial ligands were available (Cl, Br, N_3, NCS) [51] a linear

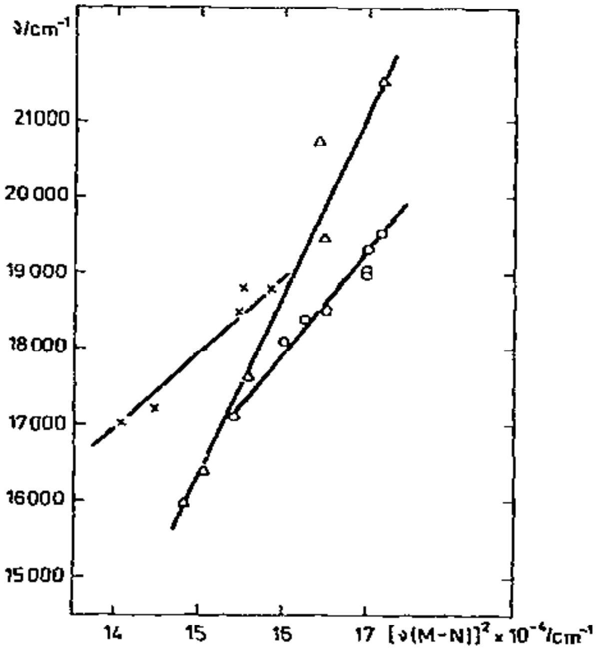


Fig. 8. The electronic transition maximum vs. the square of the frequency of the highest energy metal–nitrogen stretching mode for complexes of the type $[Cu(N-N)_2X_2]$; (N–N) = ○, en; ×, Asym. Me_2en; △, Asym. Et_2en [62].

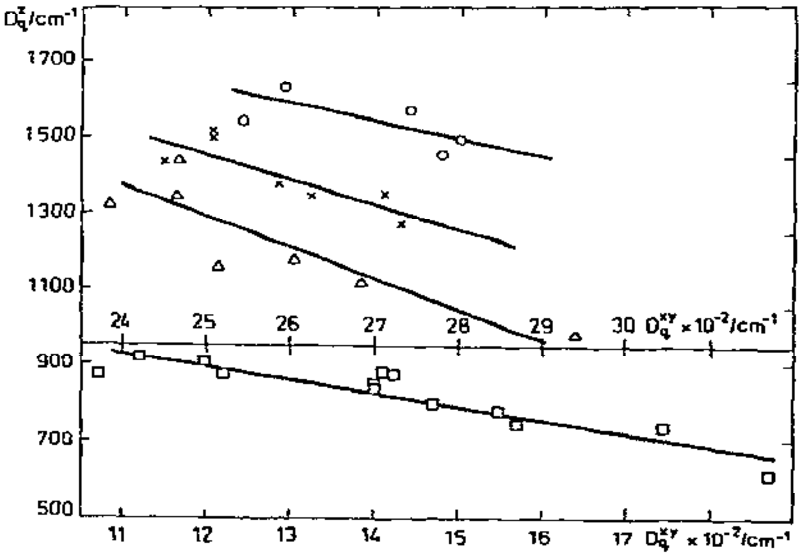


Fig. 9. Plot D_q^z vs. D_q^{xy} for complexes: $[Co(MAC)X_2]^{n+}$ for various X = ○, H_2O; ×, Cl; △, Br; and $[Ni(MAC)(NCS)_2]$: □, NCS.

dependence between D_q^{xy} and D_q^z was again found. These changes are not so clearcut as those previously.

An analysis of 65 complexes of Co(III), Fe(II), and Ni(II) with saturated and non-saturated macrocycles was described elsewhere [63]. By means of electron absorption spectra the parameters D_q^{xy} and D_q^z were calculated and positions of spectral bands for 38 as yet undescribed compounds were predicted. On the basis of these data we tried to verify the existence of an "equ–ax" influence for complexes $[\mathrm{Co(III)}\ (\mathrm{MAC})\mathrm{X}_2]^{n+}$ .This is illustrated in Fig. 9. Regression analysis for X = Cl and Br has shown a linear correlation (correlation coefficients $R_1 = 0.83$ for X = Cl and $R_2 = 0.87$ for X = Br). A similar dependence was reported for Ni(II) complexes [51]. However, if the axial ligand is changed with constant macrocyclic ligand, no such dependence was observed for Co(III) complexes (in contrast to Ni(II) complexes).

(v) "Equ–ax" influence on the coordination mode of thiocyanate ligand

The coordination modes of pseudohalogenide ligands in solid heterogeneous complexes depends on several factors, the effects of which in individual compounds may have different order of priorities [64]. Such factors are the internal disposition of pseudohalogenide ligands (which results from its bonding possibilities) as well as the internal disposition of the central atom (which depends on its characteristic as a soft or hard Pearson acid [65]). The bonding and steric properties of other ligands present in the coordination sphere may also play a role. The effect of the central atom in some complexes can be shielded by suitable combination of ligands in the coordination sphere [66,67].

A comparison of the thiocyanate coordination mode in homogeneous and heterogeneous complexes (Table 6) has shown that σ-donor ligands do not change the disposition of the central atom for the thiocyanate coordination mode, which has been observed in homogeneous thiocyanates. A change in this mode can be expected only when some thiocyanate ligands in homogeneous thiocyanates are substituted by ligands with π-acceptor properties.

Replacement of a σ-donor ligand by a ligand with π-acceptor properties is not, however, always a sufficient condition for a change in the coordination mode of the remaining thiocyanate ligands for the individual central atoms. For instance, in the compounds $\mathrm{PdL_2(NCS)_2}$, where L are π-acceptor but only *N*-donor ligands (such as py [68], 4-pic [69], 4-$\mathrm{NO_2}$py [68], 4-CNpy [68], 4-Clpy [70]) the dominant effect of the central atom is retained and the thiocyanate ligand is always bound to Pd(II) through the sulphur atom. On the other hand, a great number of heterogeneous Pd(II) thiocyanates is known which contain π-acceptor but *P*-donor ligands and the thiocyanate

TABLE 6

The coordination mode of monodentate thiocyanate ligands [64,66]

Transition metal	Coordination mode of thiocyanate ligands in		
	Homogeneous thiocyanates	Heterogeneous thiocyanates with	
		σ-donor ligand	π-acceptor ligand
Class a	–NCS	–NCS	–SCN
Class b	–SCN	–SCN	–NCS

ligand is bound via the nitrogen atom [64,66,71,72].

The authors' studies have shown that thiocyanate Cu(II) complexes are suitable for the study of the mutual influence of ligands on NCS bonding [73] for the following reasons:

(1) Considering the pseudohalogenides NCX (X = O, S, Se) thiocyanate exhibits not only the greatest variability of bonding properties in complexes but also similar behaviour for coordination via nitrogen or sulphur. In the case of cyanate ligands this trend is shifted more towards the nitrogen atom and in the case of the selenocyanate ligand more to the selenium atom [73–75].

(2) The plastic features of the Cu(II) polyhedra [11,12] create conditions for a sensitive transfer of bonding interactions in the equatorial plane versus axial positions via the central atom. As Cu(II) occupies in Pearson's classification of transition metals a border position [65,72] there are preconditions for the variability of bonding of the NCS ligand to this central atom.

(3) The thiocyanate ligand in Cu(II) complexes can be bound in equatorial plane as well as in the axial position. In the equatorial plane it is always bonded via nitrogen; in the axial positions coordination with both nitrogen and sulphur atom has been observed [73]. The change in the coordination mode of the thiocyanate ligand is influenced by the other ligands in the coordination sphere and can thus only be observed in the axial positions.

The manifestation of the "equ–ax" influence in Cu(II) thiocyanates (with monodentate thiocyanate) can be demonstrated by means of the compounds given below. With equatorial ligands such as ammonia, en, tn, and tnol, NCS coordination via sulphur atom is observed (Chart II). On the other hand, in the case of such ligands as py or aep, NCS coordination via nitrogen was reported (Chart III).

In order to explain this observation the π-bonding hypothesis seems to be acceptable [64,71]. It is obvious that the groups of ligands mentioned above differ in their π-acceptor capacity. Ligands without π-acceptor bonding

Chart II

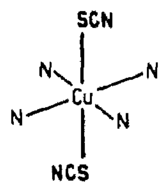
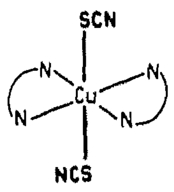
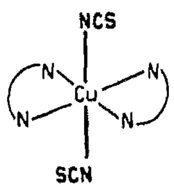
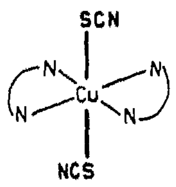
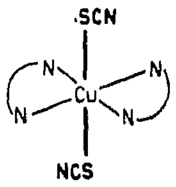
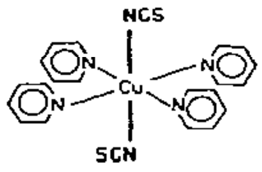
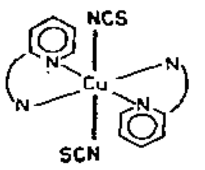
$[Cu(NH_3)_4(-SCN)_2]$ [41]	$[Cu(en)_2(-SCN)_2]$ [76]	$[Cu(Me_2en)_2(-NCS)_2]$ [77]	$[Cu(tn)_2(-SCN)_2]$ [78]	$[Cu(tnol)_2(-SCN)_2]$ [79]
				

Chart III

$[Cu(py)_4(-NCS)_2]$ [80]	$[Cu(aep)_2(-NCS)_2]$ [81]
	

properties more distinctly reduce the effective charge on the central atom Cu(II) weakening, thus, its "hard" character. Such a change results generally in an increased tendency of thiocyanate ligand coordination via sulphur [82]. The exception to this conclusion (the case of $Cu(Me_2en)_2(NCS)_2$ [77]) leads us to further study.

The consequences of "equ–ax" influence on the coordination mode of the thiocyanate ligand can also be demonstrated by means of Cu(II) thiocyanates with bridging thiocyanate ligands [73]. In this case a decrease of π-acceptor properties of the equatorial ligand leads to an increase in the number of coordination bonds via sulphur situated in axial positions (Charts IV and V). Compounds with py and 4-pic in the equatorial plane contain two equivalent thiocyanate ligands. They contain bridges formed by double-bonded sulphur atoms in the axial positions (Chart IV). The increased tendency towards coordination via sulphur occurs in NH_3 and en containing Cu(II) complexes with bridging thiocyanate ligands and is manifest by an increased number of sulphur bonds (Chart V).

Chart IV

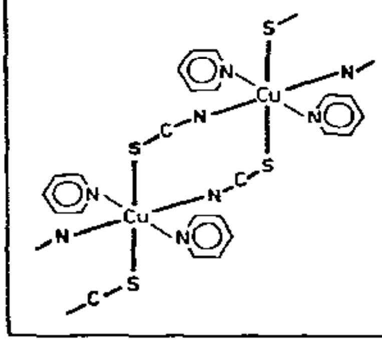
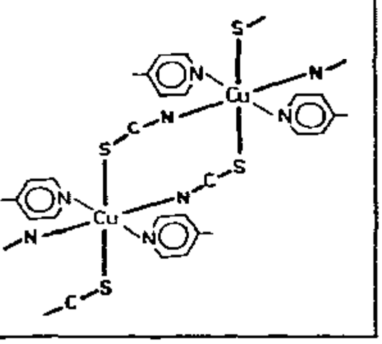
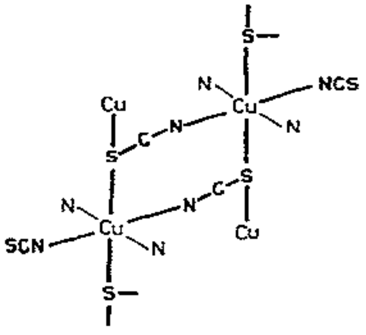
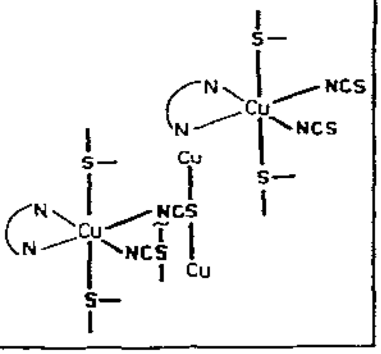
$[Cu(py)_2(-NCS-)_2]$ [83]	$[Cu(4\text{-pic})_2(-NCS-)_2]$ [84]
	

Chart V

$[Cu(NH_3)_2(\text{-}NCS)(\text{-}NCS\text{-})]$ [85]	$[Cu(en)(\text{-}NCS)(\text{-}NCS\text{-})]$ [86]
	

C. THEORETICAL ASPECTS OF THE "EQU-AX" INFLUENCE

The rarity of octahedral Cu(II) complexes was the subject of various, theoretically oriented reviews [12,47,87–89]. The most usual approach to elucidate this phenomenon is based on the Jahn–Teller theorem [90], or more exactly, on consideration of the E_g–e_g vibronic interaction (see below). In the following text, systems with the doubly degenerate electronic state E_g will be termed "E_g-active" complexes. As explained in more details elsewhere [89] a strictly degenerate E_g state in an octahedron is not required for distortion by the "Jahn–Teller" mechanism (pseudoJahn–Teller effect).

Distortions of coordination polyhedra are not observed only in E_g-active complexes. Significant distortions were also reported in complexes with the non-degenerate electronic state A_{1g}. Examples can be found among complexes with the chromophore $[NiO_6]$, $[NiN_6]$ or in hexafluoro complexes $^4[Cr(III)]$, $^6[Fe(III)]$, $^6[Mn(II)]$, and $^3[Ni(II)]$ (see Section B). For instance, in the high-spin complex La_2NiO_4 with chromophore $[NiO_6]$ the following nickel–oxygen distances were found: $R_e = 193.4$ and $R_a = 224.2$ pm [91]. Moreover NMR measurements in the solid state have shown [92] that the tendency to tetragonality should be considered a general property of complexes of the type $[MF_6]^q$. In this connection it has been found that with increasing external pressure tetragonal distortion of the coordination polyhedron increases [21,92].

It should be noted that in spite of the fact that consideration of the E_g–e_g vibronic interaction results in prediction of the distortion of coordination polyhedra in the E_g-active complexes, no satisfactory explanation of the R_a versus R_e correlations (along a smooth curve) was given until now. Relationships R_a versus R_e can hardly be attributed only to the Jahn–Teller effect as they can be observed also in those complexes where the E_g–e_g vibronic interaction does not occur. On the other hand, it is impossible to disregard the fact that the greatest variations within R_a versus R_e correlations are observed just in E_g-active complexes. For instance, among hexafluoro complexes the greatest distortions were found in the case of ^{2}[Cu(II)], ^{5}[Cr(II)], and ^{5}[Mn(III)] complexes [49]. In complexes of the $[MX_6]^q$ type probably a certain intrinsic disposition to undergo such distortion exists. At the same time, however, the secondary application of the cooperative Jahn–Teller effect in the solid state may result in strengthening the distortion caused by the "equ–ax" influence.

A theoretical (quantum-chemical) description of stereochemical manifestation of the "equ–ax" influence is to be started from the general concept of interrelationships among internal coordinates, describing the geometry of the coordination polyhedron, by means of the function $E_T = E_T(\ldots R_n \ldots)$, where E_T is the total energy of the investigated system. This is the adiabatic potential represented in a multi-dimensional space of internal coordinates by a surface of a certain shape and is called the adiabatic potential surface (APS). There are at least two reasons for such an approach. First, the knowledge that a different amount of total energy, for instance, in hexanitro complexes, results in tetragonal distortion. Second, there is the possibility of implicit involvement of stereochemical consequences of the E_g–e_g vibronic interaction in a concrete APS shape.

Problems studied by theoretical methods in the next section can be formulated as follows:

(1) Investigation of the APS shape obtained by quantitative quantum-chemical calculations and deducing a generally valid R_a versus R_e relationship for quasi-octahedral complexes of transition metals.

(2) Specification of dominant interactions directing the stereochemical manifestation of the "equ–ax" influence.

(3) The attainment of APS characteristics applicable for quantitative description of plasticity and/or rigidity of the coordination polyhedron.

(4) Demonstration of the central atom effect on the relationships followed.

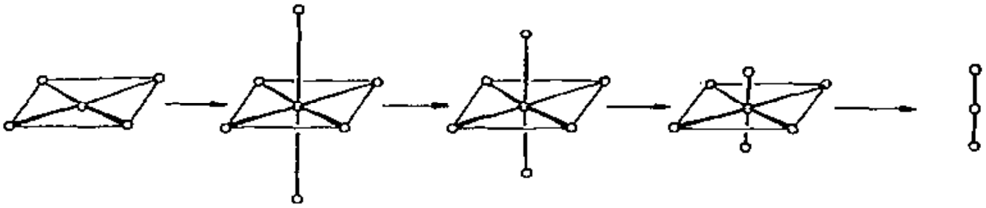
(5) Formulation of a relationship between the quantitative characteristics of the "equ–ax" influence on the one hand and the set of Jahn–Teller parameters (parameters of the E_g–e_g vibronic interaction) on the other.

(6) Demonstration of the solid state effects on the properties of coordination polyhedron and its "equ–ax" characteristics.

Now, it is necessary to mention some limitations of the theoretical investigation. First, only the chromophore $[MX_6]$ is examined. Second, its octahedral geometry is taken as the basis and only tetragonal distortions are followed, i.e. four central atom–ligand distances in the equatorial plane R_e, as well as two axial, R_a, distances are considered to be equivalent. Finally, a limiting case of tetragonal distortion for $R_a \to \infty$ is the square-planar arrangement in the coordination polyhedron and for the case $R_e \to \infty$ is the linear configuration. The above restrictions reduce considerably the number of internal degrees of freedom in the $[MX_6]$ polyhedron from $3 \times 7 - 6 = 15$ to only two, and thus APS will be considered as a simple function of the type $E_T = E_T(R_a, R_e)$. This APS shape is sufficient for description of the properties of the system along "the reaction pathway"

$$\underset{D_{4h}}{[MX_4]^{2-}} \overset{+2X^-}{\rightarrow} \underset{D_{4h}}{[MX_6]^{4-}} \rightarrow \underset{O_h}{[MX_6]^{4-}} \rightarrow \underset{D_{4h}}{[MX_6]^{4-}} \underset{-4X^-}{\rightarrow} \underset{D_{\infty h}}{MX_2} \tag{4}$$

(oxidation number of the central atom is in this case M(II) and that of ligand is X^{-1}), or in a scheme:



When taking into account the electronic factors it is necessary to add to APS several discrete variables specifying particularly the type of the central atom, M, its oxidation state, n, spin state, m, as well as the type (quality) of ligands, X, with the following form for APS $E_T = E_T(R_a, R_e; M, n, m, X)$. Some characteristics of various octahedral complexes are given in Table 7.

(i) *Adiabatic potential surfaces and "equ–ax" approach*

Within the framework of the theoretical study the central atoms M = Mn, Fe, Co, Ni, and Cu were chosen with oxidation numbers M(II) and M(III) ($n = 2, 3$) and spin multiplicities in the octahedral complexes varying within a range of $m = 1, 2, 3, 4, 5$, and 6. The ligand sphere was represented by the following halogens: X = F, Cl, and Br. For mapping the APS shapes for the complexes ${}^m[MX_6]^{4-}$ and ${}^m[MX_6]^{3-}$ the CNDO/2 version of MO–LCAO–SCF calculations was used within the UHF approach [93–95]. Some preliminary results together with details of the method are published elsewhere [45,96–98].

The calculated APS shape is schematically presented in Figs. 10 and 11. That means:

(1) APS of the type $E_T = E_T(R_a, R_e)$ exhibits one absolute minimum in the octahedral configuration for the electronic state A_{1g}. Similarly, it shows two energy minima corresponding to a slightly compressed ($R_e > R_a$) and

TABLE 7

Electron configurations and states of octahedral d^4–d^9 complexes

d^n system	Low-spin complexes			High-spin complexes		
	Configuration	State	Examples	Configuration	State	Examples
d^4	$t_{2g}{}^4e_g^0$	$^1T_{1g}$	^{1}[Cr(II)] ^{1}[Mn(III)]	$t_{2g}{}^3e_g^1$	^5E_g	^{5}[Cr(II)] ^{5}[Mn(III)]
d^5	$t_{2g}{}^5e_g^0$	$^2T_{2g}$	^{2}[Mn(II)] ^{2}[Fe(III)]	$t_{2g}{}^3e_g^2$	$^6A_{2g}$	^{6}[Mn(II)] ^{6}[Fe(III)]
d^6	$t_{2g}{}^6e_g^0$	$^1A_{1g}$	^{1}[Fe(II)] ^{1}[Co(III)]	$t_{2g}{}^4e_g^2$	$^5T_{1g}$	^{5}[Fe(II)] ^{5}[Co(III)]
d^7	$t_{2g}{}^6e_g^1$	^2E_g	^{2}[Co(II)] ^{2}[Ni(III)]	$t_{2g}{}^5e_g^2$	$^4T_{2g}$	^{4}[Co(II)] ^{4}[Ni(III)]
d^8	$t_{2g}{}^6e_g^2$	^1E_g	^{1}[Ni(II)] ^{1}[Cu(III)]	$t_{2g}{}^6e_g^2$	$^3A_{1g}$	^{3}[Ni(II)] ^{3}[Cu(III)]
d^9	$t_{2g}{}^6e_g^3$	^2E_g	^{2}[Cu(II)]			

elongated ($R_a > R_e$) tetragonal bipyramid for the systems having a degenerate electronic state E_g or T_{2g} in the octahedral configuration. (A fine map of APS for the complex $^2[CuF_6]^{4-}$ is given elsewhere [45].)

(2) APS shows a valley connecting the absolute minimum with dissociation limits, e.g. with $[MF_4]^{2-}$ and MF_2 for the case of $[MF_6]^{4-}$ complexes. This valley, V, represents a reaction pathway according to the scheme (4)

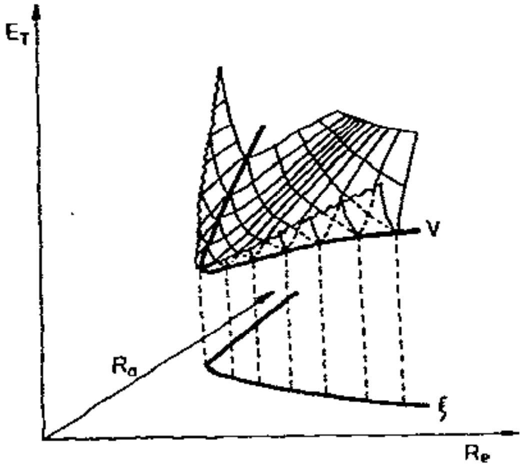


Fig. 10. Main feature of APS of the form $E_T = E_T(R_a, R_e)$. ξ is the projection of a valley, V – the R_a vs. R_e correlation curve.

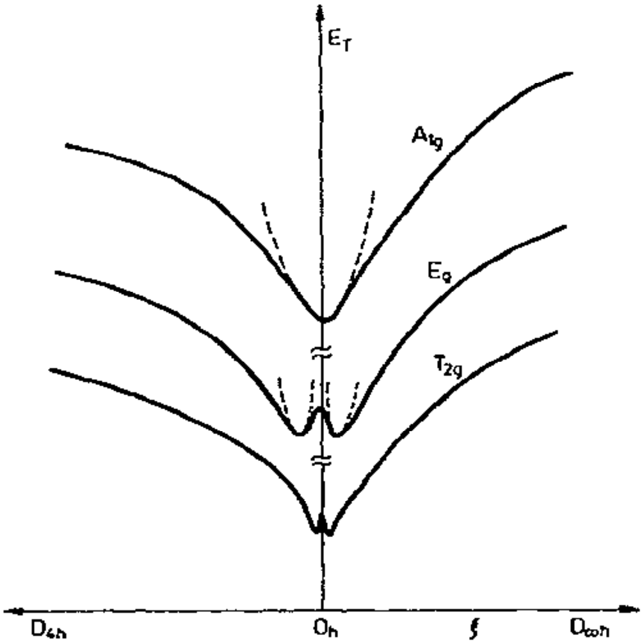


Fig. 11. Detailed shape of a valley on APS of the $E_T = E_T(R_a, R_e)$ form for various electronic states. Dashed lines represent a harmonic approximation.

and is illustrated in Fig. 10. Projection of the valley V into the plane of coordinates $\{R_a, R_e\}$ represents a smooth curve.

If the system is isolated (i.e. a free ion) then a specific equilibrium geometry corresponds to it, given by the minimum position of APS. Due to an external perturbation the position of the energy minimum can be removed in the direction of the minimum energy gradient—along the valley V on APS. The couple of corresponding coordinates $\{R_a, R_e\}$ is changing along the curve, ξ, i.e. according to the R_a versus R_e dependence. Thus, it has been demonstrated that in complexes of the type $[MX_6]^q$ a certain intrinsic disposition for distortion according to the R_a versus R_e dependence exists and is given by the APS shape. An external perturbation can be exemplified by actual arrangement of the particles in the crystal structure, i.e. by additional electrostatic potential in the first approximation. This is the situation found, for instance, in hexafluoro complexes. Another example is the effect of temperature demonstrated by hexanitro complexes.

The method of finding the valley in the case of two-dimensional APS is described in detail elsewhere [45,96]. Both calculated parts of the R_a versus R_e correlation curve represent the "minimum energy path" in the harmonic approximation [99–102]. The case of complexes $^3[NiF_6]^{4-}$ and $^2[CuF_6]^{4-}$ are

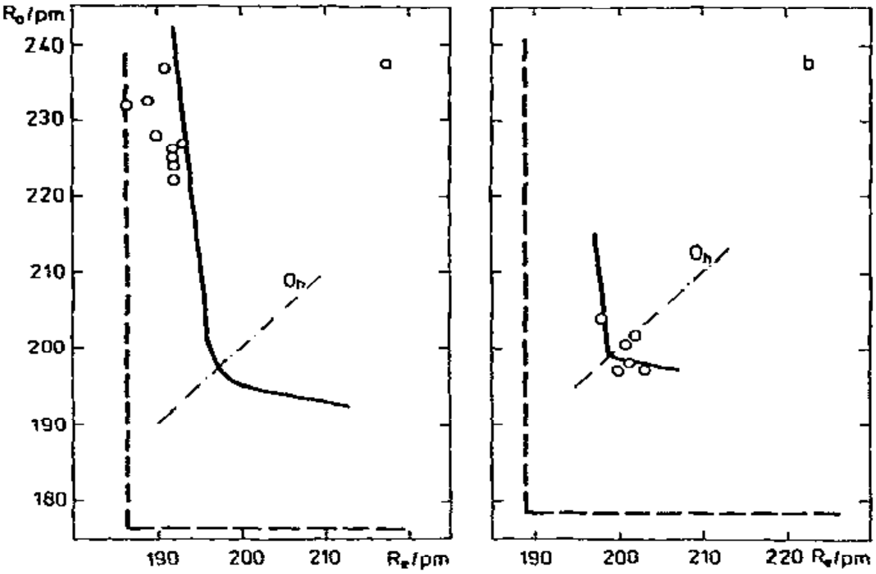


Fig. 12. The calculated R_a vs. R_e dependences (full lines) between dissociation limits (dashed lines). (a) $^2[CuF_6]^{4-}$, (b) $^3[NiF_6]^{4-}$, O, experimental data.

illustrated in Fig. 12. Here, the experimental points resulting from the X-ray structural analysis are included also and the calculated R_a versus R_e correlation curve is in good agreement with experimental data.

(ii) Energy partitioning – possibility for revealing the MIL relevancy

The above procedure represents only one of several approaches to explain the tendency of some complexes to be tetragonally distorted rather than octahedral. Some other methods used for Cu(II) complexes can be found in the literature [87,88]. However, these are often limited only to qualitative considerations. In contrast to the angular overlap method, or the extended Hückel calculations, the simple analysis of orbital energies in not recommended for the CNDO method. The total energy partitioning into one-centre, ligand–ligand and metal–ligand two-centre contributions appears to be more convenient. The last term seems to be decisive for complex stabilization as was demonstrated first in ref. 103.

The importance of the c.a. effect for the above experimental correlations and dependences proved indirectly the decisive function of the central atom. However, this observation was of a qualitative character and did not enable one to make a quantitative decision on the share of the interaction of ligands through the central atom and of the direct ligand–ligand interaction. Therefore, quantum-chemical calculations for determination of the relevancy of MIL for these correlations were performed. The dependence of individual terms of the energy on the complex geometry may provide a picture of which types of interactions in the complex are responsible for its stabilization.

The total molecular energy, E_T, can be easily partitioned, when using the CNDO method, into one-centre, E_A, and two-centre, E_{A-B}, terms

$$E_T = \sum_A E_A + \sum_{A<B} E_{A-B} \tag{5}$$

The corresponding formulae for the *d*-*s*-*p*-basis set are given elsewhere [103]. In complexes of the $MX'_4X''_2$ type (D_{4h} symmetry) it is quite interesting to follow the energy terms

$$E_T = E_{mono} + E_{L-L} + E_{M-L} \tag{6}$$

where E_{mono} is a sum of one-centre terms

$$E_{M-L} = 2E_{M-X'} + 4E_{M-X''} = 2E_{M-L_a} + 4E_{M-L_e} \tag{7}$$

is the total metal–ligand interaction energy, and

$$E_{L-L} = 6E_{X'-X'} + 8E_{X'-X''} + E_{X''-X''} \tag{8}$$

is the total ligand–ligand interaction energy.

Using the above approach, a detailed analysis of the energy stabilization of $^2[CuF_6]^{4-}$, $^2[CuCl_6]^{4-}$, $^2[CuBr_6]^{4-}$, and $^2[Cu(H_2O)_6]^{2+}$ complexes was performed [103]. The last case is shown in Fig. 13. The equilibrium R_e value at R_a = const. is defined by the minimum of the function $E_T = E_T(R_e;\ R_a = \text{const.})$. The analysis of individual energy terms proves that the dominating factor for equilibrium geometry stabilization is the E_{M-L} term. From comparison of the dependence for various R_a values the shift of the minimum on the E_T curve is directed by the shift of the minimum on the E_{M-L} curve. This is a result of the ligand–metal–ligand interaction (MIL).

The total energy E_T and its terms E_{mono}, E_{M-L}, and E_{L-L} were followed for $^2[CuF_6]^{4-}$ and $^3[NiF_6]^{4-}$ along the valley V on the APS. Corresponding plots are given in Figs. 14 and 15. The ligand–ligand interaction energy in these complexes is approximately constant and not very sensitive to the change of the complex geometry. On the other hand the terms E_{mono} and E_{M-L}, especially the last term, are definitely dependent on the complex geometry. The term E_{M-L} exhibits a minimum along the valley V at the same point as E_T and thus it is the dominating term of the complex stabilization. (The E_T course for $^2[CuF_6]^{4-}$ shows, of course, double minima, however, with the chosen scale, these minima are not distinct in Fig. 14.)

A more detailed analysis shows within the interval of the interatomic distances followed, the E_{M-L_a} term decreases with increasing E_{M-L_e}. The reciprocal course between E_{M-L_e} and E_{M-L_a} gives a reason for the "equ–ax"

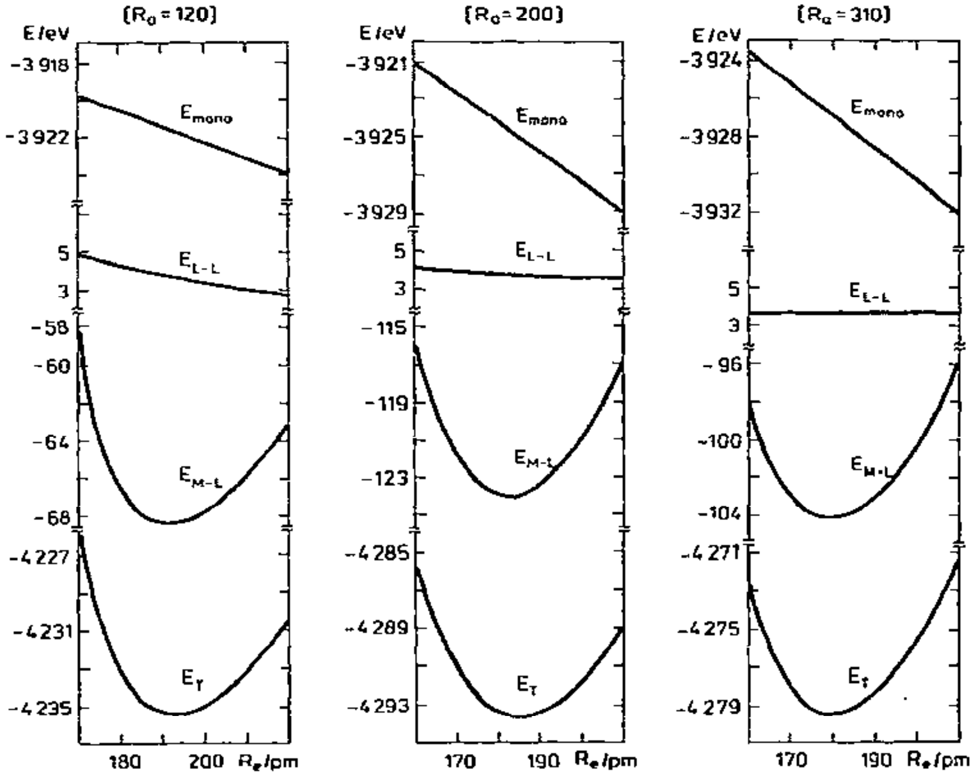


Fig. 13. The energy partitioning for the $[Cu(H_2O)_6]^{2+}$ complex.

influence approach, while the fact that the above interaction is mediated via the central atom proves the relevancy of the MIL conception.

(iii) Quantification of the "equ–ax influence

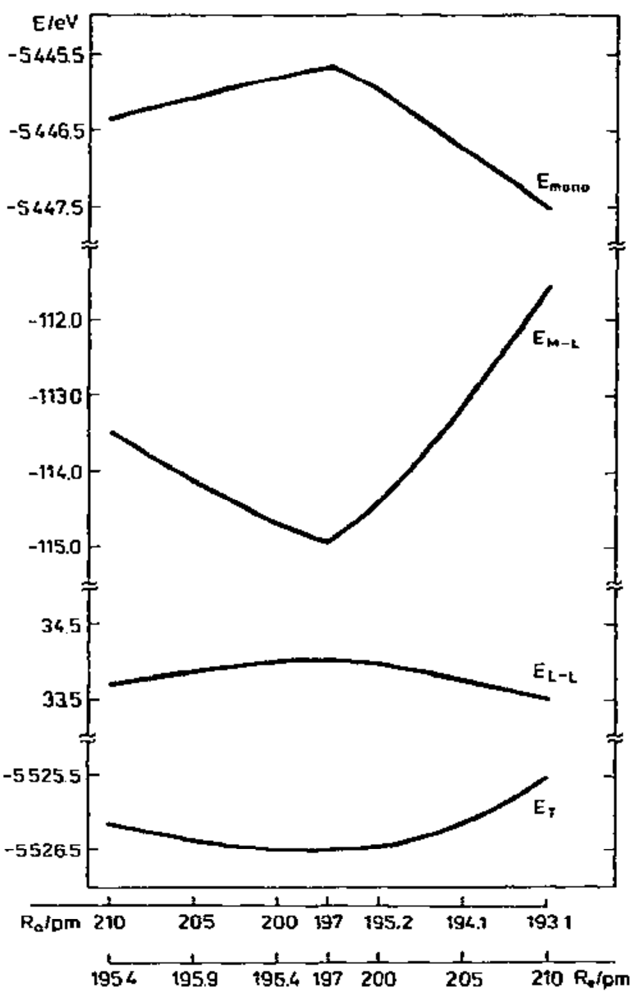
The map of numerical APS values was transformed to an analytic form. Starting from the Taylor power expansion in the point of energy minimum the following form of the harmonic approximation can be obtained.

$$E_T(R_a, R_e) = A + BR_e + CR_a + \tfrac{1}{2}k_{ee}R_e^2 + \tfrac{1}{2}k_{aa}R_a^2 + k_{ae}R_aR_e \tag{9}$$

To determine six constants, at least six numerical APS values are required. The equilibrium geometry is then estimated as follows: $R_a^0 = (Bk_{ae} - Ck_{ee})/(k_{aa}k_{ee} - k_{ae}^2)$ and $R_e^0 = (Ck_{ae} - Bk_{aa})/(k_{aa}k_{ee} - k_{ae}^2)$.

The harmonic force constant matrix

$$\mathbf{K} = \begin{pmatrix} k_{aa} & k_{ae} \\ k_{ae} & k_{ee} \end{pmatrix}$$



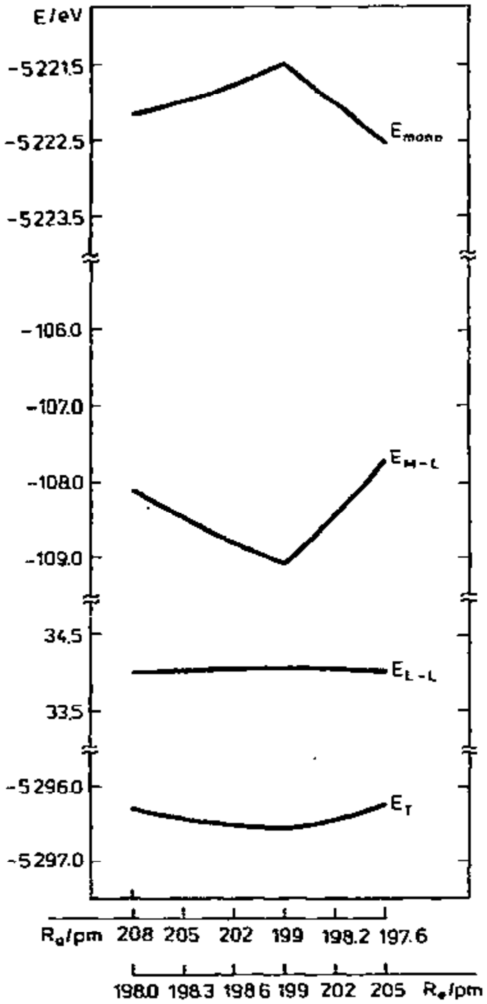


Fig. 14. The energy partitioning for the $^2[CuF_6]^{4-}$ complex.

Fig. 15. The energy partitioning for the $^3[NiF_6]^{4-}$ complex.

involves information on the APS properties in the neighbourhood of the energy minimum. However, resolution of this information into chemical significance requires application of the following procedure. By inversion of the force constant matrix the primary, c_{ii}, and interaction, c_{ij}, compliants are obtained ($\mathbf{C} = \mathbf{K}^{-1}$). These are used for defining the interaction displacement coordinates (IDC):

$$(d_j)_i = c_{ij}/c_{ii} \tag{10}$$

Finally the minimum energy coordinates (MEC) are defined as follows [99–102]:

$$D_i = R_i + \sum_{j \neq i} (d_j)_i R_j \tag{11}$$

This should mean that D_i provides a picture of the change of coordinates ($j \neq i$) in the case of a change in one of them, let us say the R_i coordinate. Thus, MEC D_i is a harmonic approximation to the minimum energy path being shown as linear around the energy minimum.

In two-dimensional space $\{R_a, R_e\}$ the relationships (10) and (11) are simplified as follows

$$D_a = R_a + (d_e)_a R_e = R_a - R_e(k_{ae}/k_{ee}) \tag{12}$$

$$D_e = R_e + (d_a)_e R_a = R_e - R_a(k_{ae}/k_{aa}) \tag{13}$$

and their meaning is illustrated in Fig. 16. For instance, the calculated value of $(d_e)_a = 0.107$ for the $^3[\mathrm{NiF_6}]^{4-}$ complex means that the R_e coordinate will be compressed by 10.7% of the elongation of R_a. In such a case the complex will relax to the energy minimum. Analogously, the value of $(d_a)_e = 0.240$ for the same complex indicates that R_a will be compressed by 24.0% of the length of elongation of the R_e coordinate. In view of such an interpretation the calculated MEC can be accepted as the quantitative criterion describing plasticity (or rigidity) of the coordination polyhedron in the harmonic approximation. The term plasticity means here the ability to undergo tetragonal distortion.

The calculated characteristics of the $[\mathrm{MX_6}]^q$ octahedral complexes in the A_{1g} (or A_{2g}) electronic state are listed in Table 8. On the basis of the interaction displacement coordinates the following conclusions can be drawn:

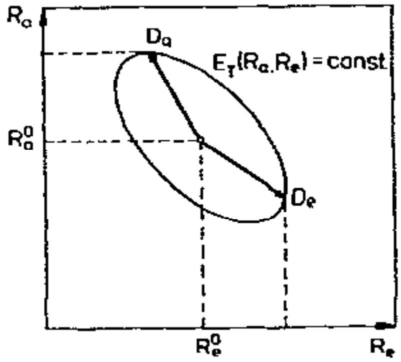


Fig. 16. The meaning of the minimum energy coordinates D_a and D_e.

TABLE 8

Calculated characteristics of octahedral $[MX_6]^q$ complexes in A_{1g} or A_{2g} electronic state

d^n	Complex	$R^0_a = R^0_e$ [a]	Harmonic force constants [b]			IDC [c]	
			k_{aa}	k_{ae}	k_{ee}	$-(d_e)_a$	$-(d_a)_e$
d^5	$^6[MnF_6]^{4-}$	222.7	5.65	1.59	12.91	0.123	0.281
	$^6[FeF_6]^{3-}$	208.5	8.47	1.89	18.84	0.100	0.223
d^6	$^1[FeF_6]^{4-}$	214.9	6.71	1.63	15.04	0.108	0.242
	$^1[CoF_6]^{3-}$	195.5	11.28	2.33	24.89	0.094	0.207
	$^1[CoCl_6]^{3-}$	228.9	8.92	2.30	20.14	0.114	0.258
	$^1[CoBr_6]^{3-}$	245.9	10.28	3.19	23.75	0.134	0.310
d^8	$^3[NiF_6]^{4-}$	198.9	10.68	2.56	23.92	0.107	0.240
	$^3[NiCl_6]^{4-}$	231.1	8.30	2.80	19.40	0.144	0.337
	$^3[NiBr_6]^{4-}$	248.2	9.28	3.54	22.11	0.160	0.381

[a] Distances in pm.

[b] Force constants in N cm^{-1}.

[c] IDC, interaction displacement coordinates.

(1) The complexes with $q = -3$ (the oxidation number of the central atom is M(III)) are more rigid than those with $q = -4$ (that is, M(II)).

(2) In the series of ligands X = F, Cl, and Br the rigidity of the complexes is decreasing, or in other words, their plasticity is increasing.

(3) In the case of the same oxidation number the rigidity of the coordination polyhedron is increasing with increasing proton number.

Complexes with degenerate electronic state E_g or T_{2g} in the octahedral configuration require a more detailed analysis. As the APS exhibits here two minima corresponding to an elongated and compressed tetragonal bipyramid (see Fig. 11), then the polynomial approximating the analytic form of APS in the vicinity of an octahedral arrangement should be at least of the fourth power. Quantitative calculations of this kind are not presented in this paper. We would like to mention briefly only a simplified approach. First, each minimum can be separately fitted by a two-dimensional parabola of the type (6). This situation is illustrated by a dashed line in Fig. 11. By this method the characteristics for the first minimum (elongated bipyramid) and for the second minimum (compressed bipyramid), were obtained and are listed in Table 9. However it is rather difficult to compare some characteristics, such as interaction displacement coordinates with the non-degenerate state.

TABLE 9

Calculated characteristics of square-bipyramidal $[MX_6]^q$ complexes having in the octahedral configuration a degenerate electronic state, as follows from independent two-dimensional parabolic fit of the individual energy minimum

d^n	Complex	Minima [a]	Distances [b]		Harmonic force constants [c]			IDC [d]	
			R_a^0	R_e^0	k_{aa}	k_{ae}	k_{ee}	$-(d_e)_a$	$-(d_a)_e$
A. Electronic state E_g in octahedral configuration									
d^4	$^5[MnF_6]^{3-}$	I	214.6	208.0	7.10	1.81	16.94	0.107	0.255
		II	205.7	212.4	7.74	1.75	16.56	0.106	0.227
d^7	$^2[CoF_6]^{4-}$	I	208.3	204.7	8.60	2.19	19.98	0.115	0.255
		II	203.6	207.1	8.66	1.92	19.55	0.098	0.222
d^8	$^1[NiF_6]^{4-}$	I	203.2	196.5	10.41	2.83	23.42	0.121	0.272
		II	194.3	201.0	11.31	2.21	24.25	0.091	0.195
d^9	$^2[CuF_6]^{4-}$	I	199.1	196.4	11.84	2.98	26.84	0.111	0.252
		II	195.4	198.2	12.00	2.67	27.04	0.099	0.222
	$^2[CuCl_6]^{4-}$	I	229.9	228.3	9.28	3.19	22.47	0.142	0.344
		II	227.8	229.4	9.60	3.06	22.41	0.137	0.319
	$^2[CuBr_6]^{4-}$	I	247.4	245.9	9.95	3.93	23.92	0.164	0.395
		II	245.4	246.9	10.42	3.82	23.67	0.161	0.367
B. Electronic state T_{2g} in octahedral configuration									
d^5	$^2[MnF_6]^{4-}$	I	219.9	219.5	5.69	1.48	13.08	0.113	0.260
		II	219.5	219.7	5.79	1.48	12.73	0.116	0.256
	$^2[FeF_6]^{3-}$	I	204.8	204.1	8.62	1.93	19.22	0.101	0.224
		II	204.1	204.5	8.59	1.96	18.82	0.104	0.228
d^6	$^5[CoF_6]^{3-}$	I	199.6	199.2	10.62	2.20	23.90	0.092	0.208
		II	198.8	199.6	10.60	2.22	23.37	0.096	0.210
d^7	$^4[CoF_6]^{4-}$	I	207.6	207.2	8.53	2.14	19.58	0.109	0.250
		II	207.2	207.4	8.72	2.13	19.04	0.112	0.244

---

[a] The first minimum, I, corresponds to an elongated bipyramid, the second one, II, to a compressed.

[b] Distances in pm.

[c] Force constants in N cm^{-1}.

[d] IDC, interaction displacement coordinates.

(iv) E_g–e_g vibronic coupling and the "equ–ax" approach

Consideration of the vibronic interaction of the degenerate electron state E_g with the vibrational modes of e_g type in octahedral complexes leads to a prediction of APS shape around the octahedral geometric configuration. APS is analytically expressed by the function of symmetric coordinates: $E_T = E_T(Q_1, Q_2, Q_3)$. In this case, the coordinate Q_1 is fully symmetric a_{1g}, while Q_2 (tetragonal distortion of the octahedron) and Q_3 (o-rhombic one) belong to e_g. The aim of this section is to find a relationship between the "equ–ax" representation of APS of the type $E_T = E_T(R_a, R_e)$ and a better known representation of the type $E_T = E_T(Q_1, Q_2, Q_3)$ found using the Jahn–Teller theorem.

Let the following limitations be accepted for the vibronic interaction: (i) E_g state interacts only with vibrations of the e_g symmetry (Q_2 and Q_3); (ii) normal vibrations are harmonic; and (iii) in the Taylor's expansion of the vibronic interaction operator only quadratic terms are taken into consideration. Then, the analytic expression for APS is as follows [89].

$$E_T(Q_1, Q_2, Q_3) = E_0 - \rho\left(A_1^2 + A_2^2\rho^2 + 2A_1A_2\rho\cos 3\varphi\right)^{1/2} + \tfrac{1}{2}K_1Q_1^2 + \tfrac{1}{2}K_2\rho^2 \tag{14}$$

where $\rho = (Q_2^2 + Q_3^2)^{1/2}$ and $\varphi = \arctan(Q_3/Q_2)$ are polar coordinates, E_0 is the total energy of the "optimum" octahedral configuration and $A_1(A_2)$ is the linear (quadratic) e_g vibronic constant. For Q_1 = constant this APS is often represented by the shape of the so called "Mexican hat" with warping. A cut of this Mexican hat for the case $Q_3 = 0$ is given in Fig. 17. Then, the

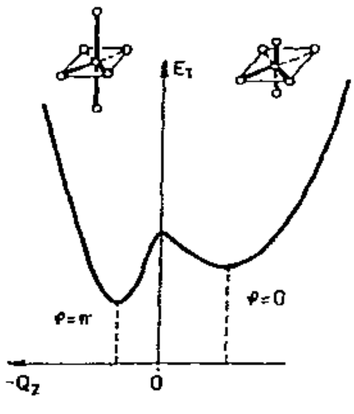


Fig. 17. A cut of the Mexican hat for $Q_3 = 0$.

analytic expression for APS is simplified as follows

$$E_{\mathrm{T}}(Q_1, Q_2; Q_3 = 0) = E_0 - |Q_2|(A_1 \pm A_2|Q_2|) + \tfrac{1}{2}K_1Q_1^2 + \tfrac{1}{2}K_2Q_2^2 \qquad (15)$$

where the negative sign in front of A_2 corresponds to the case $\varphi = \pi$ (elongated bipyramid) and the positive sign to the case $\varphi = 0$ (compressed form). Energy minima are not equivalent: the lower one is absolute, while the higher minimum is local for the cut $Q_3 = 0$. The latter corresponds in the $\{Q_2, Q_3\}$ representation to the saddle point of the warped Mexican hat [89].

Between the internal and symmetric coordinates simple linear relationships are valid. When substituting them into the harmonic approximation of individual APS minima (9), after simple algebraic operations, expressions for K_1, K_2, A_1, and A_2 can be obtained [98]. Numerical data for the $^2[\mathrm{CuF_6}]^{4-}$ complex are given in Table 10. The initial set of the "equ–ax" parameters R_a^0, R_e^0, k_{aa}, k_{ae}, and k_{ee} for individual minima (I and II) was transformed into the symmetric coordinates. Finally, Jahn–Teller parameters K_1, K_2, A_1, and A_2 were obtained. It should be noted that the theoretical APS shape (14) or (15) deviates from the shape found numerically. Otherwise, the following relationships should be valid: $(Q_1^0)_{\mathrm{I}} = (Q_1^0)_{\mathrm{II}}$, $(K_1)_{\mathrm{I}} = (K_1)_{\mathrm{II}}$ and $(A_1)_{\mathrm{I}} = (A_1)_{\mathrm{II}}$. The numerically determined APS shape is more

TABLE 10

The characteristics of APS for $^2[\mathrm{CuF_6}]^{4-}$

Quantity	Unit	Minimum I ($\varphi = \pi$)	Minimum II ($\varphi = 0$)
A. The "equ–ax" parameters			
R_a^0	pm	199.134	195.441
R_e^0	pm	196.357	198.207
k_{aa}	N cm^{-1}	11.84022	12.00045
k_{ae}	N cm^{-1}	2.98009	2.66768
k_{ee}	N cm^{-1}	26.83680	27.03727
R_0	pm	197.356	
B. The Jahn–Teller parameters			
Q_1^0	pm	−0.17962	−0.17391
Q_2^0	pm	−3.2066	3.1939
$\partial^2E_{\mathrm{T}}/\partial Q_2^2$	N cm^{-1}	5.18977	5.36403
$K_1 = (\partial^2E_{\mathrm{T}}/\partial Q_1^2)$	N cm^{-1}	7.43953	7.39551
A_1	10^{10} eV m^{-1}	1.03867	1.06929
A_2	N cm^{-1}	+0.043564	
K_2	N cm^{-1}	5.27690	

complex than that resulting from the simple approximate formula (15). The non-zero equilibrium coordinate Q_1^0 indicates that besides the E_g–e_g vibronic coupling the E_g–a_{1g} vibronic coupling is also significant and thus the real situation is better expressed by the E_g–$(a_{1g}+e_g)$ vibronic interaction. Questions of this kind are published elsewhere [104,105].

The E_g–a_{1g} vibronic coupling does not result in distortion of the ideal octahedral structure. However, in combination with the E_g–e_g vibronic coupling (taking into consideration the E_g–$(a_{1g}+e_g)$ vibronic coupling) it affects the values of the Jahn–Teller parameters not only quantitatively, but can result even in a qualitatively different picture. Such a situation was recently demonstrated [104,105] for the $^2[CuX_6]^{4-}$ type, where $X = F$, Cl, and Br. First, a mapping of the APS in the vicinity of the octahedral structure was carried out for three independent coordinates: Q_1, Q_2, and Q_3. From theoretical analysis of the vibronic Hamiltonian (by utilization of the perturbation theory) a more complicated expression than (14) resulted for APS. Here several constants appear. These constants acquire a characteristic value in individual complexes having a degenerate electronic state E_g in the octahedral geometry. Actual values of these constants were obtained by fitting the numerical APS values to the analytic form. For this purpose the modified method of non-linear regression was used [106]. The results obtained have shown that when passing from the E_g–$(a_{1g}+e_g)$ vibronic coupling towards a more approximate E_g–e_g one, the sign of the quadratic vibronic A_2 constant can be changed. This results in an interchange of the energy minima and saddle points of $^2[CuF_6]^{4-}$ (in the approximate illustration of APS as a warped Mexican hat). In both cases, however, the calculated Jahn–Teller distortion in free ions is relatively small: 10^{-1}–1 pm in length.

(v) Solid state effects and the "equ–ax" influence

The experimentally found distortions of the coordination polyhedra of the $[MX_6]^q$ type with respect to the ideal octahedron are of the order 10 pm (see Section B). However, the systems under study are in the solid state. The distortion found is higher than the calculated values in the free ions. Thus, the solid state does result in additional effects evoking either distortion (in the case of the non-degenerate A_{1g} states) or in strengthening the Jahn–Teller distortion of the free ion. To the main effects of the solid state the following facts should be mentioned:

(1) Mutual electrostatic interaction of individual ions, eventually dipoles in the crystal structure.

(2) Cooperative Jahn–Teller effect in the case of degenerate or pseudo-degenerate electronic states.

(3) The spatial distribution of individual components in the crystal lattice.

An influence of the cooperative Jahn–Teller effect (being, in the electrostatic model, an interaction of the quadrupole–quadrupole type) is probably lower than the direct interaction of ions or dipoles in the solid phase (in the electrostatic model it is the interaction of the charge–charge, charge–dipole, or dipole–dipole type). The most obvious effect of the solid state, the charge–charge interaction, was demonstrated by the following simple model approach.

In the axial positions of the ${}^{m}[MX_6]^{q}$ type complex two Na^+ cations were localized 500 pm above the central atom (Fig. 18). Systems of the type ${}^{m}[Na\ldots MX_6\ldots Na]^{q+2}$ for X = F and Cl were taken into consideration. At the same time, the geometry optimization was carried out with respect to two geometrical degrees of freedom: R_a and R_e. The calculated characteristics of the models studied are given in Table 11. On the basis of the results presented one can state that the simple model of the solid state considered considerably affects the properties of the $[MX_6]^q$ coordination polyhedron. The most important conclusion results from the equilibrium geometry found: the calculated tetragonal distortion in the model complexes is approximately 10 pm and this range is in good agreement with experiment. One cannot

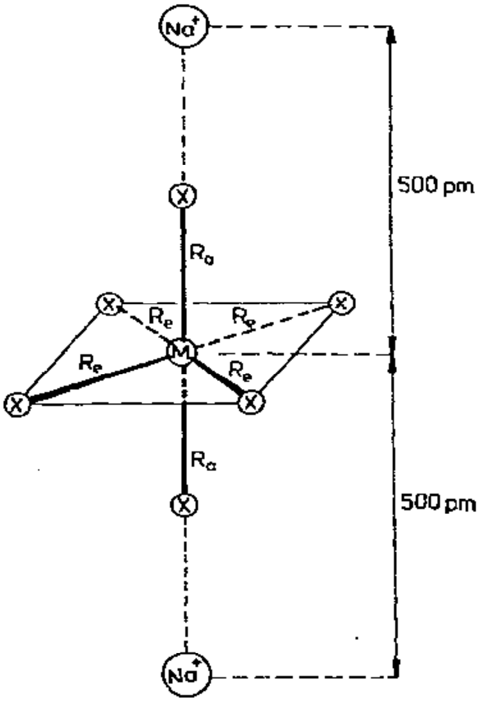


Fig. 18. A model complex of solid state influences.

TABLE 11

Calculated distortions of coordination polyhedra referring to optimum octahedral central atom–ligand distances[a]

System	State	Multiplicity	$R_0(O_h)$	Distortion	
				ΔR_e	ΔR_a
CuF_6^{4-}	^2E_g	2	197.4	1.0	−1.8
CuF_6^{4-} +2Na$^+$		2		−5.5	−19.5
$CuCl_6^{4-}$	^2E_g	2	229.0	−0.7	−1.1
$CuCl_6^{4-}$ +2Na$^+$		2		−10.6	−4.5
CoF_6^{4-}	$^5T_{2g}$	5	199.4	0.2	−0.3
CoF_6^{4-} +2Na$^+$		5		−11.6	−9.0
$CoCl_6^{4-}$	$^5T_{2g}$	5	230.8	0.2	−0.3
$CoCl_6^{4-}$ +2Na$^+$		5		−3.6	2.2
NiF_6^{4-}	$^3A_{1g}$	3	198.9	0.0	0.0
NiF_6^{4-} +2Na$^+$		3		−18.3	−16.8
$NiCl_6^{4-}$	$^3A_{1g}$	3	231.1	0.0	0.0
$NiCl_6^{4-}$ +2Na$^+$		3		−11.0	−7.2

[a] Distances in pm.

exclude that the application of another method (e.g. of more sophisticated ab initio calculations) could provide other numerical values of complex distortion. However, the distortion ratio 1:10 in the free ions and in model complexes of the solid state can hardly be changed.

From the above facts it is clear that, in the case of the simple model, the effects of the solid state prevail over the Jahn–Teller effect. It can be expected, however, that with the increasing number of unit cells (with E_g-active centres) the cooperative Jahn–Teller effect takes place (this leads to distortion strengthening), while the ion–ion interactions become compensated. This was illustrated by the situation observed in the case of the hexafluoro complexes where the greatest tetragonal distortion of the coordination polyhedra were observed for the E_g active complexes. Therefore, the results presented here should be considered as the first stage in an investigation of the mutual proportionality of the solid state and the Jahn–Teller effect which influence distortion of coordination polyhedra within the equ–ax approach.

In spite of the fact that use of the MIL study in isolated complexes (or in systems with weak interactions with the environment) is often advantageous, such limitation deprives knowledge about the consequences of MIL on the complex structure and properties. For instance, the study of MIL in connection with its chemical consequences is practically impossible without considering the interaction of the complex with its surroundings. In some cases the interaction between the complex and its environment intensifies those effects which are consequences of MIL. In such a case the function of the environment can be compared with the function of a developer by which a latent picture hidden in the photo-material is developed.

D. CONCLUDING REMARKS

On the basis of data dealing with the properties of a large number of different complexes a collective interaction of equatorial ligands versus axial ligands has been demonstrated. This has consequences in stereochemistry, physical properties, and reactivity as well as on the coordination mode of the thiocyanate ligand. The experimental data and theoretical (quantum-chemical) calculations have shown that in the equatorial–axial interactions investigated the central atom has an important function. The consequences of the equatorial–axial interactions are understood as one form of the MIL manifestation.

The investigation of the "equ–ax" interaction is a new, more integral approach within the MIL conception, in which the collective interaction between certain groups of ligands in the coordination sphere is taken into consideration (unlike the case of the *cis* effect, *cis* influence, *trans* effect, and *trans* influence). Such an approach to the MIL problems is more appropriate to reality at least in the cases considered above. It relates to current conceptions of the theory of chemical structure which try to explain the properties of a chemical compound elucidating its structure as a whole and not only by description of interactions in its fragment.

More precise limitation of the applicability of the equatorial–axial approach requires further experimental and theoretical investigations. Its stimulating importance for the development of the theories on MIL consists particularly in its collective respect of the interactions of all ligands through the central atom in the coordination polyhedron.

The experimental data and theory discussed here indicate that the "equ–ax" interactions manifest themselves mainly in those complexes having degenerate or pseudo-degenerate states and in the complexes with metallocycles (including macro-cycles) in the equatorial plane. The latter complexes, due to their theoretical attractiveness and practical importance, emphasize the relevancy of the "equ–ax" influence.

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