

EQUATORIAL-AXIAL INTERACTIONS: A MORE INTEGRAL APPROACH TO THE
PROBLEMS OF MUTUAL INFLUENCE OF LIGANDS IN COMPLEXES

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Abstract - Equatorial-axial interactions in complexes of some transition metals have been studied. The consequences of equ-ax interactions on stereochemical properties, coordination mode of NCS groups, some spectral properties, activation of small molecules and the reactivity of complexes, as well as theoretical interpretations of equ-ax approach within the MIL conception are presented.

INTRODUCTION

Significant changes in experimental techniques as well as the contemporary possibilities of theoretical chemistry allow to obtain information pointing to various consequences of the mutual influence of ligands in complexes via central atom (the MIL conception). Recently, the amount of information of the MIL consequences increases so much that the formulation of new rules may be expected which could find their use in experimental and theoretical coordination chemistry similarly as it has been the case of trans-effect.

The present work brings experimental results and theoretical interpretations of equatorial-axial interactions in complexes within the MIL conception. These interactions have been observed on the so-called static properties of complexes (equ-ax influence) as well as in their chemical changes (equ-ax effect). While the former covers mainly the stereochemistry, spectroscopy, thermodynamics and electronic structure, the latter involves first of all the chemical reactivity, activation processes, chemical kinetics and catalysis. Some more detailed information on equ-ax influence is presented in our paper [1].

The equ-ax approach within the MIL conception represents a study of integral interactions of all ligands through the central atom in the coordination sphere of complexes. It means the collective interaction of equatorial ligands with those in axial positions through the central atom in such complexes in which the equatorial plane and axial positions can be delimited. The equ-ax study differs from that applied to the problems of trans-influence and trans-effect, because the latter have been mostly studied fragmentarily as the MIL manifestations on one coordinate only.

STEREOCHEMICAL CORRELATIONS OF R_a VERSUS R_e

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 [2], several years ago the authors studied the changes in the central atom - ligand distances in the equatorial plane and those in axial positions and their relationship [3]. The mentioned analysis was limited to tetragonal distortions of octahedral and pseudo-octahedral Cu(II) complexes. It was found that for a given chromophore the mean values of central atom - ligand distances in the equatorial plane (R_e or R_S - short) and of those in axial positions (R_a or R_L - long) correlate along a smooth curve in such a way that the values of R_a decrease with increasing R_e and vice versa.

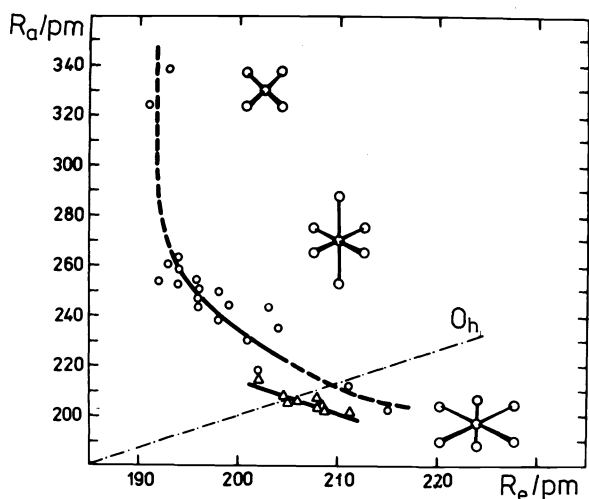
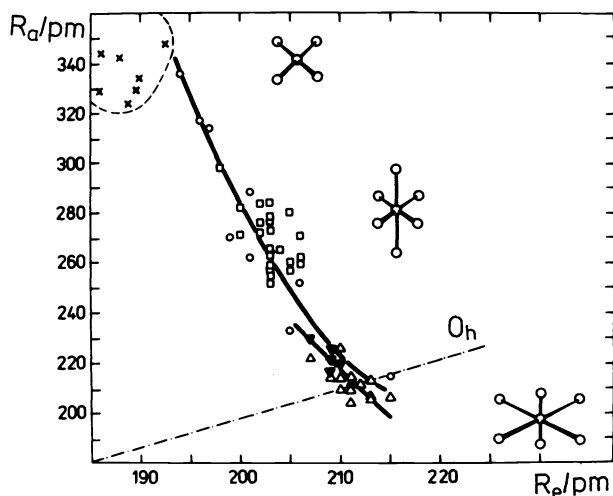


Fig. 1. Plot R_a vs. R_e for Cu(II) and Ni(II) complexes.
 O, chromophore $[\text{CuO}_6]$;
 Δ , chromophore $[\text{NiO}_6]$.

Fig. 2. Plot R_a vs. R_e for Cu(II) and Ni(II) complexes.

O, chromophore $[\text{CuN}_6]$;
 \square , chromophore $[\text{CuN}_4\text{O}_2]$;
 Δ , chromophore $[\text{NiN}_6]$;
 \blacktriangledown , chromophore $[\text{NiN}_4\text{O}_2]$;
 \times , chromophore $[\text{NiN}_4]$.



The analysis of X-ray structure data was later extended into three directions [1,4-6], namely:

(1) Statistical treating and comparison of R_a vs. R_e dependence for complexes with chromophores of $[\text{CuO}_6]$, $[\text{CuN}_6]$, $[\text{CuN}_4\text{O}_2]$, $[\text{NiO}_6]$, $[\text{NiN}_6]$, and $[\text{NiN}_4\text{O}_2]$;

(2) Investigation of axial interactions in dependence on the type of metallo-cycle in the equatorial plane;

(3) Study of the central atom effect on the degree of tetragonal distortions in complexes with a homogeneous ligand sphere.

The most significant results may be summed up as follows (Figs. 1-3).

(i) The correlation of R_a vs. R_e is non-linear for chromophores $[\text{CuO}_6]$ and $[\text{CuN}_6]+[\text{CuN}_4\text{O}_2]$, and approximately linear (in the studied interval) for chromophores $[\text{NiO}_6]$ and $[\text{NiN}_6]+[\text{NiN}_4\text{O}_2]$. When changing the central atom of Cu(II) for Ni(II), the range of the R_a - R_e interval expressively decreases. Unlike to Cu(II) complexes, for $[\text{NiN}_6]$ and $[\text{NiN}_4\text{O}_2]$ chromophores, the tetragonal distortion does not change continuously towards the square-planar configuration of $[\text{NiN}_4]$. This indicates that the "plasticity" of Cu(II) complexes [3] manifests itself in a greater adaptability of their coordination polyhedra to tetragonal distortions when compared with Ni(II) complexes.

(ii) The tetragonal distortions of coordination polyhedra occur to the greatest extent in Cu(II) complexes with planar metallo-cycles having π bonds in the equatorial plane. On the contrary, comparatively short axial bonds were found in complexes with five-membered or non-planar six-membered metallo-cycles (e.g. in chair conformations). In Fig. 3, the zone corresponding to planar metallo-cycles is limited by a dashed line. An analogous behaviour was not found for Ni(II) complexes [1,5]. It means that a certain factor influencing the R_a vs. R_e dependences need not find its manifestation to the same extent in analogous complexes, but with different central atoms.

(iii) It was found [1,7] that the tetragonal distortions of Cu(II) coordination polyhedra in a series of hydrated 2-substituted Cu(II) carboxylates are very sensitive to changes of electronic density caused by a change of the substituent in the equatorial plane.

(iv) An expressive central atom effect on the R_a vs. R_e dependence [1,6] was observed in complexes with homogeneous ligand sphere of the type of $^m[\text{MX}_6]^q$. That effect means not only the influence of proton number of the central atom M but also that of oxidation, and spin states, q , and m , respectively. Taking hexafluoro complexes for example (Fig. 4), it may be concluded that the R_a vs. R_e dependence has to be considered as a general manifestation of the innercomplex ability to undergo tetragonal distortions. The greatest tetragonal distortions of R_a - R_e were observed for complexes with doubly degenerate electronic state E_g with the hypothetical octahedral configuration, i.e. for complexes of $^5[\text{Cr}(\text{II})]$, $^5[\text{Mn}(\text{III})]$, and $^2[\text{Cu}(\text{II})]$. On the other hand, the studied systems with triply degenerate electronic state T_{2g} (or T_{1g}) e.g. $^5[\text{Fe}(\text{II})]$, as well as with non-degenerate electronic state A_{1g} (A_{2g}), e.g. $^3[\text{Ni}(\text{II})]$, exhibit tetragonal distortions within R_a vs. R_e dependence in an essentially smaller extent. An analogous behaviour has been recently found for a series of hexaqua and hexachloro complexes [6c].

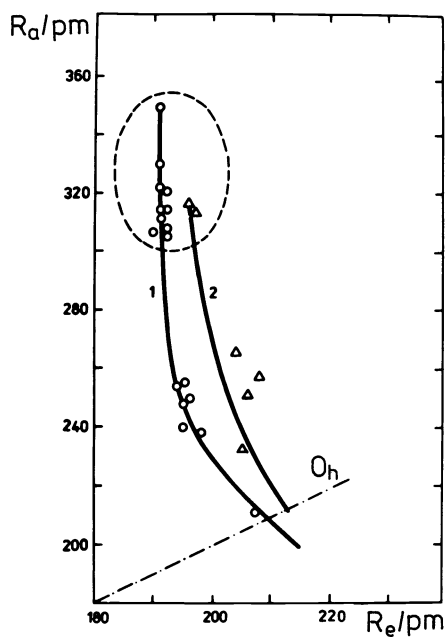


Fig. 3. Plot R_a vs. R_e for Cu(II) complexes of the chelate type.
 O, chromophore $[\text{CuO}_6]$;
 Δ , chromophore $[\text{CuN}_6]$.

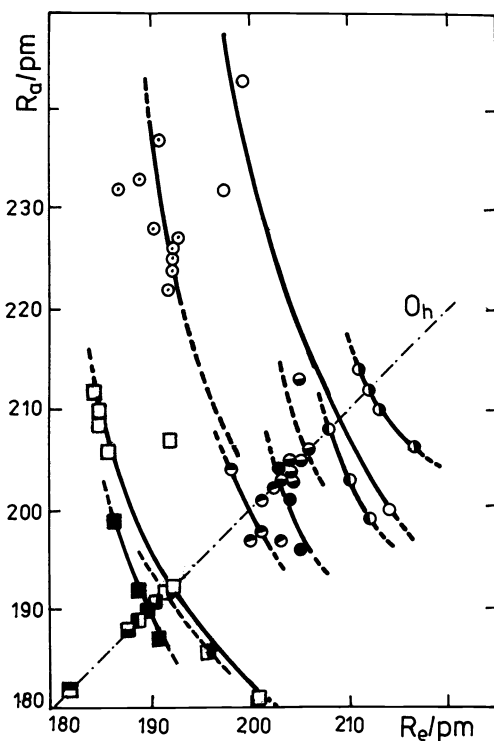
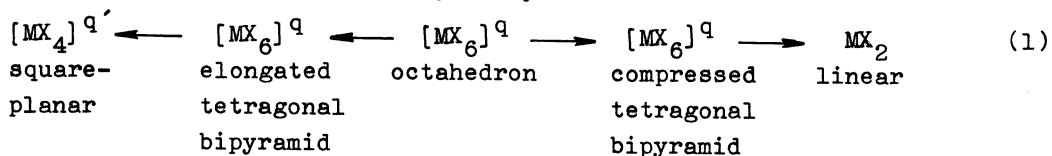


Fig. 4. Plot R_a vs. R_e for hexafluoro complexes.
 O - Cr(II), ● - Mn(II), ◐ - Fe(II),
 ◑ - Co(II), ◒ - Ni(II), ◓ - Cu(II),
 O - Zn(II), ■ - Cr(III), □ - Mn(III),
 ◑ - Fe(III), ◒ - Co(III), ◓ - Ni(III),
 ◔ - Cu(III).

(v) It was found that for Cu(II) and Co(II) hexanitro complexes, the R_a vs. R_e dependence may be applied to different temperature induced phases of the same compound [6b] differing in the amount of their total energy. This justifies the assumption according to which R_a vs. R_e dependences are in a relation with energy criteria.

In the above connection quantum-chemical computations were used (applying a semi-empirical, molecular-orbital method of CNDO and INDO) to investigate the function of the $E_T = E_T(R_a, R_e)$ type, where E_T means the total energy of $^m[\text{MX}_6]^q$. Such an adiabatic potential surface (APS) describes tetragonal distortions along the reaction pathway:



Based on the computations for various central atoms M, for different oxidation states q , spin states m , and ligands X, it was found [1,8-10] that:

(i) The above type of APS exhibits a single absolute minimum in the octahedral configuration for non-degenerate electronic states A_{1g} (or A_{2g}), and two minima (corresponding to a somewhat compressed and an elongated tetragonal bipyramid) for systems with degenerate electronic states E_g and T_{2g} (T_{1g}). Essentially higher values of tetragonal distortions were obtained for the E_g state when compared with T_{2g} (Fig. 5).

(ii) The APS exhibits a valley connecting the energy minimum with the dissociation limits, i.e. with $[MF_4]^{2-}$ and MF_2 for complexes of $[MF_6]^{4-}$. This valley, V, represents the reaction pathway according to scheme (1) and it is roughly shown in Fig. 6. The projection of the valley V into the plane of $\{R_a, R_e\}$ coordinates is a smooth curve ξ . As has been shown in former papers [1,8], the correlation curves of R_a vs. R_e computed in this way, are in a good agreement with experimental points.

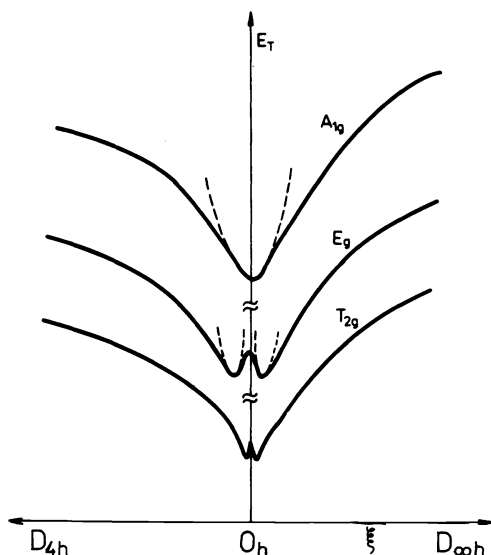


Fig. 5. Detailed shape of a valley on APS of the $E_T = E_T(R_a, R_e)$ form for various electronic states.

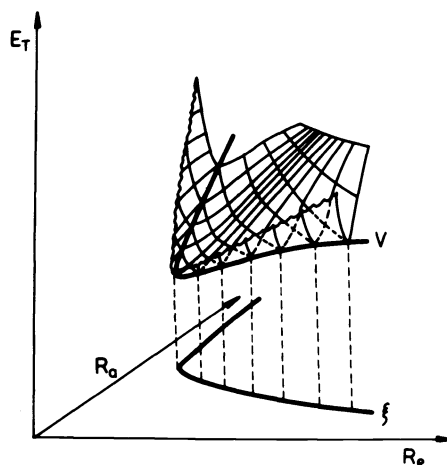


Fig. 6. Main feature of APS of the form $E_T = E_T(R_a, R_e)$. ξ is the R_a vs. R_e correlation curve.

The R_a vs. R_e behaviour of complexes may be explained in such a way that due to an extrinsic influence (e.g. owing to additional electrostatic lattice potential in the solid state or due to the temperature influence), the position of the energy minimum of APS will change according to the minimum energy gradient - along the valley on APS. Consequently, the coordinates R_a and R_e will change along the curve ξ , i.e. according to the dependence of R_a vs. R_e . The presented theoretical approach of APS mapping proved to be advantageous for the following reasons:

(i) On the basis of interaction displacement coordinates [11] quantitative characteristics may be deduced, describing the degree of plasticity or

rigidity of coordination polyhedra [1,10].

(ii) The characteristics of APS may be transformed to conventional parameters describing the $E_g - e_g$ vibronic coupling. Moreover, such a transformation may be applied to a more complicated potential type than the well-known "Mexican hat", when the vibronic coupling of $E_g - (a_{1g} + e_g)$ type is considered [10,12].

(iii) In the individual geometries of APS the total energy E_T may be partitioned into monocentric E_A and bicentric E_{A-B} contributions [13]. Thus, it has been found that the bicentric part of the total energy E_{M-L} (Fig. 7) is the controlling member of stabilization of the equilibrium geometry as well as of shifting the local minima along the R_a vs. R_e curve. This allows to classify the R_a vs. R_e behaviour within the MIL conception.

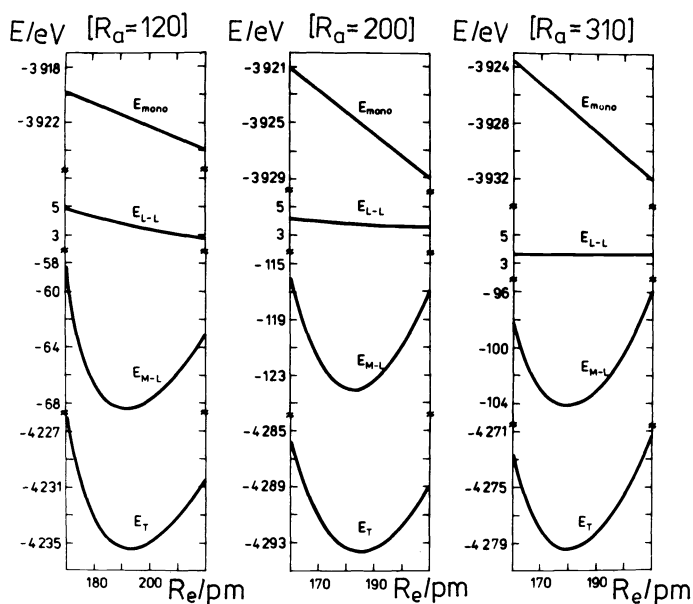


Fig. 7. The energy partitioning for the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex [13].

(iv) An analogous treating allows to investigate the APS behaviour for more complicated aggregates in which the influence of solid state effects on the distortion of coordination polyhedra is studied [1]. Thus, it may be evaluated not only the influence of ion - ion interactions on the distortion degree but also the transition from the local Jahn-Teller effect to a cooperative one.

THE COORDINATION MODE OF NCS GROUPS IN Cu(II) COMPLEXES

The influence of equatorial ligands on the coordination mode of NCS groups situated in axial positions is also one of the consequences of equ-ax interactions in complexes. It was found that for Cu(II) complexes with the same donor atoms (i.e. nitrogen) in the equatorial plane differing, however, in

the ligand ability to be bonded by π bonds, the coordination mode of NCS groups in axial positions of mononuclear and polynuclear Cu(II) complexes is different [1,14,15]. Such a behaviour was not observed for a number of complexes with other central atoms for which apparently the disposition of the central atom to be bonded with the NCS group either through its sulphur or nitrogen atoms, becomes dominant. It is worthy to mention that Cu(II) lies on the boundary between the a and b classes of Pearson's classification of metals [16].

The Cu(II) complexes with metallo-cycles in the equatorial plane and with NCS groups in axial positions were also studied in connection with the investigation of the significance of integral or fragmental ligand interactions. If, for example, in $\text{Cu(en)}_2(\text{SCN})_2$ complex [17a] (en = ethylenediamine) one NCS group is substituted by perchlorate ligand, the coordination mode of the remaining NCS group will change. The coordination of a perchlorate group in the sixth position in the tetragonal-pyramidal complex of Cu(den)(NCS)_2 [17b] (den = di(2-aminoethyl)amine) causes the change of the coordination mode of the axial NCS group in the resulting dimer complex. Both these cases are of that kind that no significant deformation of equatorial ligands occurs and they can be rationalized by means of the trans-influence. There are, however, cases when the substitution of one NCS group in axial position of the six-coordinate complex causes not only a change of the coordination mode of the remaining NCS group but also a change of the whole polyhedron geometry. Such conversion from the tetragonal-bipyramidal to a distorted trigonal-bipyramidal configuration has been originally observed for the $\text{Cu(tn)}_2(\text{SCN})_2$ (tn = 1,3-diaminopropane) when converted to $[\text{Cu(tn)}_2(\text{NCS})]\text{ClO}_4$ [17c]. Based on electronic and infrared spectra, such a conversion may also be assumed for complexes of CuL(NCS)X type where L = sym-N,N'-dimethylethylenediamine, 1,3-diaminopropane, N-(3-aminopropyl)cyclohexylamine and X = NO_3^- , ClO_4^- and BF_4^- . The latter apparently ought to be expected for complexes with metallo-cycles which are more sterically variable.

Although the integral approach within the MIL conception on investigation of the NCS group coordination mode seems to be more general, under certain conditions only changes in fragments of complexes may be registered. This is the case when the equatorial plane is "fixed" by a rigid, polydentate equatorial ligand.

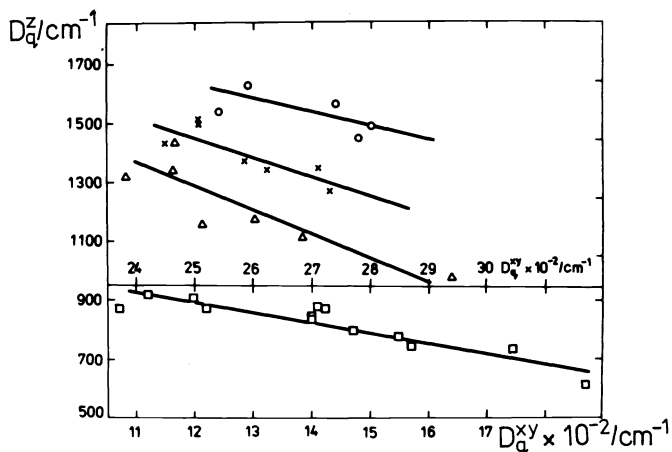
EQU-AX INTERACTIONS AND SPECTRAL PROPERTIES

The manifestations of equ-ax interactions in electronic absorption spectra were studied especially for tetragonal-bipyramidal complexes of Ni(II) and Co(II). Conclusions on equ-ax interactions were drawn from spectral parameters D_q^Z vs. D_q^{XY} dependences.

It was found for example, that an increase of the ligand field strength in the equatorial plane of $\text{Ni(R-aniline)}_4(\text{ClO}_4)_2$, in dependence on the substituent R, causes a decrease of the ligand field strength of ClO_4^- ligands

being coordinated in axial positions [18]. An analogous correlation of D_q^Z and D_q^{XY} parameters was also observed for Ni(II) complexes with saturated and unsaturated macrocycles (abbreviated as MAC) in the equatorial plane [1,19] - Fig. 8.

Fig. 8. Plot D_q^Z vs. D_q^{XY} .
 $\text{Co}(\text{MAC})\text{X}_2^q$ for $\text{X} = \text{H}_2\text{O}, \text{Cl}$,
 Br: \circ, \times, Δ .
 $\text{Ni}(\text{MAC})(\text{NCS})_2$: \square .



A gradual increase of the ligand field strength in the equatorial plane of Ni(II) complexes above a certain D_q^{XY} value leads to a discontinuous change under the formation of square (diamagnetic) complexes; simultaneously the axial ligand field strength is expressively weakened. Such a behaviour has been observed for Ni(II) complexes with pyridine and its derivatives [20,21]. The absence of such stereochemical changes in analogous Co(II) complexes [22,23] confirms that the mutual equatorial - axial conditionality is influenced by properties of the central atom.

It is not possible to determine D_q^Z and D_q^{XY} values for tetragonally distorted Cu(II) complexes from their electronic spectra. Nevertheless, a linear dependence of the electronic transition maximum vs. the square of the frequency of the highest energy metal-nitrogen stretching mode was observed for $\text{Cu}(\text{R-en})_2\text{X}_2$ type complexes [24].

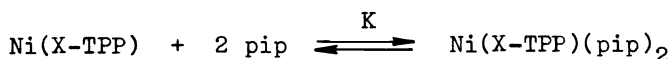
EQU-AX INTERACTIONS AND CHEMICAL CHANGES OF COMPLEXES

The existence of static and dynamic manifestations of the MIL (influence and effect, respectively) was observed for the first time for Pt(II) complexes, being known as trans-influence and trans-effect. The knowledge obtained until now allows to assume that the equ-ax effect operates in chemical reactions as well. Though the relationship between static and dynamic manifestations of the MIL apparently are not simple, yet it may be expected.

Recently quantum-chemical computational methods were used to study extensive series of dioxygen [25] and dinitrogen [26] complexes of the type $^m[\text{M}(\text{L}_e)_4\text{L}_a(\text{X}_2)]^q$ in different oxidation and spin states. It was found that the degree of activation of molecule $\text{X}_2 = \text{O}_2$ or N_2 (presupposition of their

chemical reactivity) expressively depends on the equatorial ligands ($L_e = \text{NH}_3, \text{H}_2\text{O}, \text{PH}_3, \text{SH}_2, \text{CN}^-, \text{OH}^-$ and SH^-). The degree of activation can achieve a value of one or two whole electrons (e.g. $\text{O}_2^-, \text{O}_2^{2-}, \text{N}_2^-, \text{N}_2^{2-}$) thus forming assumptions for the course of certain chemical reactions and catalysis. Since the actual manifestations of equ-ax influence depend also on central atom characteristics of $^m\text{M}^q$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ and Cu), it allows to classify certain types of activation processes as consequences of mutual influence of ligands mediated by the central atom.

The integral influence of equatorial ligands on the central atom - axial ligand bonding was proved in the study of reactions of substituted tetraphenylporphyrinato Ni(II) complexes with piperidine [27]:



The greater the electron density on the central atom is (determined by the position and properties of substituent X on the phenyl ring), the smaller is the value of the equilibrium constant K. If, e.g., $p\text{-X} = \text{OCH}_3$ (a strong donor of electron density), then $\log K = -0.69 \pm 0.04$; for $p\text{-X} = \text{NO}_2$ (a strong acceptor), $\log K = 0.65 \pm 0.04$.

The influence of equatorial ligands on the kinetics of the axial ligand substitution was studied in several papers. For example [28], the rate constants of substitution of Cl^- for OH^- ligand in trans- $[\text{Ru}(\text{N}_4)\text{Cl}_2]^+$ complexes increase in series of (N_4) = 4NH_3 , 2 en, 3,7-diazone-1,9-diamine and 1,4,8,11-tetra-aza-cyclotetradecane (abbreviated as cyclam) as follows: $k = 0.0061, 0.6, 72$ and $110 \text{ M}^{-1}\text{s}^{-1}$, respectively.

The equ-ax effect approach may also be used to interpret results of photochemical reactions of complexes. A decrease of quantum yield values was observed when photosubstitution of Cl^- or I^- ligands for water molecules takes place on irradiation of trans- $[\text{Rh}(\text{N}_4)\text{X}_2]^+$ complexes within the series of (N_4) = 4NH_3 , 2en, cyclam [29-31]. An expressive influence of central atom properties on quantum yields and stereochemistry of complexes is manifested in such a way that analogous photosubstitution reactions of $[\text{M}(\text{N}_4)\text{X}_2]^+$ give cis-isomers for Cr(III), trans-isomers for Rh(III) while a mixture of cis- and trans-isomers for Co(III) complexes.

In studying the electrochemical redox properties, Co(II) and Cu(II) complexes with ethylene bis(thioacetylacetonate) dianion ligand and its derivatives, abbreviated as R-sacacen where $\text{R} = \text{CH}_3, \text{CF}_3, \text{C}_6\text{H}_5, p\text{-CH}_3\text{OC}_6\text{H}_4,$ and $p\text{-BrC}_6\text{H}_4$, have been chosen to be investigated [32-34]. The interaction of axial ligands in Cu(II) complexes has been found to be weak; the exchange of the axial ligands (triphenylphosphane and its derivatives, solvent molecules) effects the $E_{1/2}$ value of the complex oxidation only to a very slight extent. A significant influence on the electrochemical properties of Cu(II) complexes is exerted by a change of a ligand in equatorial plane (e.g. the exchange of CH_3 for CF_3 groups causes a shift of $E_{1/2}$ as much as 390 mV). A contrary situation has been observed for Co(II) complexes. Here, the redox

properties are expressively influenced by properties of axial ligands. For example, an exchange of a solvent causes the above shift by as much as 320 mV. The change of the properties of R-sacacen is manifested only weakly (e.g. the exchange of CH_3 for CF_3 in the equatorial ligand shifts $E_{1/2}$ value by 90 mV only). The above results were correlated with electronic structure of these complexes [35,36]. For Co(II) complexes, an unpaired electron is localized in the out-of-plane (d_{yz} - like orbital) and thus, it is strongly influenced especially by ligands in axial positions. The unpaired electron in Cu(II) complexes lies, however, in the in-plane (d_{xy} - like orbital) and it is screened from the surroundings by a π -system of the R-sacacen ligand. Therefore, it is predominantly influenced by changes in the equatorial plane of the complex (the x-y plane). Consequently, the electrochemical oxidation of Co(II) complexes is expected to be more influenced by properties of axial ligands. It is not the case of Cu(II) complexes where the influence of equatorial ligands prevails.

FRAGMENTAL AND INTEGRAL APPROACH WITHIN THE MIL CONCEPTION

Two approaches within the MIL conception can be distinguished: a fragmental approach (e.g. trans-influence, trans-effect, cis-influence, cis-effect) and an integral approach (equ-ax influence, equ-ax effect). Such a classification though corresponding to the present level of experimental and theoretical knowledge, does not claim to be exhaustive and definitive and it is open to further development. The integral approach to the study of the MIL appears to be more general and considering the present experimental and theoretical knowledge, also more justified. In many actual cases, however, the fragmental approach is relevant and expresses well the essential manifestation of the MIL. Thus, for example, the fragmental approach to the study of the MIL consequences for the kinetics of substitution reactions of Pt(II) complexes was fully justified and useful. Experimental data prove that the interactions of ligands in trans-positions appear to be prevailing in the kinetics of substitution reactions of these complexes. The later experiments show that cis-effect takes place also in Pt(II) complexes, but it has only a secondary significance when compared with the trans-effect. Recently it has been found that both the trans- and cis-influences are to be considered, side-by-side, also for Ni(II) complexes [37].

This work emphasizes the significance of the central atom effect for quantitative manifestations of equ-ax interactions. It has been shown that for complexes of various central atoms equ-ax interactions manifest themselves in different quantitative extent. It has been also found that even for complexes of the same central atom, e.g. Cu(II), equ-ax interactions can be observed in different behaviour of complexes.

Further experimental and theoretical activity can lead to a more complete and deeper understanding of the manifestations of the MIL. Such knowledge will allow to exploit either integral or fragmental ligand interaction rules for their purposeful use in the coordination chemistry.

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