

THE LIGAND MUTUAL INFLUENCE IN COORDINATION COMPOUNDS

K. B. YATSIMIRSKII

*The L. V. Pisarzhevsky Institute of Physical Chemistry, Ukrainian SSR
Academy of Sciences, Prospekt Nauki 97, Kiev-28, USSR*

ABSTRACT

Three possible types of ligand mutual influence (LMI)—*trans*-influence, *cis*-influence and nondirecting influence—are discussed. Numerous thermodynamic, kinetic, structural and spectral quantitative characteristics of the LMI are presented.

The model proposed based on the simple LCAO allows orbitals to be grouped according to their ability to transmit the different LMI and an assessment to be made of the factors which determine the magnitude of the LMI.

A comparison of changing parameters of the M—Hal (Cl^- or I^-) bonds in the nickel, palladium, platinum series has been made. The variations of the coordinated molecule under the action of other ligands are considered. These variations are revealed by changes in acid-base properties of ligands, in chemical shifts of their nuclei ^1H and ^{19}F , and also by changes in structural and spectral data of coordinated polyatomic species.

The ligand mutual influence (LMI) in coordination compounds represents one of the most important problems in modern coordination chemistry.

The LMI is generally utilized in the synthesis of new coordination compounds of a desired geometric structure. The LMI affects the whole complex of physicochemical characteristics of coordination compounds (and, in the first place, thermodynamic and kinetic) and their physical parameters (bond length, angles, vibration frequencies, spectra, etc.). The introduction of a given ligand into the coordination sphere changes the electron density distribution both in bonds and in each coordinated species.

Therefore, while considering changes caused by a given ligand in the coordination sphere, it is expedient to distinguish, at least, between the two important aspects, namely, the variation in metal-ligand bonds and the variation in the coordinated molecule itself. The second aspect of the LMI is of great significance in the treatment of many cardinal problems and, in particular, those of catalysis and biology.

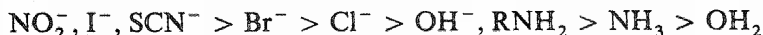
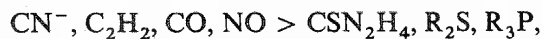
The LMI was formulated for Pt^{II} complexes by Chernyaev in 1926 in terms of the directing influence known as the *trans*-influence¹. Later on, this phenomenon was designated as the *trans*-influence rule.

The essence of this phenomenon is that ligands in the inner coordination

sphere affect each other providing their mutual *trans*-position. The *trans*-influence was revealed in all coordination compounds having ligands located at vertices of tetragon and, therefore, in *planar* or *octahedral* complexes. Various ligands have different *trans*-influences.

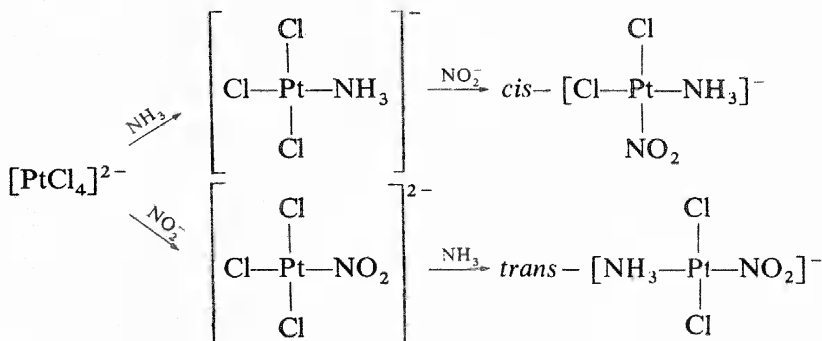
For this reason, Chernyaev proposed to arrange ligands in a definite order depending on the extent of weakening of their bond with the central atom of a ligand at the opposite end of the diagonal.

This order of decreasing *trans*-influence supplemented with recent data is given by Grinberg in his monograph²:



It holds for Pt^{II} complexes and is about the same in several authors' works³.

The *trans*-influence rule was, above all, widely used in the synthesis of coordination compounds with a given spatial position of ligands. For instance, chloroplatinite affected by nitrite or ammonia yields mono-substituted complexes, trichloronitroplatinite and trichloroaminoplatinite, respectively. Trichloronitroplatinite under the action of ammonia gives *trans*-dichloronitroamine-platinum (the *trans*-effect of the nitro group is greater than that of the chloro group) and trichloroaminoplatinite affected by chloride forms *cis*-dichloronitroamine-platinum (the *trans*-effect of chlorine is greater than that of ammonia):



Thus, the same substance affected by the same reagents but in different degrees yields substances with various spatial positions of species. These and some other facts indicate that the mutual influence of species, in the first place, affects, to a great extent, the kinetic properties of coordination compounds: under the action of thermodynamic factors alone the yield of final products must not depend on the order of reagent addition.

The above example also shows how the *trans*-influence can be employed in the synthesis of various geometric isomers of coordination compounds.

Using the *trans*-influence rule Chernyaev and Andrianova⁴ synthesized all five possible geometric isomers for a compound of the composition $[\text{Pt}(\text{en})\text{NH}_3\text{NO}_2\text{ClBr}]^+$. Gelman⁵ with co-workers synthesized three possible isomeric compounds of the general composition $[\text{PtNH}_3 \text{ pyClBr}]$ using the same *trans*-influence rule.

The utility of the *trans*-influence rule in the synthesis of coordination compounds is covered in a number of works and their review can be a topic of a special communication. The existence of the *trans*-influence and its display in numerous coordination compounds of platinum(II), platinum(IV), palladium, iridium, rhodium, cobalt were unambiguously proved.

Since the fifties a new stage has begun in the investigation of this significant phenomenon, namely, a search for quantitative characteristics of the *trans*-influence in coordination compounds.

First attempts of this kind were thermochemical measurements of cobalt(III) complexes^{6,7} made in our laboratory. The results obtained were used in the calculations of substitution reaction heats for various ligands in six-coordinated Co^{III} complexes which are in the *trans*-position towards different substituents. These substitution reactions may be designated as follows:

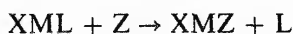


Table 1 presents data on reaction heats. These data, in the first place, point to great differences in the heats of substitution of ligand L on Z depending on the ligand, X, in the *trans*-position. Thus, it became possible to correlate the magnitude of the *trans*-effect with a value that could be measured—the substitution reaction enthalpy.

Table 1. The heats of substitution of NO₂⁻ in cobalt(III)^{6,7} compounds.

| Initial <i>trans</i> -coordinate | Substituting ligand | <i>Cis</i> -ligands | $\Delta H/\text{kcal mol}^{-1}$ |
|---|---------------------|--|---------------------------------|
| NO ₂ —Co ^{III} —NO ₂ | NH ₃ | 4 NH ₃ | 0.0 |
| NH ₃ —Co ^{III} —NO ₂ | NH ₃ | 3 NH ₃ , NO ₂ ⁻ | +0.8 |
| NH ₃ —Co ^{III} —NO ₂ | NH ₃ | 4 NH ₃ | +1.2 |
| Cl—Co ^{III} —NO ₂ | NH ₃ | 4 NH ₃ | +7.6 |
| NO ₂ —Co ^{III} —NO ₂ | H ₂ O | 4 NH ₃ | +7.5 |
| NO ₃ —Co ^{III} —NO ₂ | H ₂ O | 4 NH ₃ | +8.1 |
| NO ₂ —Co ^{III} —NO ₂ | Cl ⁻ | 4 NH ₃ | +3.8 |
| NH ₃ —Co ^{III} —NO ₂ | Cl ⁻ | 4 NH ₃ | +11.4 |
| Cl—Co ^{III} —NO ₂ | Cl ⁻ | 4 NH ₃ | +17.3 |

Table 1 also shows that ligands in the *cis*-position far less affect the heat value of the substitution reaction in a complex than those in the *trans*-position.

The *trans*-influence series for Co^{III} complexes (NO₂⁻ > NH₃ > Cl⁻) differs from that for Pt^{II} complexes.

However, it is in keeping with the theory and experimental results. The nature of the atom 'transmitting' the LMI must greatly affect this phenomenon itself. Chernyaev and co-workers⁸ found that for the same element

in various oxidation states (Pt^{II} and Pt^{IV}) the *trans*-influence series can be essentially different.

Finally, one can reveal that relative *susceptibility* of various ligands to the *trans*-influence markedly differs: the vibrational amplitude for heats of substitution reactions of the nitro group by ammonia and water is much less than that for the Cl^- ion.

Especially sensitive to the nature of the ligand in the inner coordination sphere proved to be kinetic characteristics of ligand substitution reactions. Such measurements for Pt^{II} complexes were carried out by many authors⁹⁻¹². Table 2 lists the results obtained.

Table 2. The rate of substitution⁹⁻¹² of Cl^- by L in complexes $[\text{X}-\text{Pt}(\text{Cl})-\text{Y}(\text{Z})]$ ($\log k + 5$)

| Trans-substituent | Cis-substituent | Entering ligands - L | | |
|-------------------|------------------------------|----------------------|---------------|------|
| | | OH^- | NH_3 | Py |
| NH_3 | 2NH_3 | 0.35 | 1.57 | |
| | NH_3, Cl^- | 0.70 | | |
| Cl^- | 2NH_3 | 1.00 | 2.46 | |
| | NH_3, Cl^- | 0.78 | 2.06 | 2.56 |
| | Py, Cl^- | | 2.24 | 2.76 |
| | 2Cl^- | 0.60 | 1.62 | 2.23 |
| Br^- | NH_3, Cl^- | | | 3.05 |
| NO_2 | NH_3, Cl^- | | | 3.60 |
| | $\text{NH}_3, \text{NO}_2^-$ | | | 3.57 |

Table 2 shows that the *trans*-influence can actually be characterized by kinetic parameters and, in particular, by the rate constant of the substitution reaction: for example, the rate of the substitution of the Cl^- ion in the inner sphere by other ligands (OH^- , NH_3 , pyridine) depends on the nature of a ligand in the *trans*-position and decreases in the order: $\text{NO}_2^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3$.

This order parallels that of the *trans*-influence series established earlier on the basis of data on the synthesis of Pt^{II} complexes. Kinetic characteristics of substitution in coordination compounds proved, however, so sensitive that Grinberg and Kukushkin¹¹ have managed to establish the *cis*-effect, i.e. the influence of the nature of ligand situated in the *cis*-position on the substitution reaction rate.

Table 2 shows that the variation of the nature of ligand in the *cis*-position towards a substituting ligand can lead to a change in the reaction rate

constant by about an order of magnitude; the order of the *trans*- and *cis*-influence series may significantly differ from each other.

Kinetic data¹⁰ for Pt^{IV} complexes (Table 3) appreciably differ from those for Pt^{II} not only quantitatively (the rate constant is about one order of magnitude less) but also qualitatively: the order of decreasing the *trans*-influence for Pt^{IV} complexes is $\text{Br}^- > \text{Cl}^- > \text{NO}_2^-$. The *cis*-influence in Pt^{IV} complexes is displayed to a lesser extent (Table 3).

One of the reasons for the differences in the order of *trans*-influence series lies in the fact that mechanisms of substitution in Pt^{II} and Pt^{IV} compounds are considerably different.

It is associative, S_N2 , for planar Pt^{II} complexes and dissociative, S_N1 , for octahedral Pt^{IV} complexes. In the first case, the possibility of *addition* of the fifth ligand to Pt^{II} complex is a decisive factor; in the second one, the possibility of the *dissociation* of a leaving ligand. Therefore, while changing the mechanism of substitution in a complex the *trans*-influence series must also be essentially changed.

Table 3. The rate of substitution¹⁰ of Cl^- by pyridine in Pt^{IV} complexes ($\lg k + 5$)

| <i>Trans</i> -substituent | <i>Cis</i> -substituent | $\lg k + 5$ |
|---------------------------|-------------------------------------|-------------|
| Br^- | 2 NH_3 , 2 NO_2^- | 1.88 |
| | 3 NH_3 , Cl^- | 1.72 |
| Cl^- | 2 NH_3 , 2 NO_2^- | 1.45 |
| | 3 NH_3 , Cl^- | 1.28 |
| NO_2^- | 2 NH_3 , 2 NO_2^- | 1.10 |
| | 3 NH_3 , Cl^- | 0.88 |

One cannot expect the parallelism in the *trans*-influence series obtained from kinetic and thermodynamic data, as the former characterize the activated state energetics, the latter, the bond energy in the ground states (initial and final). The nature of the transition activated complex can be different depending on the reaction mechanism. The activated complex composition can be close either to the initial substance composition or to the composition of reaction products, or be quite a new one. Extensive investigations of the kinetics of substitution reaction have been carried out for cobalt(III) complexes. On the basis of the data obtained one can do an extra analysis of the kinetic aspects of the LMI. Table 4 presents kinetic characteristics of the LMI for cobalt(III) complexes^{13, 14}. The *trans*-influence is quite evident in Co^{III} compounds: in passing from such a *trans*-substituent as OH^- to NCS^- in the above series the reaction rate is changed by several orders of magnitude.

The *trans*-influence series differs from that for Pt compounds, presumably, due to electrostatic factors (shorter distances, more ionic bond). A special

Table 4. The rate of substitution^{13, 14} of Cl⁻ by H₂O in complexes [Co(en)₂LCl] (*k* in s⁻¹)

| L: | OH ⁻ | NO ₂ ⁻ | N ₃ ⁻ | CN ⁻ | Br ⁻ | Cl ⁻ | H ₂ O | NH ₃ | NCS ⁻ |
|---|-----------------|------------------------------|-----------------------------|-----------------|-----------------|-----------------|------------------|-----------------|------------------|
| <i>trans</i> -[Co(en) ₂ LCl] | 160 | 98 | 22 | 8.2 | 4.5 | 35 | 0.25 | 0.034 | 0.005 |
| <i>cis</i> -[Co(en) ₂ LCl] | 1200 | 11 | 20 | | 14 | 24 | 0.16 | 0.05 | 1.1 |

position of NCS⁻ in the *trans*-influence series seems to be due to a pronounced π -acceptor character of this ligand.

The *trans*- and *cis*-influences displayed by the same ligands are about of the same order (except for NCS⁻, OH⁻ and NO₂⁻ ions). The increasing *cis*-influence of the hydroxyl ion appears to be concerned with the possibility of the formation of the hydrogen bond with a suitable water molecule. A greater value of the *cis*-effect of Cl⁻ compared with that of Br⁻ is evidently due to steric factors of the species mentioned (a greater volume of the Br⁻ ion).

The LMI is clearly seen from such an important characteristic as the kinetics of inner and outer sphere water exchange studied by n.m.r. technique¹⁶ (Table 5).

Table 5 shows that the introduction of such ligands as Cl⁻ and NH₃ almost equally accelerates the exchange of water molecules in both cobalt(II) and nickel(II) compounds.

The introduction of two ammonia molecules gives the same results as in the case of introducing one ethylenediamine molecule. On introducing a similar π -acceptor ligand, bipyridine, one obtains the opposite results: the rate of water molecule exchange increases and even exceeds the initial value (a free aquo ion).

The data quoted, being far from complete, show how sensitive kinetic parameters of coordination compounds are to the introduction of various ligands into the inner sphere. Kinetic characteristics of coordination compound conversions reveal the detailed LMI.

The LMI in kinetics proves, however, to be a characteristic depending on specific features of the coordination compound reaction mechanism itself. The theories proposed to account for kinetic effects of the *trans*-influence were based on strictly defined mechanisms of substitution reactions¹⁷.

Table 5. The kinetics of H₂O exchange for nickel and cobalt complexes¹⁶

| Composition | 10 ⁵ <i>k</i> for Ni ²⁺ /s ⁻¹ | 10 ⁷ <i>k</i> for Co ²⁺ /s ⁻¹ |
|--|--|--|
| M(H ₂ O) ₆ ²⁺ | 0.3 | 0.2 |
| M(H ₂ O) ₅ Cl ⁺ | 1.4 | 1.7 |
| M(H ₂ O) ₅ NH ₃ ²⁺ | 2.5 | 1.6 |
| M(H ₂ O) ₄ (NH ₃) ₂ ²⁺ | 6.1 | 6.5 |
| M(H ₂ O) ₄ en ²⁺ | 4.4 | |
| M(H ₂ O) ₂ en ₂ ²⁺ | 5.4 | |
| M(H ₂ O) ₄ bipy ²⁺ | 0.4 | |

The LMI also affects the geometry of bonds. The ligands which are in the *trans*-position towards a given ligand and weakening its bond with the central atom, as a rule, cause lengthening of the bond distance between a given ligand and the metal. The existing variation of the bond length was designated as 'trans-lengthening' and observed for the first time in Pt^{II} compounds^{18, 19}. It is true that the Pt—Cl or Pt—Br bond distance, in the case when NH₃, a *trans*-substituent, was replaced by ethylene, increases only by 4 to 5% (Table 6).

Table 6. The Pt—Hal bond distances¹⁷ in $\begin{array}{c} \text{Y} \\ | \\ \text{X—Pt—Hal} \\ | \\ \text{Z} \end{array}$

| Bond | <i>Trans</i> -substituent | <i>Cis</i> -substituent | Bond length/Å |
|-------|-------------------------------|---|---------------|
| Pt—Cl | NH ₃ | 2 Cl ⁻ | 2.32 |
| | Cl ⁻ | Cl ⁻ , NH ₃ | 2.35 |
| | Cl ⁻ | Cl ⁻ , C ₂ H ₄ | 2.32 |
| | C ₂ H ₄ | 2 Cl ⁻ | 2.42 |
| Pt—Br | NH ₃ | 2 Br ⁻ | 2.42 |
| | Br ⁻ | Br ⁻ , C ₂ H ₄ | 2.42 |
| | C ₂ H ₄ | 2 Br ⁻ | 2.50 |
| | H | 2 PR ₃ | 2.56 |

The *trans*-effect in octahedral compounds involving Os≡N and Mo=O bonds is shown in the works by Atovmyan with co-workers²⁰ and in some other publications given in a detailed review²¹.

The central atom is always more distant from a ligand in the *trans*-position towards these groups than from ligands in the *cis*-positions (the difference is up to 10%)(Table 7). *Cis*-effects are also observed on the M—OH₂ bond; however, they, as a rule, are much weaker, and so far no regularities can be derived.

Table 7. Bond lengths^{19, 20} in octahedral complexes of the type *trans*-[MZ₂X₄]

| MZ | M—Z | Bond length/Å | |
|-------------------|------|-------------------------|-------------------------|
| | | <i>trans</i> -(M—X) | <i>cis</i> -(M—L) |
| OsN ³⁺ | 1.73 | 2.50 (Cl ⁻) | 2.36 (Cl ⁻) |
| | 1.74 | 2.50 (H ₂ O) | 2.35 (Cl ⁻) |
| | 1.67 | 2.42 (H ₂ O) | 2.48 (Br ⁻) |
| MoO ⁴⁺ | 1.66 | 2.03 (F ⁻) | 1.86 (F ⁻) |
| | 1.67 | 2.63 (Cl ⁻) | 2.40 (Cl ⁻) |
| | 1.72 | 2.27 (H ₂ O) | 2.38 (Cl ⁻) |
| | 1.78 | 2.39 (H ₂ O) | 2.51 (Br ⁻) |
| | 1.86 | 2.83 (Br ⁻) | 2.55 (Br ⁻) |

Finally, it was clearly shown by Chatt, Duncanson and Shaw²² that the vibration frequency of the Pt—H bond affected by a substituent, X, in the *trans*-position towards this hydrogen atom in $[\text{HPt}^{\text{II}}\text{XL}_2]$ complexes is markedly changed (Table 8). The order of changes in the vibration frequencies of the Pt—H bond series does roughly parallel that of the *trans*-influence series established by Chernyaev. The *cis*-effect is also observed in the vibration frequencies; when PEt_3 is replaced by AsEt_3 (both ligands are in the *cis*-position towards the Pt—H bond) the vibration frequencies are decreased.

Table 8. Vibration frequencies²² of the Pt—H bond in complexes $[\text{X}-\text{Pt}-\text{H}]$

| L \ X | $\begin{array}{c} \text{L} \\ \\ \text{X}-\text{Pt}-\text{H} \\ \\ \text{L} \end{array}$ | | | | | | | |
|-----------------|--|---------------|---------------|--------------|-----------------|----------------|---------------|------------------|
| | NO_3^- | Cl^- | Br^- | I^- | NO_2^- | SCN^- | CN^- | |
| PEt_3 | 2242 | 2183 | 2178 | 2156 | 2150 | 2112 | 2041 | cm^{-1} |
| AsEt_3 | | 2174 | 2167 | 2139 | | 2108 | | cm^{-1} |

The distinct LMI was displayed in the vibration frequencies of Pt—Cl bonds opposite to the corresponding ligands²³⁻²⁵ (Table 9). In this case π -acceptor ligands strengthen the Pt—Cl bond (increasing vibration frequencies) while σ -donor ligands weaken it.

Table 9. Vibration frequencies²³ of the Pt—Cl bond in complexes *cis*- $[\text{PtX}_2\text{L}_2]$

| X: | Phen | Bipy | 2 Py | Et_2S | NH_3 | Ph_3P | En | Et_3P | |
|---------|------|------|------|-----------------------|---------------|-----------------------|-----|-----------------------|------------------|
| ν_1 | 355 | 351 | 343 | 330 | 324 | 316 | 311 | 305 | cm^{-1} |
| ν_2 | 339 | 338 | 329 | 318 | 317 | 294 | 290 | 283 | cm^{-1} |

Somewhat unexpected in our opinion is the position of ammonia and ethylenediamine molecules in the above series.

Numerous data presented support the existence of the LMI and the possibility of obtaining its quantitative characteristic by means of such fundamental bond parameters as bond length, bond energy and vibration frequency which, in their turn, determine thermodynamic and kinetic properties of substitution reaction of one ligand by another.

While considering the mutual influence in a coordination compound the X—M—L fragment is usually isolated, in which M is a metal, and X and L are ligands mutually influencing each other. The most pronounced

effect of mutual influence is observed when all three species are located on one line (*trans*-influence); it is much less in the case when the angle in the X—M—L fragment is 90° (*cis*-influence). The LMI can, however, be found at any other angle values in the X—M—L fragment (non-directing influence).

The formation of common three-centre molecular orbitals of the type:

$$\psi = C_1\varphi_X + C_2\varphi_M + C_3\varphi_L \quad (1)$$

(where φ_M , φ_X and φ_L are overlapping atomic orbitals of the metal and X and L ligands, respectively, and C_1 , C_2 and C_3 are coefficients) mostly accounts for the LMI.

A three-centre model²⁶ was proposed by the author in 1968 and then was further developed²⁷. It is a set of some molecular orbitals for the XML fragment and, hence, the mutual influence is 'transmitted' along a multi-orbital (multi-channel) system.

An attempt to distinguish between the σ - and π -influences was earlier made by Langford and Gray³. A more detailed division of orbitals 'transmitting' mutual influence is presented in this report. In addition, our scheme covers all types of the LMI (*trans*-, *cis*- and non-directing).

A three-centre model is successfully being developed in works by Shustorovich and other authors²⁸.

The energy of each three-centre orbital may be evaluated as a first approximation using the Hückel determinant:

$$\begin{vmatrix} \alpha_X - E & \beta_{MX} & 0 \\ \beta_{MX} & \alpha_M - E & \beta_{ML} \\ 0 & \beta_{ML} & \alpha_L - E \end{vmatrix} = 0 \quad (2)$$

which, in its turn, may be expressed as the sum of the energy bond determinant M—L and a second term

$$\begin{vmatrix} \alpha_M - E & \beta_{ML} \\ \beta_{ML} & \alpha_L - E \end{vmatrix} - \beta_{MX}^2 \frac{\alpha_L - E}{\alpha_X - E} = 0 \quad (3)$$

where α_M , α_X and α_L are Coulomb integrals, β_{ML} and β_{MX} are resonance integrals, E is the energy of molecular orbitals.

If one assumes that the M—X bond is more ionic than the M—L bond (i.e. $\alpha_X < \alpha_L$)*, the orbital mainly located on the L ligand will have an intermediate value in energy:

$$E_2 \approx \alpha_L - \Delta \quad (4)$$

The value of Δ , bonding energy, is calculated from a first determinant† in the left part of equation (3) and proves to be about²⁹:

$$\Delta = \frac{\alpha_M^2 \cdot S_{ML}^2}{\alpha_M - \alpha_L} \quad (5)$$

where S_{ML} is the integral of orbital overlapping on the M—L bond.

* All coulomb and resonance integrals are negative values.

† Equation 5 approximately holds, if a determinant in equation (3) equals zero.

In the absence of influence of the ligand, X, on the M—L bond, a second term in equation (3) must be equal to zero; hence, its value (deviation from zero) approximately characterizes the effect of the ligand X influence on the M—L bond and shows by what factors this influence is determined. Taking account of equation (4), we obtain for a second term of equation (3):

$$\chi \approx \beta_{MX}^2 \cdot \frac{\Delta}{\alpha_L - \alpha_X} \quad (6)$$

$$(\Delta \ll \alpha_L - \alpha_X)$$

Equation (6) shows the importance of various factors which determine the LMI magnitude. Above all, the LMI should markedly be observed only in the presence of the covalent M—L bond (in the case when the M—L bond is ionic, $\Delta = 0$).

The influence of the ligand, X, on the M—L bond is also determined by the covalence of the M—X bond characterized by the resonance integral β_{MX} and the proximity of α_X and α_L levels (decreasing this difference, i.e. denominator, in equation (6) increases the value of X).

We have made analogous conclusions earlier using the same model somewhat differently^{26, 27}. If atomic orbital φ_X is higher in energy than φ_M and φ_L orbitals, it turns out to be the most antibonding (vacant, as a rule). In this case, the energy of the whole complex ($E_1 + E_2$) decreases and the ligand, X, displays stabilizing action on the M—L bond. For instance, A is the dative interaction between the central ion and ligand.

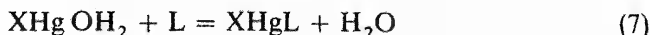
The model proposed can be applied to all types of mutual influence and it can be tested with the most different complexes.

For illustration, let us consider the simplest complexes of the MXL type for mercury(II) (Table 10³⁰).

Table 10. Log k for the reaction³⁰ $\text{XHg}^{II} + \text{L}^- = \text{XHgL} + \text{H}_2\text{O}$

| X \ L | Cl ⁻ | Br ⁻ | I ⁻ | CN ⁻ |
|---|-----------------|-----------------|----------------|-----------------|
| H ₂ O | 6.8 | 9.1 | 12.9 | 18.0 |
| Cl ⁻ | 6.6 | 9.5 | 12.5 | 17.8 |
| Br ⁻ | 7.2 | 8.2 | 12.1 | 16.9 |
| I ⁻ | 6.4 | 8.3 | 11.9 | 15.9 |
| CN ⁻ | 6.6 | 8.0 | 10.8 | (16.7)? |
| $\Delta \log k_{\text{CN-H}_2\text{O}}$ | 0.2 | 1.1 | 2.1 | ~2 |

One may think that the order of increasing bond covalence of ligands is H₂O, Cl⁻, Br⁻, I⁻, SCN⁻, CN⁻. The change in free energy in the reaction:



increases in the same sequence.

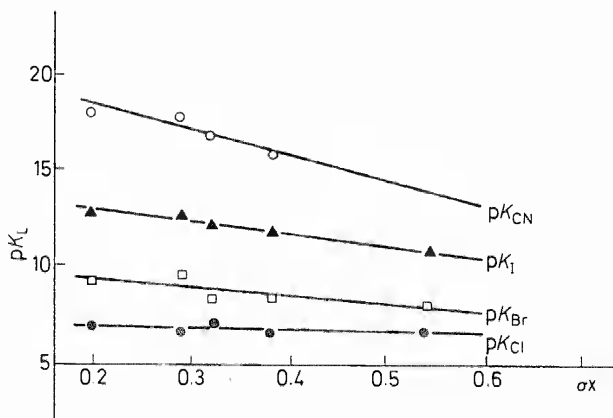


Figure 1. Plots of pK_L against Hammett's σ -constants.

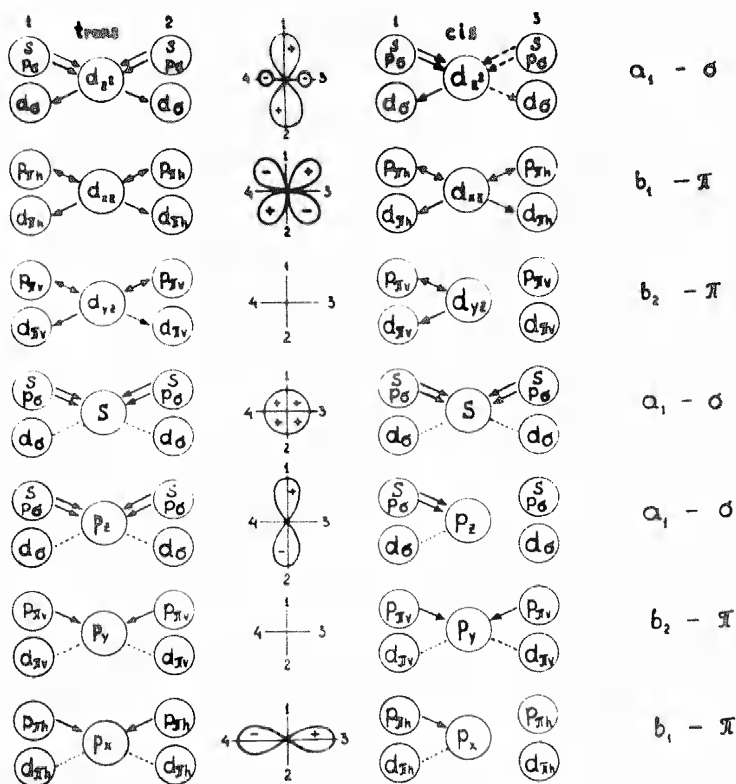


Figure 2. The interaction of various orbitals of ligands located in the XOZ plane in terms of a set of topological graphs.

On introduction of different ligands X, the bond Hg—L weakens in the same order.

As one should expect, the most sensitive to changes in the nature of ligand X proved to be covalently linked I^- and CN^- ligands, and practically insensitive to the $Hg^{II}-Cl$ bond.

In analogous cadmium compounds the same qualitative relationships are observed, but all effects are far weaker due to a greater bond ionicity compared with mercury compounds³¹.

The pK_L constants obtained satisfactorily correlate with Hammett's σ -constants observing linear relationship.

$$pK_L = \text{const} - \rho\sigma_X \quad (8)$$

The coefficient ρ increases with increasing bond covalence (Figure 1).

The above approaches may be useful in analysis, selection and systematization of data on stability of mixed complexes.

Let us come back to a multi-orbital mode of the LMI transmitting in the XML fragment. Table 11 presents the scheme of the interaction of various orbitals of ligands located in the XOZ plane. All ligands are either in the *trans*-position to each other (on the Z axis), or in the *cis*-position (on the Z and X axes).

Table 11. The common molecular orbital formation by the atoms situated in the plane XOZ at the vertices of the tetragon; numerators and denominators are *trans*- and *cis*- ligands, respectively

| Metal orbital | Ligand orbital | | | | | | | |
|---------------|----------------|------------|-------------|-------------|------------|-------------|-------------|-------|
| | s | p_σ | $p_{\pi h}$ | $p_{\pi v}$ | d_σ | $d_{\pi h}$ | $d_{\pi v}$ | |
| d_{z^2} | 1/1 | 1/1 | 0/0 | 0/0 | 1/1 | 0/0 | 0/0 | 3/3* |
| d_{xz} | 0/0 | 0/0 | 1/1 | 0/0 | 0/0 | 1/1 | 0/0 | 2/2 |
| d_{yz} | 0/0 | 0/0 | 0/0 | 1/0 | 0/0 | 0/0 | 1/0 | 2/0 |
| s | 1/1 | 1/1 | 0/0 | 0/0 | 1/1 | 0/0 | 0/0 | 3/3 |
| p_z | 1/0 | 1/0 | 0/0 | 0/0 | 1/0 | 0/0 | 0/0 | 3/0 |
| p_x | 0/0 | 0/0 | 1/0 | 0/0 | 0/0 | 1/0 | 0/0 | 2/0 |
| p_y | 0/0 | 0/0 | 0/0 | 1/1 | 0/0 | 0/0 | 1/1 | 2/2 |
| | 3/2 | 3/2 | 2/1 | 2/1 | 3/2 | 2/1 | 2/1 | 17/10 |

* Overlapping is less at the *cis*-position than that at the *trans*-position.

The relations given in Table 11 may be also expressed with the help of a set of topological graphs (Figure 2). At the graph apices, ligand and central atom orbitals are placed; graph edges connect interacting (overlapping) orbitals. Arrows indicate possible directions of shifting in electron density.

Figure 2 also presents the symmetry of the central atom orbitals in the point group C_{2v} (a_1, b_1, b_2) and the type of orbital interaction (σ or π).

Seven orbitals of the central atom participate in 'transmitting' of mutual influence.

The $d_{x^2-y^2}$ and d_{xy} orbitals do not take part in the interaction of this type as they cannot form common orbitals with *cis*-ligands.

When ligands are in the *trans*-position the formation of the δ -bonds does not contribute much to the coordination compound energy. The d_{z^2} orbital ($d\sigma$) forms common orbitals both with *trans*- and *cis*-ligands; however, its overlapping with a *cis*-ligand is somewhat weaker.

The two d_π orbitals (d_{xz} and d_{yz}) behave differently: d_{xz} interacts with ligands in the *trans*- and *cis*-positions, while d_{yz} interacts only with orbitals of the ligand in the *trans*-position and does not interact with orbitals of the ligand located in the *cis*-position towards a given ligand. This orbital is responsible for the *trans*-directing influence.

The s orbital interacts with all orbitals of ligands of the σ -type located towards each other at any angles. The non-directing influence is displayed via this orbital.

The p_z orbital forms common orbitals solely with ligands which are in the *trans*-position towards each other (the σ *trans*-influence).

The p_π metal orbitals are also different in mutual influence 'transmitting', as *trans*-influence is transmitted via both orbitals (p_x and p_y), the *cis*-influence via the p_y orbital alone.

Thus, the *trans*-influence is displayed through the formation of a greater number of orbitals compared with the *cis*-influence. In transmitting of the *trans*-influence seventeen orbitals can partake and in transmitting of the *cis*-influence only ten. Table 12 presents the classification of the mutual influence.

Table 12. The types of ligand mutual influence

| Types of influence | Metal AO transmitting a given type of influence |
|-----------------------------|---|
| (1) Non-directing | s |
| (2) σ - <i>cis</i> | d_{z^2}, s |
| (3) π - <i>cis</i> | d_{xz}, p_y |
| (4) σ - <i>trans</i> | d_{z^2}, s, p_z |
| (5) π - <i>trans</i> | d_{xz}, d_{yz}, p_x, p_y |

The simple scheme of the σ or π mutual influence, however, does not cover all possible cases of orbital interactions. Actually, the p_z orbital does not participate in the formation of orbitals common with the *cis*-ligands according to the σ -type.

Yet, the p_z orbital can interact with $p_{\pi h}$ orbitals of the *cis*-ligands according to the π -type whereby parameters of the p_z orbital change. The same applies

Table 13. Overlap integrals³²⁻³⁴ for the M—Cl bonds and orbital ionization potentials (OIP) (M=Ni, Pd, Pt)*

| OIP/eV | | 24.55 | 12.98 | 1.87 | | |
|-------------|-----------------------|-------|-----------------|-----------------|-----------------|-----------------|
| and orbital | | 3s | 3p _z | 3p _x | 3d _σ | 3d _π |
| Ni 13.93 | nd _σ | 0.046 | 0.070 | | 0.021 | |
| Pd 13.32 | | 0.106 | 0.136 | | 0.049 | |
| | | 0.166 | 0.186 | | 0.082 | |
| Pt 10.61 | nd _π | | | 0.022 | | 0.097 |
| | | | | 0.049 | | 0.178 |
| | | | | 0.079 | | 0.247 |
| Ni 8.67 | (n + 1)s | 0.277 | 0.165 | | | |
| Pd 8.33 | | 0.268 | 0.124 | | V | |
| Pt 9.8 | | 0.272 | 0.115 | | | |
| Ni 3.97 | (n + 1)p _σ | 0.443 | 0.231 | | | |
| Pd 3.88 | | 0.412 | 0.171 | | V | |
| | | 0.423 | 0.150 | | | |
| Pt 5.35 | (n + 1)p _π | | | 0.132 | | |
| | | | | 0.122 | | V |
| | | | | 0.125 | | |

* Upper, middle and lower values are given for Ni—Cl, Pd—Cl and Pt—Cl bonds, respectively. V are virtual orbitals.

to the p_x orbital which forms a common π orbital only with the *trans*-ligands, but is still able to interact with the *cis*-ligands according to the σ type. Thus, except for the 'pure' σ and π interaction, there exist cases of the original combined $\sigma\pi$ interaction without formation of any common orbital though with indirect display of the mutual *cis*-influence.

The proposed model allows us to pass over to the elucidation of necessary conditions for the *trans*-influence to be displayed: the σ *trans*-influence is displayed only in the presence of the low located p_z orbital.

The π *trans*-influence requires either availability of low-located p orbitals of a metal atom or that of vacant π type orbitals on ligands (p_π or d_π).

So far the *trans*-influence was observed solely in square and octahedral complexes; one can assume that influence of the same type would be observed in other complexes involving linear ligand disposition, as well (polar ligands in all types of bipyramids, linear complexes with two ligands, etc.).

The angle magnitude in the XML fragment is rather significant for the LMI: it is maximum, if the angle is 180° (*trans*-influence) and minimum, if the angle is 90° (*cis*-influence). With intermediate values of the XML angle, the LMI should have intermediate values.

To assess the role of different factors which determine the LMI, Tables 13 and 14 present ionization orbital potentials and overlap integrals characterizing the M—Hal bonds of nickel, palladium and platinum and, also, of chlorine and iodine. The ionization orbital potentials are taken from the literature^{32, 33}. The overlap integrals were obtained using Slater exponents from tables³⁴.

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 Table 14. Overlap integrals³²⁻³⁴ for the M—I bond and OIP (M = Ni, Pd, Pt*)

| OIP/eV and orbital | 20.61 | | 10.45 | | 2.25 | |
|---------------------------------|-----------------------|-----------------|-----------------|-----------------|-----------------|--|
| | 5s | 5p _σ | 5p _π | 5d _σ | 5d _π | |
| Ni 13.93 Pd 13.32 Pt 10.6 | nd _σ | 0.033 | 0.053 | | 0.021 | |
| | | 0.087 | 0.126 | | 0.060 | |
| | | 0.133 | 0.171 | | 0.089 | |
| Ni 8.67 Pd 8.33 Pt 9.8 | (n + 1)s | 0.273 | 0.234 | | V | |
| | | 0.295 | 0.204 | | V | |
| | | 0.272 | 0.177 | | V | |
| Ni 3.97 Pd 3.88 | (n + 1)p _σ | 0.395 | 0.321 | | V | |
| | | 0.439 | 0.285 | | V | |
| | | 0.465 | 0.245 | | V | |
| Pt 5.35 | (n + 1)p _π | | | 0.136 | V | |
| | | | | 0.147 | V | |
| | | | | 0.156 | V | |

* Upper, middle and lower values are given for Ni—Cl, Pd—Cl and Pt—Cl bonds, respectively. V are virtual orbitals.

Almost in all cases the overlap integrals for the M—Hal bonds are increased in the order Ni < Pt < Pd, except for weakly bonding orbitals. Besides, in these cases, the overlap integrals for the M—Hal bonds differ little from each other.

If one takes into account that the *d* and *s* levels of palladium are located not much higher than those of nickel, the conclusion about bond covalence increasing in the order Ni—Hal, Pd—Hal, Pt—Hal proves evident. Especially pronounced increase in covalence growth must be observed in passing over to platinum halogenides due to a drastic decrease in energy on *s* and *p* orbitals.

Dative interaction increases in the series nickel, palladium and platinum halogenides.

An appreciable contribution of σ -dative interaction into the orbital involving d_z^2 metal orbitals, i.e. the transfer of a portion of electron density from the *d* metal orbitals to the *d* halogen orbital according to the σ type attracts attention.

Comparing chloride and iodide compounds, one can see that bond covalence increasing going from the M—Cl bond to the M—I bond is mainly due to higher energy levels of the corresponding *ns* and *np* orbitals of iodine compared with those of chlorine and to decreasing level of *nd* iodine orbitals. The overlap integrals for orbitals corresponding to the M—Cl and M—I bonds differ little from each other. However, the overlap integrals on the orbitals responsible for transmitting *trans*-influence ($6p_\sigma$ and $6p_\pi$)

Table 15. Overlap integrals³²⁻³⁴ for Pt—Cl and Pt—I bonds and OIP*

| OIP/eV and orbital | 24.55; 20.61 | 12.98; | 10.45 | 1.87; | 2.25 |
|-----------------------|------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | <i>ns</i> | <i>np_σ</i> | <i>np_π</i> | <i>nd_σ</i> | <i>nd_π</i> |
| 10.6 | 5 <i>d_σ</i> | 0.166 | 0.186 | | 0.082 |
| | | 0.133 | 0.171 | | 0.089 |
| | 5 <i>d_π</i> | | | 0.079 | 0.247 |
| | | | | 0.068 | 0.197 |
| 9.8 | 6 <i>s</i> | 0.272 | 0.115 | | V |
| | | 0.306 | 0.177 | | |
| 5.35 | 6 <i>p_σ</i> | 0.423 | 0.150 | | V |
| | | 0.465 | 0.245 | | |
| | | | | 0.125 | |
| | 6 <i>p_π</i> | | | 0.156 | V |

* Upper values are given values of *s* for Pt—Cl bonds, lower for Pt—I bonds, V are virtual orbitals.

on the Pt—I bonds are appreciably greater than those on the Pt—Cl bonds (Table 15).

In many works to interpret the LMI in coordination compounds scientists widely use concepts of ligand influence on the effective charge of the central atom. Such an approach is, to a certain extent, suitable to explain the non-directing mutual influence of ligands but it fails to elucidate directing effects.

The concept of common orbital formation accounts for directing effects not only by variation of charges but also by variation of population of metal—ligand bonds in common orbitals: the greater the population of the

Table 16. The acid dissociation constants of NH₃ and H₂O situated in the inner spheres of platinum coordination compounds³⁵⁻³⁷

| Pt ^{II} complexes | | | | Pt ^{IV} complexes | | | |
|----------------------------|-------------------------------|------------------------------------|------|----------------------------|---------------------------|------------------------------------|------|
| Dissociating ligand | <i>Trans</i> -substituent | <i>Cis</i> -substituent | pK | Dissociating ligand | <i>Trans</i> -substituent | <i>Cis</i> -substituent | pK |
| NH ₃ | DMSO | 2 NH ₃ | 9.06 | NH ₃ | Cl ⁻ | Cl ⁻ , 3NH ₃ | 9.37 |
| NH ₃ | C ₂ H ₄ | 2 NH ₃ | 8.56 | NH ₃ | Cl ⁻ | 4NH ₃ | 8.10 |
| H ₂ O | NH ₃ | H ₃ , H ₂ O | 5.52 | NH ₃ | Br ⁻ | 4NH ₃ | 8.25 |
| H ₂ O | Py | Py, H ₂ O | 4.50 | H ₂ O | I ⁻ | 4NH ₃ | 5.76 |
| H ₂ O | Et _m | Et _m , H ₂ O | 3.68 | H ₂ O | Br ⁻ | 4NH ₃ | 3.60 |
| H ₂ O | H ₂ O | 2NH ₃ | 4.45 | H ₂ O | OH ⁻ | 4NH ₃ | 3.07 |
| H ₂ O | H ₂ O | 2Py | 3.82 | H ₂ O | NO ₂ | 4NH ₃ | 2.97 |
| H ₂ O | H ₂ O | 2 Et _m | 2.85 | | | | |

corresponding bonds, the greater the directing effects, and, conversely, the lesser the population, the lesser the strength of the directing effects.

So far we have considered the influence of one ligand on the bond of another one with the metal. Now let us discuss changes that occur in the coordinated species under the action of other atoms located in the same inner sphere.

The most measurable characteristic is acid properties of a coordinated species, i.e. the variation of its ability to dissociate involving proton splitting under the action of other ligands. The effect was studied by Grinberg and co-workers in detail.

All coordinated molecules interacting with the central atom form common molecular orbitals with it at the expense of non-bonding orbitals (lone pairs) or vacant (antibonding) orbitals available to the overlapping with the central atom orbitals.

The latter case is usually attributed to the dative interaction which as shown in *Tables 12* and *13* may be both of the σ and π types. During the interaction of this kind the energy of corresponding orbitals and electron density distribution inside the species are changed. Other coordinated ligands change orbitals of the central atom and, naturally, those common with it, either of a coordinated molecule or ion. In coordination, different electrostatic factors and, in particular, the coulomb interaction with charges on the central atom and ligands may play an important role.

Table 16 lists some data on acid dissociation of the simplest molecules, NH_3 and H_2O coordinated in Pt^{II} and Pt^{IV} complexes^{2, 35-37}. Analogous investigations were carried out for cobalt(III)³⁸ and rhodium(III) complexes³⁹ (*Table 17*).

Table 17. The acid dissociation constants of OH_2 situated in the inner sphere of complexes $\text{Co}(\text{DH})_2, \text{XH}_2\text{O}$ ³⁸

| <i>Trans</i> -substituent | OH^- | NO_2^- | Br^- | Cl^- |
|---------------------------|---------------|-----------------|---------------|---------------|
| pK | 8.07 | 7.66 | 6.44 | 6.30 |

It is seen from tables that there exists a definite conformity between series obtained from data on acid dissociation of the ligand RH located in the *trans*-position towards the ligand, X, in the X—M—R fragment. For Pt^{IV} , the series is: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3 > \text{OH}^- > \text{NO}_2^-$; for Co^{III} : $\text{OH}^- > \text{NO}_2^- > \text{Br}^- > \text{Cl}^-$.

As with kinetic data, the *trans*-influence series for Pt^{IV} and Co^{III} do not parallel, which can be due to various reasons. The d_{xz} and d_{yz} orbitals in platinum(IV) are situated at the lowest energy levels which are not able to interact with the nitro group by the π -dative mechanism. In cobalt(III) compounds, as shown above, the marked role is played by electrostatic factors.

The similarity of the *trans*-influence series for Co^{III} and Rh^{III} compounds calls attention.

In the cases studied for Pt^{II}, the *trans*-influence changes in the same direction.

Analogous information on ligand influence on protons one may obtain from n.m.r. data. Watt and Cuddebaeu⁴⁰ studied chemical shifts of protons in ethylenediamine coordinated by Pt^{II} (Table 18).

Table 18. Chemical shifts of ethylenediamine protons in complexes [Pt(en)L₂]⁴⁰

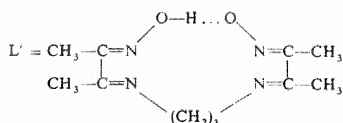
| L: | 2Ph ₃ P | Ph ₃ P I ⁻ | En | 2 SCN ⁻ | 2 NO ₂ ⁻ | 2 Br ⁻ | Bipy | Phen |
|----|--------------------|-------------------------------------|------|--------------------|--------------------------------|-------------------|------|------|
| δ: | 2.64 | 2.81 | 2.94 | 2.99 | 3.23 | 3.45 | 4.27 | 4.48 |

The series obtained is basically consistent with the series mentioned above, except for the position of ethylenediamine which is somewhat unusual. The variations in chemical shifts F¹⁹ make it possible to judge the magnitude of ligand *trans*-influence on the particles, *m*-C₆H₄F and *p*-C₆H₄F added to Pt^{II} and Co^{III} atoms^{41, 49} (Table 19).

Table 19. Chemical shifts of F¹⁹ in complexes [X PtLC₆H₄F] and [X Co^{III}L' C₆H₄F]^{41, 42*}

| X | Pt ^{II} complexes | | Co ^{III} complexes | | Difference | |
|--------------------------------|---|---|---|---|---------------------|---------------------|
| | <i>m</i> -C ₆ H ₄ F | <i>p</i> -C ₆ H ₄ F | <i>m</i> -C ₆ H ₄ F | <i>p</i> -C ₆ H ₄ F | Δ <i>m</i> Pt—Co | Δ <i>p</i> Pt—Co |
| CH ₃ | 3.93 | 11.70 | 3.05 | 11.3 | 0.88 | 0.40 |
| FC ₆ H ₄ | 3.07 | 10.80 | 2.05 | 10.6 | 1.02 | 0.20 |
| NCO | 2.30 | 10.10 | 0.98 | 9.72 | 1.32 | 0.38 |
| Cl | 2.11 | 10.10 | | | | |
| Br | 1.97 | 9.86 | 0.68 | 9.73 | 1.29 | 0.13 |
| I | 1.56 | 9.54 | 0.50 | 9.73 | 1.06 | -0.19 |
| SCN | 1.75 | 9.29 | 0.52 | 9.29 | 1.23 | 0.00 |
| CN | 2.27 | 9.32 | | | | |
| SnCl ₃ | -0.23 | 9.27 | | | | |

* L = PEt₃



The series obtained for Co^{III} and Pt^{II} are about the same; however, some discrepancies are observed for the methyl group (the 'pure' σ bond) and also for I⁻, SCN⁻ and OCN⁻ (the possibility of dative bond formation).

Appreciable changes in bond characteristics for the molecules coordinated in the form of three-centre fragments $M \begin{array}{c} \diagup X \\ | \\ \diagdown X \end{array}$ are observed during the introduction of any ligands. In three iridium complexes with the same coordination number 6*, the O—O bond distance in a coordinated oxygen molecule is either 1.30 Å, 1.51 Å, or 1.63 Å depending on the atoms occupying the other four places. In all cases there are two phosphine phosphorus atoms, but in the two first cases two vacant places occupied by CO and Cl⁻ and CO and I⁻, respectively, and, in the third case, all four places are occupied by phosphorus from phosphine (Table 20).

Table 20. The O—O distances in the coordinated O₂ molecule in chromophore Ir^{III}L₂XYO₂ (L are phosphorus atoms (phosphinic) situated on the bipyramid vertices)⁴³

| X | Y | R _{O—O} /Å |
|----|-----------------|---------------------|
| CO | Cl ⁻ | 1.30 |
| CO | I ⁻ | 1.51 |
| P | P | 1.65 |

The replacement of Cl⁻ by I⁻ leads not only to a greater distance in the O₂ molecule, but also to reversible addition of the O₂ molecule in the first case and irreversible in the second.

Marked changes are observed in the vibration frequencies of the ethylene molecule coordinated by Pt^{II} depending on the atom located in the *trans*-position towards it⁴⁴ (Table 21). Here one should bear in mind that in the case

Table 21. Vibration frequencies of C₂H₄ in compounds of the *trans*-type [Pt Y₂X C₂H₄]⁴⁴

| <i>Trans</i> -substituent | <i>Cis</i> -substituent | ν/cm^{-1} | $\Delta\nu/\text{cm}^{-1}$ |
|---------------------------|-------------------------|----------------------|----------------------------|
| O | O | 1621 | 0 |
| Cl ⁻ | 2 Cl ⁻ | 1526 | 97 |
| NH ₃ | 2 Cl ⁻ | 1521 | 102 |
| NH ₃ | 2 Br ⁻ | 1517 | 106 |
| Br ⁻ | 2 Br ⁻ | 1511 | 112 |

of the *trans*-orientation the vacant $d_{x^2-y^2}$, s and p orbitals interact with the π orbital of ethylene and ligands, while the d_{xz} orbital interacts with the free π^* orbital of ethylene. With *cis*-disposition, p_x and d_{xz} orbitals cannot form mutual molecular orbitals. Therefore, the *cis*-influence of Br and Cl is displayed, though to a much smaller degree.

* O₂ is considered as a bidentate ligand.

As one can see the chemist has at his disposal at least three different ways of influence on a coordinated molecule: (1) a choice of the coordination centre (metal atom in a given oxidation state); (2) the choice of ligands for the formation of a mixed complex; (3) the choice of their spatial arrangement.

The approaches discussed here are applicable to solving other three-centre problems in coordination chemistry and, in particular, the mutual influence of two cations divided by ligands. For instance, the CoCl_4^{2-} spectrum in melt changes depending on the nature of the outer sphere cation^{4,5}, the Dq parameter decreasing in the order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$.

To judge by the symmetry, one may assume that the interaction of e -orbital Co^{2+} with the vacant ns orbital of the alkali metal ion occurs through the chlorine ions involving energy decreasing of the e -orbital.

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