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Mutual Influence of Ligands in Complexes

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The review deals with the theoretical concepts and experimental data on the mutual influence of ligands in complexes. Studies published after 1952 are covered.
The bibliography includes 166 references.

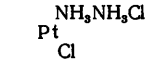
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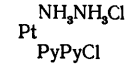
I. INTRODUCTION

The problems of the mutual influences of atoms was raised by Chernyaev in relation to inorganic chemistry. In 1925 he formulated the *trans*-influence rule [1], which, after Werner's coordination theory had been devised, became the most important generalisation in the chemistry of complexes. In recent years certain non-Soviet scientists have tended to attribute the discovery of the trans-*influence* to Werner. This tendency began with the review of Quagliano and Schubert [2], who, referring to Werner's paper [3], claimed that Werner introduced the concept of the elimination of groups in the *trans*-position.

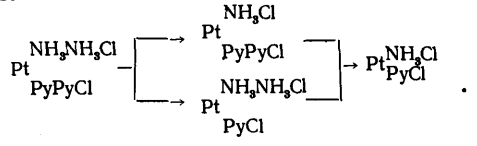
This situation apparently arose because Jørgensen, who supported Blomstrand's views on the structure of complexes, assumed that Peyrone's chloride has the structure



When it reacts with pyridine, the product is a mixed tetrabase complex to which the following structure was attributed



Its cleavage by hydrochloric acid proceeds via the following stages:



Werner laid the foundations of coordination theory [3]. In his communication he explained the isomerism of dichlorodibaseplatinum(II) complexes from the standpoint of the hypothesis, which he put forward for the first time, that platinum(II) complexes have a planar structure. He developed his planar structure hypothesis on the basis of

Jørgensen's experimental data [4]. He introduced the concept of the planar configuration of platinum(II) complexes and concluded that, when $[Pt(NH_3)_4]^{2+}$ reacts with hydrochloric acid, the complex $[Pt(NH_3)_2Cl_2]$ with the *trans*-configuration is obtained. However, the *trans*-cleavage rule (Jørgensen's rule) can in no way be regarded as the *trans*-influence rule. Chernyaev's *trans*-influence rule includes not only Jørgensen's rule but also Peyrone's and Kurnakov's rules. Thus there are no grounds for attributing to Werner the discovery of the *trans*-influence rule.

In March 1952 a conference was held on the *trans*-influence rule [5], where 25 years of the study and refinement of Chernyaev generalisation were assessed. This review presents the main achievements in this field during the last two decades.

In 1952 the *trans*-influence rule was based on complexes of bivalent and quadrivalent platinum and partly bivalent palladium [6,7]. Lebedinskii's preparative studies demonstrated *trans*-influence in compounds of tervalent rhodium and iridium (Ref. 5, p. 95). On the other hand, Ablov merely posed the question of *trans*-influence in tervalent cobalt complexes and Volshtein did the same in relation to tervalent chromium complexes. In summarising the conference proceedings, Chernyaev expressed his confidence that the *trans*-influence rule would be extended to many other elements in Mendeleev's Periodic System.

One may say that at present the vast majority of studies on *trans*-influence are carried out with platinum compounds. However, investigations of *trans*-influence in cobalt complexes have developed on a large scale and this problem is dealt with in a special review [8] published in 1969. Many studies have been made on *trans*-influence in rhodium(III) complexes and others on tervalent gold and ruthenium have been published. Isolated investigations have been made on *trans*-influence in gallium, tin, chromium, rhenium, and iron compounds.

A characteristic feature of the studies after 1952 is the change from a qualitative approach to quantitative investigation of the phenomenon. The first attempt at a quantitative characterisation of *trans*-influence was made by Gel'man and Karandasheva [9]. The development of these investigations enabled Zvyagintsev and Karandasheva to devise a quantitative *trans*-influence scale for individual ligands [10,11]. Kinetic studies on substitution reactions involving platinum(II) complexes enabled Grinberg and Kukushkin to discover in 1957 the *cis*-influence of ligands in complexes [12].

II. THEORY OF *TRANS*- AND *CIS*-INFLUENCE

The theories of *trans*-influence have been described in detail in a number of books and reviews [13-17]. Therefore they need not be considered in detail and only those which constituted important stages in the development of the *trans*-influence rule need be enumerated.

The Grinberg–Nekrasov polarisation theory [18,19] must be regarded as the first theory of this kind. Grinberg's interpretation of *trans*-influence on the basis of the oxidation-reduction interaction of the ligand with the central atom [20] extended the applicability of the polarisation theory. This theory has a considerable predictive power and is still used to account for the σ-*trans*-influence of ligands.

The next stage was Syrkin's explanation of *trans*-influence [21] on the assumption of ds-hybridisation in complexes. In recent years these views have again attracted the attention of theoreticians in relation to the phenomenon of "rehybridisation" of the hybrid dsp^2 orbitals of the central atom [22-24].

An important stage in the development of the theory of *trans*-influence was the high trans-influence of unsaturated ligands such as ethylene and carbon monoxide established by Gel'man [25]. The polarisation theory proved incapable of accounting for these facts. However, they served as the foundation for the development of the theory which was proposed almost simultaneously by Chatt and coworkers [26,27] and by Orgel [28]. The Chatt–Orgel theory refers to ligands with pronounced π-acceptor properties, such as ethylene, phosphines, or carbon monoxide. Owing to the π-acceptor properties of these ligands, the formation of metal–ligand double bonds becomes possible. A σ-bond is formed via the donor–acceptor mechanism and a π-bond is formed as a result of the overlapping of the filled d orbital of platinum having appropriate symmetry with the vacant orbital of the π acceptor (Fig. 1).

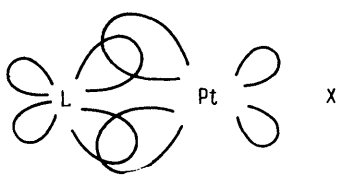


Figure 1. Schematic illustration of the formation of a metal–ligand π-bond.

In this case the ligand L can be phosphine or a sulphur-containing species. This scheme (Fig. 1) explains the enhanced rate of substitution of the ligand X. When a π-bond is formed, the attack on the Pt–X bond is facilitated and the transition state, which is an intermediate having a trigonal bipyramidal configuration, is stabilised (Fig. 2).

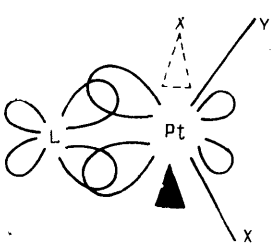


Figure 2. Schematic illustration of the stabilisation by the ligand of the intermediate with a trigonal bipyramidal configuration.

Bersuker pointed out a very significant feature of the Chatt–Orgel theory, namely he stressed the inter-relation between the σ-donor and π-acceptor properties of ligands [29]. In the donor–acceptor interaction the ligand gives up its σ electrons to the central atom and thereby reduces the

energies of its own π orbitals. As a result it becomes a stronger π-acceptor. It is thus found that the more marked the σ-donor properties the greater the possibilities of the reverse charge transfer from the central atom to the π orbitals of this ligand (Fig. 3).

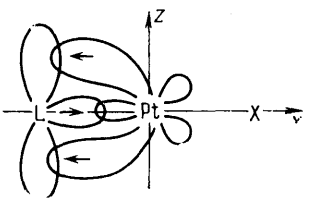


Figure 3. Schematic illustration of the σ- and π-type interactions of the orbitals of the ligand and the central atom.

Baranovskii and Sizova, who refined Bersuker's views, note[30] that the enhancement of the electron-donating capacity of the ligand in the *trans*-position with respect to L stimulates the transfer of electron density to the π^* orbital of the ligand L and at the same time hinders the shift of electrons from L to the central atom via the σ-bond. Thus, in considering the relative contributions of the donor–acceptor and dative components of the metal–ligand bond, one must also take into account the electron-donating properties of the ligand in the *trans*-position with respect to L.

On the basis of σ- and π-electronic effects, Langford and Gray[31] suggested that *trans*-influence be subdivided into σ- and π-trans-influences. Accordingly two series of ligand were obtained:

Ligand series based on the σ-effect

$$\underset{0.5169}{H^-} > \underset{0.3770}{PR_3} > \underset{0.360}{DMSO} \sim \underset{0.3574}{SCN^-} > \underset{0.3494}{CH_3^-, CO, CN^-} > \underset{0.3357}{Br^-} > \underset{0.3332}{Cl^-} > \underset{0.3139}{NH_3} > \underset{0.2877}{OH^-} > \underset{0.189}{C_2H_4}$$

Ligand series based on the π-effect

$$\underset{0.136}{DMSO} > \underset{0.096\ 0.124}{C_2H_4} > \underset{0.093}{CO} > \underset{0.088}{CN^-} > \underset{0.066}{NO_2^-} > \underset{0.052}{SCN^-}$$

The relative positions of the ligands in these series were established on the basis of the corresponding overlap integrals. The ligands in the σ-*trans*-influence series were arranged in sequence on the basis of the overlap integrals between the $6p$ orbital of platinum and the corresponding $p\sigma$ valence orbital of the ligand $[\int(6p\sigma/np\sigma)]$. The relative positions of the ligands in the π-*trans*-influence series were estimated from the overlap integrals between the $5d\pi$ orbital of platinum and the free π^* molecular orbital of the ligand. Mathematical radical functions for platinum were taken from Basch and Gray[32] and those for the ligand atoms from Clementi[33].

It has been shown[34–37] that the *trans*-influence of dimethyl sulphoxide (DMSO) in platinum(II) complexes is very close to that of ethylene. The properties of the complex ion $[Pt(DMSO)Cl_3]^-$ resemble those of the ion $[Pt(C_2H_4)Cl_3]^-$.[35,38] Baranovskii et al. calculated the corresponding overlap integrals and established the positions of DMSO and ethylene in the ligand σ- and π-*trans*-influence series[39]. The molecular orbitals of DMSO and ethylene were calculated by the LCAO-MO SCF method in terms of the CNDO approximation[40,41].

These values are indicated in the corresponding series. The overlap integral $\int(5d\pi/\pi^*C_2H_4)$ is close to the value obtained by Langford and Gray[31]. The difference between them can be explained by the different choice of the radial component of the p-function of carbon and the fact that Langford and Gray estimated the bond lengths on the basis of covalent radii, while Baranovskii et al.[39] used neutron diffraction data for the complex $K[Pt(C_2H_4)Cl_3].H_2O$.[42]

The calculations of the overlap integrals led to the conclusion that DMSO has a much greater σ-*trans*-influence than ethylene. It was concluded on the basis of the overlap integrals $\int(5d_\pi^{Pt}/\pi^*)$ for DMSO and ethylene that their π-*trans*-influences are similar and it is difficult to determine unambiguously their relative positions in the *trans*-influence series.

Bersuker's scheme[29,43] explains the *cis*-influence of ligands which was observed for platinum(II) compounds. Indeed, the shift of σ-electrons from the ligand L to the central atom should depend on the σ-donor properties of the ligands in the *cis*-position with respect to the given ligand (Fig. 3), If the σ-donor properties of the *cis*-neighbours are pronounced, the result should be a smaller shift of σ electrons from L to the central atom and this in turn should lead to a decrease of the π-acceptor interaction of the ligand with the central atom and hence to a decrease of the *trans*-influence of L. This mechanism of *cis*-influence explains satisfactorily the experimental observation that the *cis*- and *trans*-influence series are opposed. The view that the ligand which labilises the substituent on the opposite side stabilises the adjacent substituent and conversely was put forward in an earlier investigation[12]. Indeed, ammonia and pyridine have small *trans*-influences compared with chlorine, but they exhibit a marked *cis*-influence[44,45]. The studies of Grinberg and Kuz'mina on the exchange of chlorine in the complex ion $[Pt(C_2H_4)Cl_3]^-$ occupy a special place among these investigations. They showed that ethylene, which has a large *trans*-influence, fixes the *cis*-disposition of the chlorine atoms in the complex[46,47]. The opposed *trans*- and *cis*-influence series of the ligands C_2H_4, Cl^-, NH_3, and Py follows clearly from data for the rates of chlorine isotope exchange compared in Table 1.

Table 1. Rate constants for the exchange of chlorine in platinum(II) complexes.

Complex ion	Cl–Pt–Cl	L–Pt–Cl	Refs.	Complex ion	Cl–Pt–Cl	L–Pt–Cl	Refs.
$Cl\ Cl^{2-}$ Pt $Cl\ Cl$	$1.04\cdot10^{-5}$	$1.04\cdot10^{-5}$	44	$C_2H_4\ Cl^-$ Pt $Cl\ Cl$	$4.92\cdot10^{-6}$	Very rapid	46
$NH_3\ Cl^-$ Pt $Cl\ Cl$	$2.91\cdot10^{-5}$	$4.16\cdot10^{-6}$	45	$DMSO\ Cl^-$ Pt $Cl\ Cl$	$4.96\cdot10^{-4}$	Very rapid	33
$Py\ Cl^-$ Pt $Cl\ Cl$	$3.82\cdot10^{-5}$	$2.87\cdot10^{-6}$	45	$DMSO\ Cl^-$ Pt $Cl\ Cl$	$1.55\cdot10^{-4}$	Very rapid	48

Together with Kuz'mina and other coworkers, the author investigated the *cis*-influence of dialkyl sulphoxides on the rate of exchange of chlorine[35,48,49]. These studies

established that the chloride ion located in the opposite position relative to a dialkyl sulphoxide exchanges almost instantaneously, i.e. at the "zero exchange" rate. This behaviour of complex ions of the type $[Pt(R_2SO)Cl_3]^-$ in relation to the exchange of the chloride ion in the *trans*-position is analogous to the behaviour of $[Pt(C_2H_4)Cl_3]^-$.[46] This is also evidence for the closeness of the *trans*-influences of DMSO and ethylene.

The rate of exchange of the *cis*-chloride ions in the complexes $[Pt(R_2SO)Cl_3]^-$ proved to be unexpectedly high. Despite their large *trans*-influence, dialkyl sulphoxides do not fix the chloride ions in the *cis*-positions, but actually labilise them. The chloride ions on the Cl–Pt–Cl axis in the diethyl sulphoxide complex are extremely mobile, but are nevertheless approximately three times less mobile than in the dimethyl sulphoxide compound. This is probably related to the increase of the size of the alkyl groups, which should lead to the "screening" of the chloride ions.

It follows from the calculation on the electronic structure of the DMSO molecule by the LCAO-MO SCF method in terms of the CNDO approximation[49] that the oxygen $p\pi$ orbitals have a marked electron-donating capacity. The *cis*-influence of DMSO in complex ions of the type $[Pt(DMSO)Cl_3]^-$ can be accounted for by the interaction of the p_y orbitals of oxygen and the central atom, which labilises the bond between platinum and the chlorine in the *cis*-position (Fig. 4).

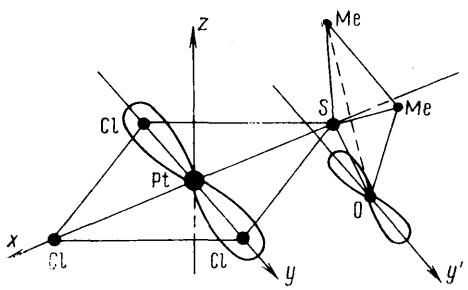


Figure 4. Schematic illustration of the interaction of the p_y orbitals of the central atom and the oxygen atom of the coordinated sulphoxide.

The majority of theories have been devised to account for the kinetic aspect of *trans*-influence. However, numerous data have now accumulated, which permits the consideration of *trans*-influence in the ground and not the transition state of the complex. Thus techniques such as X-ray diffraction, vibrational spectroscopy, NMR, etc. permit the detection of the *trans*-influence in the static state of the complex. A clear tendency to distinguish the trans-influences in the static and dynamic states has arisen in the world literature. To distinguish them, the first is referred to as the *trans*-influence and the second as the *trans*-effect. In addition one should add that two cases are also investigated in the dynamic state: on the one hand the rate of reaction and on the other the position of the reaction equilibrium. Thus in the dynamic state two aspects of the *trans*-effect are considered: the kinetic and thermodynamic aspects.

The investigation of Zumdahl and Drago[24] occupies a special place among studies on the theory of *trans*-influence. Using Hoffmann's modification of the extended Hückel methods, these workers calculated the electronic structures of a number of complexes of the type *trans*-$[PtL(NH_3)Cl_2]$. The complexes are arranged in Table 2 in order of increasing *trans*-influence of the ligand L which had been determined earlier. Some of the ligands in this series are hypothetical, for example, H_2S or PH_3. The hydrocarbon groups in these ligands have been replaced by the hydrogen atom to simplify the calculations and economise computer time. The authors[24] assume that all the ligands considered behave as σ-donors only; their π-acceptor properties are neglected.

Table 2. Overlap populations for the complexes *trans*-$[PtL(NH_3)Cl_2]$.

L	Pt–L bond length, Å	Overlap populations						
		Pt–N	Pt–Cl	Pt–L	$Pt(6p_y)$–L	$Pt(6p_y)$–N	Pt(6s)–N	$Pt(5d_{x^2-y^2})$–N
H_2O	2.00	0.3370	0.3909	0.2406	0.1114	0.1235	0.1205	0.1275
NH_3	2.00	0.3221	0.3832	0.3221	0.1313	0.1313	0.1139	0.1145
Cl^-	2.33	0.3240	0.3843	0.3322	0.1759	0.1212	0.1181	0.1225
H_2S	2.30	0.3244	0.3745	0.4235	0.2070	0.1320	0.1158	0.1154
CH_3^-	2.15	0.3009	0.3724	0.4637	0.1945	0.1431	0.1036	0.0349
PH_3	2.25	0.3032	0.3569	0.5585	0.2435	0.1490	0.1054	0.0366
H^-	1.06	0.3074	0.3641	0.6069	0.2603	0.1415	0.1046	0.1009

One of the first tasks formulated by the authors[24] was to determine the relative bond strengths. They obtained this information by analysing the Mulliken orbital populations. Analysis of the populations yields two criteria for measuring the relative bond strengths in molecules: (1) overlap populations; 2) overlap energies. We may recall that the overlap population is a measure of electron density in the region between two atomic orbitals. It follows from a consideration of the populations (Table 2) that the more marked the *trans*-influence of the ligand L the weaker the opposite Pt–N bond. This is consistent with the *trans*-influence for σ-ligands. It is interesting that the decrease of the population of the Pt–N bond is not due to the decrease of the involvement of the platinum 6*s* and $5d_{x^2-y^2}$ orbitals. Calculation shows that the involvement of this orbital in the platinum–nitrogen bond also increases when the *trans*-influence of the ligands is enhanced. On the other hand, the decrease of the population of the platinum–nitrogen bond is due to the reduced involvement of the platinum 6*s* and $5d_{x^2-y^2}$ orbitals. A similar conclusion concerning the decrease of the involvement of the 6*s* and $5d_{x^2-y^2}$ orbitals with enhancement of the *trans*-influence of the opposite substituent was reached[22] on the basis of the ^{195}Pt–^{31}P interaction constant. We may appropriately recall that the important role of the 6*s* and $5d_{x^2-y^2}$ orbitals in the transmission of *trans*-influence was first pointed out by Syrkin[21].

Another interesting conclusion is that the Pt–Cl bonds in the *cis*-position are also weakened with enhancement of the *trans*-influence of L. Both conclusions refer to molecules in the static state.

Table 2 shows that, on passing from a ligand with a weak *trans*-influence (H_2O) to one with a strong *trans*-influence (H^-), the bond is weakened only to the extent of 10%. This finding suggests that the weakening of the bond is not the fundamental cause of *trans*-influence in the kinetics of substitution reactions at least for σ-linked ligands. Therefore, like Langford and Gray[31], Zumdahl and Drago[24] conclude that the reasons for the difference between the rates of substitution over a wide range is different degrees of stabilisation of the transition state.

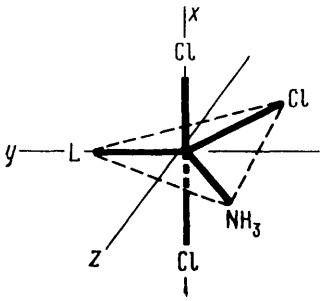


Figure 5. The directions of the Cartesian coordinate axes in the trigonal bipyramidal intermediate.

Zumdahl and Drago explained the *trans*-influence of σ-linked ligands in the following way. In the ground state the ligand L and the leaving group (NH_3) share the same platinum orbital ($6p_y$). We shall assume that Cl^- enters into the complex and that the intermediate has the trigonal bipyramidal structure illustrated in Fig. 5. In this structure the entering and leaving groups (Cl^- and NH_3) lie on either side of the Pt($6p_y$) orbital and employ both p_y and p_z orbitals for the formation of bonds. Thus L occupies more than half of the $6p_y$ orbital. This implies that, when L is a powerful σ-donor and can effectively occupy part of the vacant p_y orbital, the transition complex will be stabilised. Thus the difference between the energies of the ground and transition states will be relatively small for ligands which can effectively interact with the p_y orbital. Powerful σ-donors should behave as ligands of this kind. The calculated Pt($6p_y$)–L overlap populations (Table 2) show that there is an almost exact agreement between the capacity of the ligand to interact with the $6p_y$ orbital of platinum and its position in the experimental *trans*-influence series. The calculated overlap populations are listed in Table 3, which shows that, on passing from H_2O to H^-, the Pt–L bond is indeed strengthened, while the other bonds are weakened. The most interesting result are presented in Table 4, which includes the differences between the overlap populations of the individual bonds and orbitals in a tetracoordinate planar complex and a pentacoordinate bipyramidal complex. The difference shows that, on passing from H_2O to H^-, all the bonds are weakened to approximately the same extent. The Pt–Cl bond within the plane is missing in the ground state. Therefore, Table 4 in fact gives for it not the difference but the actual overlap population in this transition state. It is seen from Table 4 that, when L = H^-, the weakening of the Pt–L bond is much smaller than for L = H_2O. The difference refers almost completely to the Pt(6s)–L and Pt($d_{x^2-y^2}$)–L interactions. The sums of these reductions in strength are almost the same in the two cases.

Zumdahl and Drago[24] also calculated the difference between the activation energies for the transition from planar to pyramidal complexes for L = H^- and L = H_2O:

$$E_a = E_{H^-} - E_{H_2O} \ .$$

They found that the difference between the activation energies should be about 8 kcal mole^{-1}. Thus, for a ligand with a high *trans*-influence such as H^-, about 8 kcal mole^{-1} less is needed to pass from the planar to the trigonal bipyramidal configuration than for a ligand with a weak *trans*-influence (H_2O).

Table 3. Overlap populations in trigonal bipyramidal complexes.

Complex	Pt($6p_y$)–L	Pt–L
$PtH_2O(NH_3)Cl_3^-$	0.1602	0.1895
$PtH(NH_3)Cl_3^{2-}$	0.3356	0.5868
Pt–Cl (on *x* axis)	Pt–Cl (in the plane)	Pt–N
0.3441	0.3117	0.2920
0.3198	0.2859	0.2674

Table 4. Differences between overlap populations.

L	Pt($6p_y$)–L	Pt(6s)–L	Pt($5d_{x^2-y^2}$)–L
H_2O	0.0488	−0.0071	−0.0447
H^-	0.0753	−0.0142	−0.0382
Pt–L	Pt–Cl (on *x* axis)	Pt–Cl (in the plane)	Pt–N
−0,0511	−0.0468	0.3117	−0.0450
−0,0213	−0.0443	0.2859	−0.0400

Yatsimirskii recently examined the possible types of ligand interactions in complexes[50]. The analysis of the σ-type and π-type interactions of metal and ligand orbitals for the molecular fragment LMX in the *xy* plane is interesting. Tables 5 and 6 list the squares of the coefficients of the linear combinations of the corresponding atomic orbitals.

Table 5 shows that, for the *trans*-disposition of the ligands L and X, there is almost 100% orbital overlapping. On the other hand, for the *cis*-disposition, the orbital overlap is only to the extent of 50%. The same situation obtains also when π-bonds are formed.

Thus, when the dissociation of M–X bonds is considered, it follows from Tables 5 and 6 that the ligands with pronounced σ- and π-donor properties should have a labilising effect directed mainly to the *trans*-partner. With reference to the work of Zumdahl and Drago[24], one may mention that, for unequal overlap populations of the atomic orbitals, this conclusion is no longer so evident.

For ligands with electron-accepting properties, the M–X bonds should be strengthened. The ligand in the *trans*-position has greater influence than the ligand in the *cis*-position. The conclusions which follow from Chatt's Orgel's and Bersuker's ideas remain valid for the associative mechanism.

Table 5. Characteristics of the σ-type interaction of the metal orbitals with the orbitals of ligands in the *xy* plane.

Metal orbitals	*trans*-L	X	*cis*-L
$d_{x^2-y^2}$	1/4	1/4	1/4
S	1/6	1/6	1/6
P_x	1/2	1/2	0
P_y	0	0	1/2
d_{z^2}	1/12	1/12	1/12
P_z	0	0	0
Common orbitals with X	100%	—	50%

Table 6. Characteristics of the π-type interaction of the metal orbitals with the orbitals of ligands in the *xy* plane.

Metal orbitals	*trans*-L	X	*cis*-L
d_{xy}	1/4	1/4	1/4
d_{xz}	1/4	1/4	0
d_{yz}	0	0	1/4
Common orbitals with X	100%	—	50%

An important result of Yatsimirskii's study [50] is the conclusion that the *trans*- and *cis*-influence series may be reversed, depending on the reaction mechanism (dissociative or associative).

Yatsimirskii's remark [50] that, apart from the formation of common orbitals, Coulombic interactions between the ligands and the central atom are important is also significant. Naturally the Coulombic interaction is more marked the more effective the charges on the central atom in the ligand. This interaction leads to non-directional effects. The decrease of the effective charge on the central atom of the complex should facilitate dissociation and weaken association and conversely.

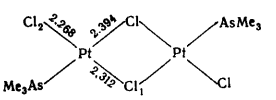
III. CRYSTAL-CHEMICAL MANIFESTATION OF *TRANS*-INFLUENCE

The number of studies undertaken to establish a relation between the *trans*-influence of individual ligands and the corresponding bond lengths increased considerably in recent years. The earlier investigations in this field were carried out exclusively on platinum complexes. The studies carried out up to 1962 have been analysed in Kukina's review [51]. Later studies are described in other reviews [52,53]. Bokii and Kukin's study [54] is one of the first where it was shown convincingly that interatomic distances depend on the nature of the ligand in the *trans*-position. In the complex $K[Pt(C_2H_4)Br_3].H_2O$ the bromine atom in the *trans*-position relative to ethylene is approximately 0.1 Å further away from the platinum atom than the bromine atom located opposite another bromine atom. A difference between the Pt–Br distances was observed also in the salt *cis*-$[Pt(C_2H_4)(NH_3)Br_2]$. Here too the platinum–bromine bond length on the C_2H_4–Pt–Br axis is greater by approximately 0.1 Å than that on the NH_3–Pt–Br axis [55,56].

A change in interatomic distances probably occurs only for a large difference between the *trans*-influences of the inner-sphere ligands. Thus the Pt–Cl interatomic distances in the complex $K[Pt(NH_3)Cl_3]$ cannot be inferred. The differences are within the limits of experimental error [57,58]. It has been shown [59] that the Pt–Cl and Pt–N bond lengths in *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ are almost the same.

The Pt–Cl and Pt–Br bond lengths in complexes usually vary within fairly narrow limits. It has been found that in the hydride compounds *trans*-$[Pt(PEt_3)_2BrH]$ [60] and *trans*-$[Pt(PPh_2Et)_2ClH]$ [61] the above bond lengths are unusually large. The authors explained this by the strong *trans*-influence of the ligand H^-. An increase in the lengths of the Pt–X bonds located opposite trialkylphosphine has been observed in the trialkylphosphine complexes *trans*- and *cis*-$[Pt(PR_3)_2X_2]$ where X is a halide ion. The Pt–Cl bond length in the *trans*-isomer is 2.30 Å, while in the *cis*-isomer it increases to 2.37 Å. [62,63] From this it follows that the phosphine groups have a fairly marked *trans*-influence.

The interatomic distances and valence angles in the bridged compound $Pt_2Cl_4[As(CH_3)_3]_2$ have been determined [64,65]. It has been established that the Pt–Cl distance in the *trans*-position relative to arsenic is greater than the normal distance approximately by 0.1 Å.



These data are regarded as evidence for a marked *trans*-influence of trimethylarsine. A similar situation is observed in the dimeric tripropylphosphine complex *trans*-$PtCl_4(PPr_3)_2$. [66] We may mention that the Pt–Br distances involving the bridge and terminal bromine in $[N(C_2H_5)_4]_2[Pt_2Br_6]$ differ by 0.04 Å. [67] The difference is of the same order of magnitude as that between the Pt–Cl_1 and Pt–Cl_2 distances in $Pt_2Cl_4[AsMe_3]_2$.

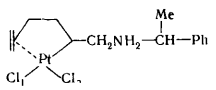
The Pt–Cl bond lengths in certain platinum(II) complexes have been compiled in the review of McWeeny et al. [68] It is interesting to quote this Table in a somewhat extended form (Table 7).

It is clear from Table 7 that the atoms can be arranged in the following sequence in terms of the *trans*-influence in platinum(II) complexes:

$$Si > C \sim H^- > P > C = C,\ Cl > O\ .$$

The much greater *trans*-influence of the σ-linked carbon atom compared with that of the olefinic π-bond merits attention. Apart from the data in Table 7, this is also indicated by the results of other investigations [72,73]. Bombieri et al. [73] studied the cyclic platinum complex [PtLPyCl], where L is methoxycyclo-octa-1,5-diene. This ligand undergoes ring closure via the σ-linked carbon atom on one side and the olefinic π-bond on the other. It was established that the Pt–N bond located opposite the Pt–C bond is unusually long (2.02 Å). This can be regarded as evidence in support of the strong *trans*-influence of the carbon atom.

It has been shown [74] that the Pt–Cl_1 bond located opposite the σ-linked carbon atom in the complex



is longer by 0.09 Å than the Pt–Cl_2 bond in the *trans*-position relative to the olefinic π-bond. A similar situation has been observed in dimeric μ-acetate complexes of palladium [75]. The Pd–O bonds located opposite the σ-linked carbon atom are longer than the Pd–O bonds located opposite the olefinic π-bond. The difference between the *trans*-influences of the olefinic π-bond and the σ-linked carbon atom has also been discussed in other reports [76,77]. Two studies in recent years established a marked *trans*-influence of the hydrocarbon groups in rhodium complexes. Thus the length of the rhodium–nitrogen bonds located opposite the ethyl group in the complex ion $[Rh(C_2H_5)(NH_3)_5]^{2+}$ is 2.256 Å, while the length of the remaining rhodium–nitrogen bonds are 2.072 Å. [78]

Very accurate measurements have shown [82] that the Ru–Cl bond in the *trans*-position relative to the water molecule in the complex $Cs[RuCl_5(H_2O)]$ is shorter than the other bonds. Presumably this is a consequence of the weak *trans*-influence of the water molecule.

Table 8. Bond lengths in compounds of the type ML_3Cl_3.

Bond	Re^{III}	Os^{III}	Ir^{III}
M–Cl (*trans* w.r.t. Cl)	2.353 (6)	2.347 (6)	2.361 (6)
M–Cl (*trans*-w.r.t. P)	2.454 (6)	2.439 (6)	2.429 (6)
M–P (*trans* w.r.t.Cl)	2.401 (6)	2.350 (6)	2.277 (6)
M–P (*trans* w.r.t.P)	2.458 (6)	2.408 (6)	2.363 (6)

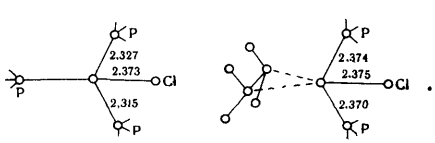
Table 7. Pt–Cl distances in the certain platinum(II) complexes.

Complex	*trans*-Ligand	Bond length, Å	Refs.
$[Pt(acac^*)_3Cl]^-$	O	2.28±0.01	69
trans- $[Pt(PEt_3)_2Cl_2]$	Cl	2.30±0.01	62
$[(C_{12}H_{17})_2Pt_2Cl_3]$	C=C	2.31±0.01	70
cis- $[Pt(PEt_3)_2Cl_2]$	P	2.37±0.01	63
trans- $[Pt(PMe_2Ph)_2Cl(CH_2SiMe)]$	C	2.415±0.005	71
trans- $[Pt(PPh_2Et)_2ClH]$	H	2.42±0.01	61
trans- $[Pt(PPhMe_2)_2(SiPh_2Me)Cl]$	Si	2.45±0.01	68

*acac = acetylacetonate ion.

A study of the structure of $\{RhPy_2Cl_2[P(o\text{-}C_6H_4CH_3)_2.(o\text{-}C_6H_4ClH_2)]\}$ showed that the Rh–Cl bond length is 2.399 Å on the Py–Rh–Cl axis and 2.531 Å on the C–Rh–Cl axis [79]. Thus, like the ethyl group, the benzyl group has a powerful *trans*-influence.

X-Ray diffraction studies on $[Rh(PPh_3)_3Cl]$ and $[Rh(PPh_3)_2(CF_2{=}CF_2)Cl]$ showed that, when triphenylphosphine is replaced by tetrafluoroethylene, there is no significant change in the Rh–Cl bond in the *trans*-position but the Rh–P bond in the *cis*-position relative to tetrafluoroethylene increases appreciably [80].



It has been shown [81] that in the octahedral complexes ML_3Cl_3 of the meridian type, where L = dimethylphenylphosphine and M = Re^{III}, Os^{III}, or Ir^{III}, the M–Cl and M–P bonds located opposite the phosphine groups are longer than those located opposite the chlorine atoms. The difference is approximately 0.1 Å (Table 8).

It has been established [83] that the dimeric complex $[Ir_2(CO)_4Me_2Cl_4]$ is formed via a double chloride bridge. It is noteworthy that the Ir–Cl bridging bonds are marked non-equivalent. The length of the Ir–Cl bond in the *trans*-position relative to Me is 2.52 Å and the length of the bond in the *trans*-position relative to CO is 2.38 Å. These results can be regarded as supporting the much greater *trans*-influence of the alkyl group compared with that of the CO molecule.

In his review [53] Porai-Koshits quotes interesting data on the influence of the Rh–Rh bond in dimeric formate and acetate complexes resulting in an increase in the length of the Rh–H_2O, Rh–Cl, and Rh–Br bonds in the *trans*-positions. In addition he notes that the *trans*-ligands in their turn also affect the Rh–Rh bond length. In halide complexes this bond is much longer than in hydride complexes (2.45–2.47 and 2.35–2.38 Å respectively).

Porai-Koshits [53] notes that the structural manifestation of the *trans*-influence of ligands are extremely delicate and depend on many factors. It is still not always possible to take into account all these factors. Thus there are very conflicting manifestations of the *trans*-influence of a multiple bond. In molybdenum compounds the Mo=O double bond causes an appreciable lengthening of the *trans*-bond with any ligand. In rhenium and ruthenium complexes the increase in the length of the bond in the *trans*-position relative to M=O occurs only for neutral ligands but not for acido-ligands. The Os=N triple bond constitutes a special case. In the complex $K_2[OsNCl_5]$ the length of the Os–Cl bond on the N≡Os–Cl axis is increased to 2.60 Å compared with the other bonds, whose length is 2.32–2.37 Å. The problem of the dependence of the strength of the metal–ligand bond located opposite a multiply-linked ligand in hexacoordinate compounds has been examined theoretically [84]. The influence of the yl oxygen on the inner-sphere fluoride ions in Group V and VI transition metal complexes has been investigated by NMR. [85,86]

The structure of the octahedral terpyridyl complex of gallium $GaCl_3$.2,2′,2″-terpyridyl has been investigated [87] and it has been established that the length of the Ga–Cl bond located opposite nitrogen is much smaller than that of the other two bonds on the Cl–Ga–Cl axis. The authors [87] attribute this finding to *trans*-influence.

IV. *TRANS*-INFLUENCE IN VIBRATIONAL SPECTROSCOPY

Force constants can serve as a measure of the strength of a chemical bond. When complexes of the same type are compared, the stretching vibration frequencies of chemical bonds are frequently used instead of force constants as a measure of the strengthening or weakening of the bonds.

We shall not consider here studies in which the relative strength of a metal–ligand bond was inferred from indirect data. They have been analysed in a monograph[16] (p. 315). Although the sensitivity of the metal ligand bond stretching vibrations to the type of ligand in the *trans*-position was established initially for Pt–H [88] and Pt–C bonds [89], it is nevertheless useful to begin the consideration of these data with studies where Pt–Cl vibrations were investigated.

Much information based on extensive experimental data concerning the influence of inner-sphere ligands on the Pt–Cl bonds was obtained by Chatt and coworkers[90]. Like Bersuker[29], the authors of this investigation concluded that there are at least two causes of *trans*-influence: the σ-electron shift from the ligand to the central atom and the π-electron shift from the central atom to the ligand. The σ-electron shift is probably the main cause of the strong *trans*-influence of hydrides and alkyl and aryl carbonions and the π-electron shift is characteristic of olefins. The σ-electronic mechanism of the transmission of *trans*-influence should weaken the bond in the *trans*-position for the molecule in the static state. On the other hand, the π-electronic mechanism should strengthen the bond in the opposite position.

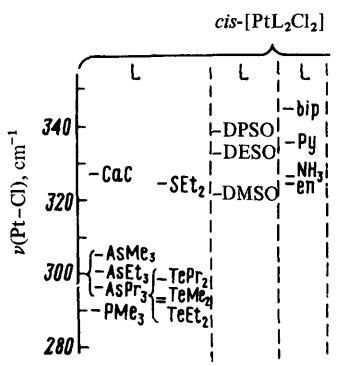


Figure 6. The spectroscopic *trans*-influence scale for ligands based on complexes of the type *cis*-$[PtL_2Cl_2]$.

A *trans*-influence scale has been set up for ligands on the basis of the Pt–Cl and Pt–Br stretching vibration frequencies[90]. The scale, supplemented by other data [91–93], is presented in Fig. 6. Compared with ammonia and pyridine (ligands with a weak *trans*-influence) phosphines and arsines lower the strength of the bonds in the opposite positions. It is claimed[23] that the *trans*-influence of phosphines is caused mainly by the σ-component, the π-component of phosphines being insignificant. Diethyl sulphide, diethyl selenide, and particularly cacodyl, which exhibit a powerful dynamic *trans*-effect (unlike phosphines), do not weaken but actually stabilise the bond in the opposite position. Basolo and Pearson[16] regard this finding as inconsistent with other experimental data (Basolo and Pearson[16], p. 316). However, bearing in mind that this scale refers to the *trans*-influence in the static state of the molecule, there is no inconsistency. Owing to the π-acceptor properties of sulphides and particularly of olefins, the effective charge on the platinum atom should increase and this should intensify the Coulombic interaction between the central atom and the ligand.

It has been shown by calculations and experimentally [36–38, 94, 95] that dialkyl sulphoxides have fairly pronounced π-acceptor properties. It was therefore interesting to establish their position in Chatt's *trans*-influence scale. Table 9 lists the vibration wave-numbers of the Pt–Cl bond in complexes of the type *cis*- and *trans*-$[Pt(R_2SO)_2Cl_2]$.

A similar Table has been compiled on the basis of studies [92, 93] on *cis*- and *trans*-$[Pt(DMSO)Cl_2L]$, where L represents amines or olefins (Table 10).

Table 9. The vibrational wavenumbers (cm^{-1}) of the Pt–Cl bond in the *cis*- and *trans*-complexes $[Pt(R_2SO)_2Cl_2]$.

Type of vibration	R_2SO				
	DMSO	DESO	DPSO		DiPSO
	cis	*cis*	*cis*	*trans*	*trans*
Pt—Cl	333 s. 309 s.	342 s. 322 s.	350 s. 326 s.	355 s.	353 s.

Table 10. The vibrational wavenumbers (cm^{-1}) of the Pt–Cl bonds in the *cis*- and *trans*-complexes $[PtL(DMSO)Cl_2]$.

Type of vibration	L							
	NH_3		NH_2CH_3		NH_2Et		C_2H_4	C_3H_6
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*cis*
Pt—Cl	346 s. 312 s.	344 s.	334 s. 313 s.	348 s.	338 312	349	338 s. 311 s.	334 306

Chatt's *trans*-influence scale (Fig. 6) was established on the basis of data for complexes with a *cis*-configuration. The value of ν(Pt–Cl) on this scale is the average of the values for two Pt–Cl bands. The scale for compounds with a *trans*-configuration might characterise the *cis*-influence, but in fact it essentially reflects the non-directional influence of the effective charge of the central atom on the ligands having the opposite charge. The *trans*-influence scale leads to the following conclusions.

1. In terms of the overall influence of the σ-donor and π-acceptor properties, sulphoxides are close to olefins, particularly to cyclo-octadiene. The similarity of the properties of olefin and sulphoxide complexes has been frequently pointed out [32, 33, 36, 37, 47, 48].

2. Comparison of the positions of diethyl sulphide and diethyl sulphoxide shows that sulphoxides tend to fix chlorine in the *trans*-position to a greater extent. The presence of oxygen at the sulphur atom should enhance the effective charge of the sulphoxide sulphur atom compared with the sulphide sulphur atom. It has indeed been shown by X-ray emission spectroscopy [96, 97] that the effective positive

charge on the sulphur atom in a sulphoxide is higher than in a sulphide. The same conclusion was reached[95] on the basis of the acid properties of analogous sulphide and sulphoxide compounds. The higher effective positive charge may be the reason for the somewhat more marked π-acceptor properties of sulphoxides compared with the corresponding sulphides.

3. In mixed dimethyl sulphoxide–amine and dimethyl sulphoxide–olefin compounds with the *cis*-configuration the arithmetical mean of the Pt–Cl bond stretching vibration frequencies is approximately the same as for the disulphoxide compounds. When two strong π-acceptors are present in the complex, the involvement of each in the interaction with the *d* orbitals of platinum probably decreases to such an extent that the effective charge of the central atom remains approximately the same.

It is interesting to note that, despite the appreciable difference between the type of ligands, the Pt–Cl bond stretching vibration wavenumbers in the spectra of compounds having the *trans*-configuration remain virtually constant and are in the range 339 ± 3 cm^{-1}.[90,91,98,99] Since *trans*-diolefine compounds are unknown, they cannot be represented on this scale. It would be interesting to supplement the series of compounds by complexes of the type *trans*-$[PtA(C_2H_4)Cl_2]$.

In the series of compounds with the *trans*-configuration, disulphoxide complexes occupy an anomalously high position. Mixed sulphoxide–amine compounds have somewhat lower Pt–Cl bond vibration frequencies. One should note that in all the compounds investigated, the Pt–Cl stretching vibration frequencies are higher for compounds with the trans-configuration than for the corresponding *cis*-compounds. This may be related to the higher symmetry of charge distribution. The ligands L in the complexes *trans*-$[Pt(PMe_2Ph)_2LCl]$ have been arranged in the following series in terms of *trans*-influence on the basis of the Pt–Cl bond vibrations: Cl^-, Me^-, Me_2SiCH_2, Ph_2MeSi.[71] On passing from Cl^- to Ph_2MeSi, the vibration wavenumber of the bond in the *trans*-position falls from 370 to 242 cm^{-1}. This series is satisfactorily consistent with data for the *trans*-influence of the given ligands obtained by ^1H NMR and X-ray diffraction. The following *trans*-influence series has been established[100] on the basis of the Pt–Cl stretching vibration frequencies in the complexes $[Pt(AsEt_3)_2LCl]ClO_4$: $CO > RNC > ArNC > P(OPh)_3 \simeq \simeq P(PMe)_3 > AsEt_3 \simeq PEt_3$.

The Pt–H bond vibration wave-numbers in the spectra of the complexes *trans*-$[PtA_2LH]$, where $A = PEt_3$ or $AsET_3$, which have been determined by Chatt and Shaw[101], made it possible to arrange ligands in the following series in terms of the strength of the *trans*-influence:

$$NO_3^- < Cl^- < Br^- < I^- < NO_2^- < SCN^- < SnCl_3^- < CN^- \ .$$

It is interesting that it coincides almost completely with the series of ligands based on the Pt–C bond stretching vibration frequencies in the compounds *trans*-$[Pt(PR_3)_2(CH_3)L]$.[102] The series is $NO_3^- < SCN^- < Cl^- < Br^- < I^- < NO_2^-$. They are both analogous to the *trans*-influence series established at an early stage by the discoverer of *trans*-influence–Chernyaev. Only the thiocyanate ion deviates from the second series. The authors[102] suggested that in this case it may be coordinated via the nitrogen atom and not via the sulphur atom.

The *trans*-influence in iridium(III) compounds has been detected[103] by infrared spectroscopy. The study of the spectra of the meridional compounds $[Ir(PMe_3Ph)_3LCl_2]$ showed that in the series $L = Cl^-$, PR_3, or AsR_3, H^- there is a steady decrease of the Ir–Cl frequency, which can indicate a relative decrease of the strength of this bond. This is consistent with the variation of the *trans*-influence of the ligands:

$$H^- > PR_3 \simeq AsR_3 > Cl^- \ .$$

It was established in the same study that in the series of ligands $L = Cl^-$, H^-, Br^-, I^-, SCN^-, CN^- there is virtually no change in the vibration frequencies of the Ir–Cl bonds in the *cis*-positions.

A study of octahedral complexes of tervalent rhodium and iridium[104] established that the stretching vibration frequencies of the Rh–Cl and Ir–Cl bonds depend mainly on the nature of the ligands in the *trans*-positions. The ν(M–Cl) frequencies increase in the following sequence of ligands:

$$Cl^- < Br^- < I^- \sim CO < Me^- \simeq PR_3 \simeq AsR_3 < H^- \ .$$

A study of the Au–C bond vibration frequencies and the deformation frequencies of the methyl group in the ion $[Me_2AuX_2]^-$ showed[105] that the *trans*-influence series for gold(III) complexes is the same as for platinum(II):

$$Me_2S > Br^- > Cl^- > en > OH^- > H_2O \ .$$

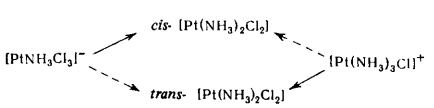
The substitution of two halide ions in the square planar ion AuX_4^- (X = Cl or Br) by two Me^- carbanions leads to the formation of complexes with the *cis*-configuration only and reduces the force constant of the bond Au–X by more than 30%.[105] Thus these data also indicate a much more marked *trans*-influence of the Me^- group compared with Cl^- or Br^-.

The infrared and Raman spectra of the complexes $Me_2SnX_4^{2-}$, where X = F, Cl or Br, have been investigated[106]. It was established that these compounds have the *trans*-configuration. After the substitution of two fluoride ions in SnF_6^{4-} by Me^-, there is some decrease of the force constant of the Sn–F bond. This happens to a smaller extent when a chloride ion is substituted and is altogether negligible in bromide compounds. The authors attribute this variation to the enhancement of the covalence of the tin–halogen bonds. They note that in transition metal compounds the bonds in the *trans*-position relative to the alkyl group are weakened, while in tin compounds the weakening is observed in the *cis*-position.

In contrast to other investigators, Ivannikova et al.[107] concluded that there is no correlation between ν(Pt–Cl) and the ligand *trans*-influence series for complexes of the type $[Pt(NH_3)_2LCl]X$. In most of the studies where such correlation has been established non-electolytic complexes were investigated. Possibly the results of Ivannikova et al.[107] can be accounted for by the fact that they employed compounds containing outer-sphere anions.

V. *TRANS*-INFLUENCE IN THE KINETICS OF SUBSTITUTION REACTIONS

The kinetic aspect of *trans*-influence follows clearly from the classical reactions of ammonia with chloroplatinate(II) to form *cis*-$[Pt(NH_3)_2Cl_2]$ and the cleavage of the tetrammine $[Pt(NH_3)_4]Cl_2$ by hydrochloric acid with formation of *trans*-$[Pt(NH_3)_2Cl_2]$. After excluding reaction stages without fundamental importance, these transformations can be represented schematically as follows:



It is difficult to imagine that the isomeric complexes *cis*-$[Pt(NH_3)_2Cl_2]$ and *trans*-$[Pt(NH_3)_2Cl_2]$ have the same free energy. Indeed, according to the literature[108] the difference between the total energies of these isomers is 3 kcal mole^{-1}, that of the *trans*-isomer being lower. It was established even earlier[109] that the *trans*-isomer is more stable from the energy standpoint, since dry solid *cis*-$[Pt(NH_3)_2Cl_2]$ is converted at 230°C into the corresponding *trans*-isomer as well as being decomposed. Thus the cleavage of the triammine by hydrochloric acid is consistent with thermodynamics and the interaction of the monoammine and ammonia with formation of *cis*-$[Pt(NH_3)_2Cl_2]$ follows the thermodynamically less favourable pathway. Consequently, kinetic factors play the main role in determining the direction of the reaction $[Pt(NH_3)Cl_3]^- + NH_3 = cis\text{-}[Pt(NH_3)_2Cl_2] + Cl^-$.[110,111] Subsequently others reached a similar conclusion[112]. It has been established[111] that a very small amount of *trans*-$[Pt(NH_3)_2Cl_2]$ is formed in the reaction between ammonia and chloroplatinate(II) in addition to *cis*-$[Pt(NH_3)_2Cl_2]$, and after the cleavage of the tetrammine the *trans*-isomer contains a small amount of *cis*-$[Pt(NH_3)_2Cl_2]$.

Subsequently it was shown[113,114] that the compounds *cis*-$[PtA_2X_2]$, where A = amine and X = Br or I, have a higher free energy than the corresponding *trans*-isomers, since on heating in the dry state the *cis* → *trans* isomerisation takes place with energy evolution. Depending on the nature of the amine, the isomerisation energies of the iodide and bromide complexes are 4–6 and 2–3 kcal mole^{-1} respectively.

The occurrence of the reaction via the thermodynamically less favourable pathway but in conformity with the *trans*-influence is probably a common phenomenon. It has been established in a number of studies[32,34,115–117] that the sulphoxide compounds *trans*-$[Pt(R_2SO)ACl_2]$ isomerise in the dry state to the more stable *cis*-isomers with energy liberation. However, the reaction of the ion $[Pt(R_2SO)Cl_3]^-$ with amines does not proceed via the thermodynamically more favourable pathway with formation of *cis*-$[Pt(R_2SO)ACl_2]$, but follows the kinetically more favourable pathway with formation of *trans*-$[Pt(R_2SO)ACl_2]$:

$$[Pt(R_2SO)Cl_3]^- \xrightarrow{+A} \begin{matrix} trans\text{-}[Pt(R_2SO)ACl_2] \\ \downarrow \\ cis\text{-}[Pt(R_2SO)ACl_2] \end{matrix}$$

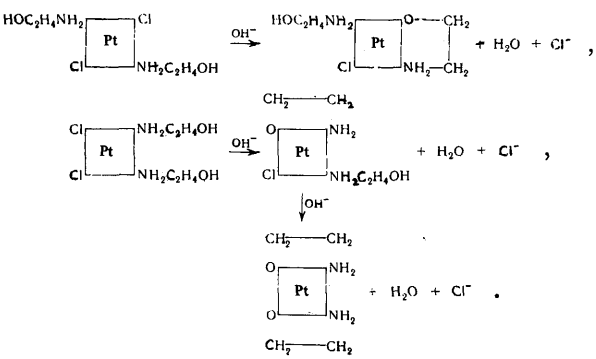
The kinetic manifestation of the *trans*-influence has been satisfactorily described in a number of books and reviews[13–16,30]. In recent years most kinetic studies of the *trans*-influence were made, as before, on platinum complexes. The exchange of labelled [^{14}C] diethylamine in complexes of the type *trans*-$\{PtL[^{14}C](NHEt_2)Cl_2\}$ in methanol and other non-aqueous solvents has been investigated[118]. The authors reached a number of interesting conclusions. Thus they established that triethylphosphine, arsine, and stibine can be arranged in the following sequence in terms of their *trans*-influence: $R_3Sb > R_3P > > R_3As$. The *trans*-influence of the alkyl derivatives of phosphorus, arsenic, and antimony in the reactions investigated is always greater than that of the aryl derivatives. The series $C_2H_4 \simeq$ i-PrCH=CHMe $\simeq Me_2C(OH)C{\equiv}CC(OH)Me_2 \gg Et_3Sb > Ph_3Sb > Me_3P > Et_3P >$ n-$Pr_3P > > Ph_3P > Et_3As \gg$ n-Pr_2S shows that the *trans*-influence of dipropyl sulphide is much smaller than that of phosphines, arsines, and stibines.

A major and interesting study[119] dealt with the kinetics of substitution in complexes of the type *trans*-$[PtL_2Cl_2]$ as a function of the nature of the inner-sphere ligand L and the entering ligand. It might have been expected that the results would make it possible to establish the ligand series in terms of the strength of the *cis*-influence. Unfortunately the rate constants are sometimes so close that the adjacent ligands in the series change places depending on the compounds investigated. For this reason, it was impossible to establish a rigorous *cis*-influence series. Nevertheless, an investigation[119] demonstrated unambiguously a greater *cis*-influence of triethylarsine compared with triethylphosphine, i.e. the opposite variation of the *trans*- and *cis*-influences of ligands was again confirmed. One should note that, among the ligands investigated, organic dialkyl sulphides exhibit both a weak *trans*-influence and a weak *cis*-influence.

Ammonia and aliphatic amines have a much weaker *trans*-influence than phosphines. It has been shown[120] that the *cis*-influence of ammonia and diethylbenzylamine greatly exceeds that of triethylphosphine. This applies both to the solvation of the complexes *trans*-$[Pt(PEt_3)_2Cl_2]$, *trans*-$[Pt(PEt_3)(NH_3)Cl_2]$, and *trans*-$[Pt(PEt_3).(NEt_2CH_2Ph)Cl_2]$ in methanol and to the chlorine isotope exchange reactions in these complexes.

Clear-cut findings indicating the manifestation of *trans*-influence were obtained in a study of the exchange of diethyl sulphoxide in the complex ions $[Pt(DESO)Cl_3]^-$ and $[Pten(DESO)Cl]^+$.[121,122] While the DESO exchange in the first complex is relatively rapid ($k = 7.6 \times 10^{-2}$ litre mole^{-1} s^{-1}), in the ion $[Pten(DESO)Cl]^+$ there is virtually no exchange. This can be undoubtedly attributed to a much weaker *trans*-influence of the amino-groups of ethylenediamine compared with the *trans*-influence of the chloride ion.

Stephen and Basolo established[123] that in the interaction of *trans*-$[Pt(NH_2C_2H_4OH)_2Cl_2]$ with alkali one of the ethanolamine molecules undergoes ring closure faster than the other. Studies have been made[124,125] on the rate of closure of ethanolamine rings in the isomeric *cis*- and *trans*-complexes $[Pt(NH_2C_2H_4OH)_2Cl_2]$. As a result, data were obtained showing that the closure of the first ring in the *trans*-complex is much faster than in the *cis*-complex. On the other hand, the second ring is formed much faster in the *cis*-complex than in the isomeric compound. This fact indicates the manifestation of *trans*-influence, which clearly follows from the following schemes.



Owing to the comparatively powerful *trans*-influence of chlorine, substitution on the Cl–Pt–Cl axis is much easier than on the Cl–Pt–NH_2R axis. Therefore, the closure of the first ring in *trans*-$[Pt(NH_2C_2H_4OH)_2Cl_2]$ is much faster. For the closure of the second ring in the *trans*- and *cis*-isomers of $[Pt(NH_2C_2H_4OH)(NH_2C_2H_4O)Cl]$, substitution on the Cl–Pt–OR and Cl–Pt–NH_2R axes respectively is necessary. The much higher rate of substitution of the second ring in the *cis*-complex is probably a consequence

of the greater *trans*-influence of the amino-group compared with the OR^- group. One may mention that in platinum(II) complexes the *trans*-influence of the amino-group of alanine bound in a cyclic form is somewhat greater than the *trans*-influence of the carboxy-group[126].

In thioethers forming metal complexes the sulphur atom is at the apex of a trigonal pyramid. Consequently there should be three conformers of platinum and palladium complexes of the type $[Pt(RSC_2H_4SR)X_2]$. An ^1H NMR study[127] has been made of the interconversion of these conformers, involving the inversion of the molecular structures relative to the sulphur atom. It was established that the rate of inversion in the complexes $[Pt(RSC_2H_4SR)X_2]$ and $[Pd(RSC_2H_4SR)X_2]$ depends on the *trans*-influence of the ligands X. The ligands X can be arranged in the following series in terms of their facilitating influence on the inversion process: $Cl^- < Br^- < I^- \ll Ph^-$. It has been shown that the inversion in the palladium complexes is much easier than in the corresponding platinum compounds.

The first kinetic study of the substitution reactions in rhodium(III) complexes was made by Zvyagintsev and Shubochkina[128]. Unfortunately, this study was not developed further subsequently. Systematic investigations, which clearly revealed *trans*-influence in complexes, were also made by Poë and coworkers[129–134]. They investigated extensively the kinetics of substitution reactions of the type

$$trans\text{-}[Rhen_2LY] + Z \rightarrow trans\text{-}[Rhen_2LZ] + Y \quad .$$

According to the results of these studies, the *trans*-influence series for rhodium(III) is as follows: $H_2O < OH^- \simeq \simeq NH_3 \leqslant Cl^- < Br^- < I^-$. In many respects it agrees with the corresponding *trans*-influence series for platinum(II).

It has been established[135] that the rate constants for the substitution of ammonia by water in the complexes $[RhEt(NH_3)_5]^{2+}$ and $[Rh(C_2F_2H)(NH_3)_5]^{2+}$ are smaller by several powers of ten than the rate constant for the substitution of ammonia in the ion $[RhH(NH_3)_5]^{2+}$. However, the analogous substitution in the ion $[RhCl(NH_3)_5]^{2+}$ is slower still. Thus the ligands investigated can be arranged in the following series in terms of their *trans*-influence in rhodium(III) complexes: $H^- \gg Et^- > C_2F_4H^- \gg Cl^-$.

It has been shown[131] that the relative *trans*-influence of ligands depends on the nature of the ligand eliminated from the complex.

The rates of substitution reactions in the iridium complexes *trans*-$[Iren_2X_2]^+$ (X = Cl, Br, or I) and *trans*-$[Iren_2LCl]^+$ (L = NO_2, Br, or I) with various nucleophiles were investigated spectrophotometrically[136]. It was established that these reactions are complicated neither by catalysis nor by stereochemical rearrangements. Their rates are independent of the nature and concentration of the entering ligand. This suggests that the reaction proceeds via a rate-determining stage:

$$trans\text{-}[Iren_2LX]^+ + H_2O \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} trans\text{-}[Iren_2LH_2O]^{2+} + X^- \quad ,$$
$$trans\text{-}[Iren_2LH_2O]^{2+} + Y^- \longrightarrow trans\text{-}[Iren_2LY]^+ + H_2O \quad .$$

It follows from the results[136] that the *trans*-influence increases in the series $NCS^- < Cl^- < Br^- < NO_2^- < I^-$. The position of the thiocyanate ion is different from that in the corresponding series for platinum(II). This is because in the iridium(III) complexes the thiocyanate ion is bound to the central atom via nitrogen[137].

The strong *trans*-influence of the hydride ion compared with the chloride ion can be inferred from the finding[138] that, when the complex $[PtH_2Cl(PEt_2Ph)_3]$ reacts with sodium iodide, the chloride ion is readily substituted by iodide. However, it has been established that the substitution for iodide of the chloride ion located opposite another chloride ion requires high temperatures and a long reaction time. The strong *trans*-influence of tertiary phosphines is indicated by the very rapid substitution of the chloride ion located opposite the phosphine in the meridional complex $[Ir(PEt_3)_3Cl_3]$. In hot acetone the substitution takes place in 3 min. On the other hand, the substitution of the two other chloride ions requires boiling for 3.5 h.

The hydrolysis of *cis*-$[Ruen_2X_2]^+$, *cis*-$[Ruen_2(OH)Cl]^+$, and $[Ru(NH_3)_5X]^{2+}$ has been investigated[139]. It was established that the hydrolysis does not entail stereochemical changes in the complexes. The authors put forward a mechanism involving a conjugate base in which *trans*-influence plays a significant role. They assumed that the rapid substitution of the halogen is associated with the *trans*-influence of the amido-group as a result of its interaction of the $p\pi-d\pi$ type.

A study[140] where the aquation of the ion $[Cr(H_2O)_5I]^{2+}$ in the presence of Cl^- ions was investigated is of interest. It was established that the main reaction products are $[Cr(H_2O)_6]^{3+}$, while $[Cr(H_2O)_5Cl]^{2+}$ is obtained in a yield of only 10–20%. In another study[141] this reaction was investigated using labelled [^{18}O] water. It was possible to show that the elimination of the ion from the complex is preceded by an appreciable exchange of water in the ion $[Cr(H_2O)_5I]^{2+}$. These findings together with the observation that the exchange of water in the ion $[Cr(H_2O)_5Cl]^{2+}$ is very slow led to the conclusion that the inner-sphere iodide ion has a labilising influence on the water molecule in the opposite position. This conclusion is quite likely and, if it is true, then the above observation can be regarded as the first reliable evidence in support of the occurrence of *trans*-influence in chromium(III) complexes.

trans-Influence in the iron(II)-phthalocyanine complex has been suggested by Jones and Twigg[142], who investigated the rate of substitution of DMSO by imidazole in the axial position in the complex $FePc(DMSO)_2$. The reaction was carried out in DMSO. It was found that the rate-determining stage is the substitution of the first DMSO molecule:

$$FePc(DMSO)_2 + Imid \rightleftharpoons FePc(DMSO)(Imid) + DMSO,$$
$$FePc(DMSO)(Imid) + Imid \rightleftharpoons FePc(Imid)_2 + DMSO.$$

The second molecule is substituted at a higher rate owing to the greater *trans*-influence of imidazole compared with DMSO.

One should note that, when there is only one possibility of substitution, (in the *trans*- or *cis*-position), it is dangerous to reach conclusions concerning directional intramolecular interaction.

Cobalt complexes undoubtedly occupy the first place as regards the number of kinetic studies on substitution reactions. Nevertheless, the problem of the applicability of the *trans*-influence rule to cobalt complexes has not been completely resolved. It is interesting that Basolo and Pearson, who contributed much to the study of the kinetics of substitution reactions in cobalt complexes, did not devote even a single chapter or paragraph to this problem in their book[16]. Although the review of Pratt and Thorp[8] is devoted to the *cis*- and *trans*-effects in cobalt complexes, it fails to elucidate this problem completely. They quote the following ligand series based on the *trans*-influence:

$$\text{alkyls, } SO_3^{2-} \gg \begin{matrix} CN^-,\ N_3^-,\ NO_2^-,\ NH_3 \\ HO^-,\ Cl^-,\ Br^-,\ I^- \end{matrix} > H_2O > NSC^- \quad .$$

Unfortunately, the *trans*-influence series for cobalt complexes depends on the type of complex used as a basis for the substitution reaction series. Any rule must have predictive power. However, for cobalt complexes the above series has so far had a comparatively low predictive power.

VI. THE MUTUAL INFLUENCE OF LIGANDS AND ACID PROPERTIES OF COMPLEXES

A great contribution to the study of the problem of the influence of inner-sphere ligands on the acid properties of complexes was made by Grinberg, who describes them in a monograph[13] (p. 388). As early as 1935, Grinberg and Ryabchikov showed[143] that in platinum(II) complexes ligands with a strong *trans*-influence reduce the acid dissociation of proton-containing groups located in the opposite positions. They studied the acid properties of the isomeric *cis*- and *trans*- complexes $[Pt(NH_3)_2(H_2O)_2]^{2+}$ and established that the first acid dissociation constant of the *trans*-isomer is higher than that of the *cis*-isomer. The second acid dissociation constants are close, but K_2 for the *cis*-isomer is somewhat higher. These findings were explained from the standpoint of the enhancement of the *trans*-influence of the ligands in the series $OH^- > NH_3 > H_2O$. According to the polarisation model of *trans*-influence, with increase of the σ-donor properties of the ligand the *trans*-ligand is depolarised with a consequent weakening of its acid properties. Since the *trans*-influence of water is weaker than that of ammonia, the first acid dissociation constant of the ion $\begin{bmatrix} NH_3 & & H_2O \\ & Pt & \\ H_2O & & NH_3 \end{bmatrix}^{2+}$ should indeed be higher than that of the ion $\begin{bmatrix} NH_3 & & H_2O \\ & Pt & \\ NH_3 & & H_2O \end{bmatrix}^{2+}$. The second dissociation constants are those of the ions $\begin{bmatrix} NH_3 & & OH \\ & Pt & \\ H_2O & & NH_3 \end{bmatrix}^{+}$ and $\begin{bmatrix} NH_3 & & OH \\ & Pt & \\ NH_3 & & H_2O \end{bmatrix}^{+}$. Since the *trans*-influence of the hydroxy-group is somewhat greater than that of ammonia, K_2 for the *cis*-isomer proved to be somewhat higher than for the *trans*-isomer.

This variation of the acid properties was confirmed[144,145] for other pairs of isomeric diaquo-complexes. A similar behaviour was discovered also for octahedral cobalt(III) and chromium(III) complexes[146]. Apart from the influence of the *trans*-ligands on the properties of inner-sphere proton-containing molecules, Grinberg and coworkers discovered the influence of the ligands in the *cis*-position with respect to the dissociating molecule[144]. In particular, they established that an inner-sphere pyridine molecule enhances the acid properties of H_2O molecules in platinum(II) complexes[144,147] and NH_3 molecules in platinum(IV) complexes[148-150]. Stetsenko systematically arranged the available information about the *trans*- and *cis*-influence of ligands on the acid properties of platinum complexes and demonstrated convincingly[151] that, following the replacement of NH_3 by another ligand, the acid properties of the *cis*- and *trans*-complexes $[PtA_2B_2]^{2+}$ change in the same direction (become stronger or weaker). However, the change in the acid properties of the *cis*-isomer is as a rule greater.

The hypothesis of the weakening of the acid properties of inner-sphere proton-containing molecules in both *trans*- and *cis*-positions with increase of the *trans*-influence of ligands is valid only for σ-donors. In 1955 Leden and Chatt[152] estimated the acid dissociation constant of the complex $[Pt(C_2H_4)(H_2O)Cl_2]$ and found it to be approximately 10^{-5}. Thus, despite the very strong *trans*-influence of ethylene, it does not weaken but actually enhances the acid properties of the inner-sphere water molecule. Grinberg postulated that *trans*-active ligands with pronounced π-acceptor properties can intensify the acid dissociation of inner-sphere ligands by increasing the effective positive charge on bivalent platinum[13] (p. 391). Numerous findings confirming this view have now been obtained[94,95,153-158]. The comparatively weak influence on the acid properties of the aquo-complexes of platinum(II) following the substitution of the ammonia molecule in the ion $[Pt(NH_3)_3(H_2O)]^{2+}$ by triphenylphosphine or triphenylstibine was somewhat unexpected[158].

The overall experimental data show that the mutual influence of ligands, shown by a change in acid properties, is relatively non-directional. If the proton-donating molecule is a σ-donor alone, then in principle the influence of the ligands on its acid properties may be reduced to the following cases (Fig. 7): I. by direct transmission of the influence of one ligand to another in the *cis*-position; II. by the transmission of the influence of σ-donors to the *trans*-position via the p_y orbital; III. by the transmission of the electron density of σ-donors in the *cis*-position via the $d_{x^2-y^2}$ orbital. Thus the increase of *trans*- or *cis*-influence, leading to an increase of electron density in the Pt–Rh bond, should weaken the acid properties of the coordinated molecule RH.

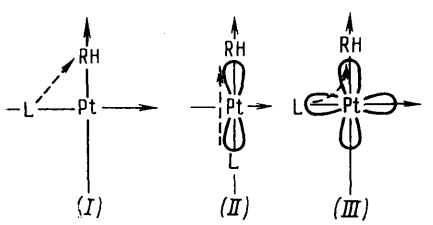


Figure 7. Schematic illustration of the transmission of the influence of a ligand with σ-donor properties.

A different situation should arise for ligands with π-acceptor properties (Fig. 8). If it is assumed that RH exhibits neither π-acceptor nor π-donor properties, then the influence of π-ligands on its acid properties can only be electrostatic. The effective charge of the central atom consists of the nuclear charge and the charges of the electrons in its orbitals. Since a limited number of orbitals are involved in interactions of the π-type, it is useful to infer the change of the effective charge from the shift of electron density in the corresponding orbitals. If the ligand L with π-acceptor properties is fixed on the X axis and the location of the ligand RH relative to it is varied, then mainly the d_{xy} and d_{xz} orbitals of the central atom will be involved in the interaction with L. When the ligands are in the *trans*-positions, the centres of gravity of the electron densities of the d_{xy} and d_{xz} orbitals will shift by a distance l to the π-acceptor and will be located on the X axis (IV*a*, IV*b*).

It is evident from Schemes V*a* and V*b* that for ligands in the *cis*-positions the centres of gravity of the d_{xy} and d_{xz} orbitals are also remote from RH but less so than for the *trans*-positions. Thus, in consequence of the π-acceptor properties of the ligand L, the acid properties of the RH molecule should be enhanced in both the *cis*- and *trans*-positions. However, the influence should be somewhat more marked for ligands in the *trans*-positions.

If the ligand L exhibits π-donor properties, then it should weaken the acid properties of RH in both the *trans*- and *cis*-positions and to a somewhat greater extent in the former case.

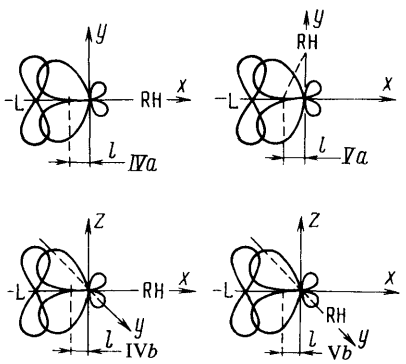


Figure 8. Schematic illustration of the transmission of the influence of a ligand with π-acceptor properties.

The mutual influence of ligands in relation to the acid properties of octahedral complexes, in particular platinum(II) complexes, is less definite. Grinberg and Gil'dengershel' established that the acid dissociation constant of the bromo-complex $[Pt(NH_3)_5Br]^{3+}$ is 5.6×10^{-9} and that of the chloro-analogue $[Pt(NH_3)_5Cl]^{3+}$ is 7.9×10^{-9}.[160] This is consistent with the polarisation model of *trans*-influence. The bromide ion, which has a stronger *trans*-influence than the chloride ion, causes a greater counter-polarisation of the ammonia molecule in the opposite position. As a result the acid properties of the bromo-complex are weaker than those of the chloro-complex. However, from this point of view the acid properties of *cis*-$[Pt(NH_3)_4Cl_2]^{2+}$ should be weaker than the acid properties of *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$, since in the first case two of the four ammonia molecules are in the *trans*-positions with respect to the chloride ions. On the other hand, experimental data indicate more marked acid properties of the *cis*-isomer[161]. From this, it follows that the difference between the *trans*-influences of chlorine and ammonia in platinum(IV) complexes is less important than the repulsion of the protons of the molecules in the *cis*-positions or the polarity of the complex ion.

Spitsyn et al. established that the ligands can be arranged in a definite series in terms of their influence on the acid properties of certain platinum(IV) aquo-complexes. On this basis, they proposed a *trans*-influence scale for ligands[162].

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In conclusion, one must say that so far there is no theory which explains all the experimental facts and which embraces all the aspects of the mutual influence of ligands in complexes. One of the problems which still awaits solution is the manifestation (or absence) of the mutual influence of ligands in equilibrium systems involving ligand substitution. Systematic studies on this problem are being made by Peshchevitskii[112,163-166].

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