Directing Effects in Inorganic Substitution Reactions. Part I. A Hypothesis to Explain the trans-*Effect.*

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The hypothesis that *trans*-directing ligands in square planar and octahedral complex compounds exert their directing effects in substitution reactions because they co-ordinate by double bonds is developed, and it is shown how the general phenomenon of the *trans*-effect can be explained. It is supposed that the forces responsible for the directing effect originate mainly in the electron withdrawal, occasioned by dative π-bond formation, from a d_{xz}-orbital of the metal towards the ligand A of high *trans*-effect (Fig. 2). This electron withdrawal will increase the electron affinity of the metal atom and perhaps the strength of σ-bonding to all the other ligands B. However, the electrons are withdrawn mainly from the antinodes remote from A of the *d*-orbital, thus decreasing any tendency of the ligand B in *trans*-position to A to form a dative π-bond. The whole M=B bond will thus be drastically weakened (*i.e.*, more subject to heterolytic fission) if the dative π-bond is an essential component. However, if B, *trans* to A, has little tendency to form dative π-bonds its attachment to the metal could be strengthened by the presence of A.

The operation of the rapid and readily reversible elimination of groups *trans* to ligands A of high *trans*-effect (*i.e.*, high double-bonding capacity) is readily explained if we suppose that *trans*-substitution occurs by an S_N2 (bimolecular) mechanism. Increasing double bonding by A increases the electron affinity of the metal atom and hence the ease of nucleophilic attack. Also, because the electron withdrawal occasioned by A occurs from the antinodes remote from A of the d_{xz}-orbital, the attack takes place there, preferentially displacing the ligand *trans* to A (Fig. 2). Electronically platinum(II) is uniquely constituted for the origin and transmission of a strong *trans*-effect.

CHERNYAEV (*Ann. Inst. Platine, U.S.S.R.*, 1926, **4**, 243; 1927, **5**, 118) observed that, in the substitution reactions of the complex compounds of platinum(II), the position of substitution depends on the groups or ligands already present in the complex and not on the entering group. Subsequent developments in preparative co-ordination chemistry have served to confirm that strong directing forces operate in guiding the course of substitution in square planar platinous complexes; also that similar, but probably weaker, forces may influence the course of substitution in all complex compounds of inert type, especially of planar palladium(II), and octahedral cobalt(III), rhodium(III), and platinum(IV). The subject of these directing effects and current hypotheses as to their nature have recently been reviewed by Quagliano and Schubert (*Chem. Rev.*, 1952, **50**, 201). However, the effects have received extensive study only in the platinous series of complexes. So far all studies have been essentially qualitative; it is the object of the present series of papers to find a quantitative basis, and extend the study to metals other than platinum.

The laws of substitution as they apply in platinous chemistry may be illustrated by the two reactions :

$$\mathrm{K[NH_3,PtCl_3] + C_2H_4 \longrightarrow \textit{cis}\text{-}[NH_3,C_2H_4,PtCl_2] + KCl}$$
$$\mathrm{K[C_2H_4,PtCl_3] + NH_3 \longrightarrow \textit{trans}\text{-}[NH_3,C_2H_4,PtCl_2] + KCl}$$

In these, ammonia directs the entering group into a *cis*-position and substitution is slow; ethylene directs it into the *trans*-position, and this substitution is rapid and readily reversible. The analogy between the above substitution reactions and the familiar substitution of benzene is very striking. The *cis*-substitution reaction corresponds to *meta*, and the *trans* to *ortho*- and *para*-substitution reactions. It should therefore be possible to place the common ligands of inorganic complex chemistry in order of their tendency to direct a second substituent into the *trans*-position. This has been done by chemists of the Russian school but only qualitatively, and a series in approximate order of increasing *trans*-directing effect is as follows :

$$\mathrm{H_2O < OH < NH_3 \sim R{\cdot}NH_2 < pyridine < Cl < Br < CNS \sim I}$$
$$\mathrm{\sim NO_2 \sim SO_3H \sim PR_3 \sim R_2S \sim SC(NH_2)_2 < NO \sim CO \sim C_2H_4 \sim CN}$$

The groups at the CN end of this series are said to have a high *trans*-influence or high *trans*-effect and the general phenomenon of these directing effects is known as the *trans*-effect. The exact order of substituents in the series is not known with certainty; *e.g.*, a recent semiquantitative study by Hel'man and Karandashova [*Doklady Akad. Nauk S.S.S.R.*, 1952, **87**, (4), 597] places CN in the position occupied by the nitro-group in the above series and the latter between Cl and Br.

The way in which a ligand exerts its directing influence is unknown, but it has been generally assumed that groups of high *trans*-directing effect weaken the bond in the *trans*-position to themselves, *i.e.*, increase the tendency of that bond to heterolytic fission. This belief is so strongly held that Quagliano and Schubert (*loc. cit.*) use it to define the *trans*-effect : " The *trans*-effect stipulates that the bond holding a group *trans* to an electronegative or other labilising group is weakened." There is, however, no unequivocal evidence of a general weakening of the bond in the *trans*-position to a group of high *trans*-effect; we now find evidence that, in certain circumstances to be described, the bond may be strengthened. We prefer to define the *trans*-effect as follows : " The *trans*-effect or *trans*-influence of a group (A) co-ordinated to a metal ion is the tendency of that group to direct an incoming substituting group into the *trans*-position to itself (A)." Chemists of the Russian school refer to the labilisation of the *trans*-group by A, which does not necessarily mean that the bond in *trans*-position to A is weakened, although it is usually assumed. In discussing a co-ordinate bond, " bond weakening " means increasing tendency for the ligand-to-metal bond to break so that the ligand carries away with it the bonding electrons as a lone pair, *i.e.*, increasing tendency of the bond to heterolytic fission.

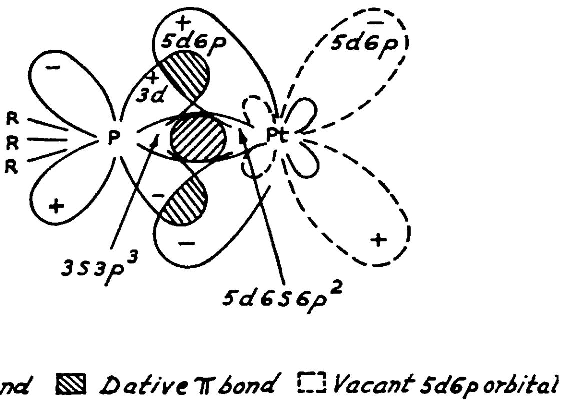
Various hypotheses, summarised by Quagliano and Schubert (*loc. cit.*), have been put forward by Russian chemists to explain the operation of the *trans*-effect but all assume and explain a weakening of the *trans*-bond. The latest, by Syrkin (*Izvest Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1948, 69), serves as a useful mnemonic for deciding the position of substitution in a platinous complex.

Chatt (*J.*, 1949, 3340) suggested that many more donor atoms than had previously been supposed might be bound to the later transition metals of each period, and especially to platinum(II), by bonds of partial double-bond character; also that there might be some direct correlation between the tendency of a ligand to bind by a double bond and the magnitude of its *trans*-effect (*Nature*, 1950, **165**, 637; Chatt and Williams, *J.*, 1951, 3061). The existence of such double bonding is now generally recognised (for summary of the present position see Craig *et al.*, *J.*, 1954, 332; Jaffé, *J. Phys. Chem.*, 1954, **58**, 185). In this paper we shall put forward a development of the idea that the amount of double bonding between a metal and a ligand through inductive and mesomeric effects is the main cause of the *trans*-effect, and the consequences of this hypothesis. Syrkin's hypothesis relegates double bonding to a subsidiary position in its relation to the *trans*-effect, which he supposes to be due primarily to a change in hybridisation of the σ-bonds.

The σ- and π-components of a double bond binding a ligand to a suitable transition metal may be visualised as follows. The σ-bond is formed by donation of a lone pair of electrons from the donor atom or group to the metal. The π-type bond (dative π-bond) is formed by the overlap of a filled *d*- or *dp*-hydrid orbital of the metal and a vacant *p*-, *d*-, or *dp*-hybrid orbital of the donor. The specific example of a C_2H_4–Pt bond where the dative π-bond is an essential part of the co-ordinate bond is shown schematically by Chatt and Duncanson (*J.*, 1953, 2939). In the case of the R_3P–Pt bond a similar schematic representation is given in Fig. 1, which also shows the vacant non-bonding *dp*-hybrid of the platinum atom.

Origin of the Force causing the trans-*Effect.*—In co-ordinate double bonds there can arise much greater inductive and mesomeric effects than are found in aromatic compounds. In theory the σ-bond may range from a strong bond with complete sharing of the lone pair and transfer of one electronic charge to the acceptor metal atom, to a weak bond with little transfer of charge (*e.g.*, in H_3BCO) and still further to no bond at all and no charge transfer. In fact the upper limit of charge transfer of single co-ordinate bonds between electrically neutral molecules or atoms appears to be about 0·65*e* (Phillips, Hunter, and Sutton, *J.*, 1945, 146). Also, since the lower limit of zero is only attained when there is no bond at all between the ligand and metal, the stable and very dipolar co-ordinate bonds which exist in the common platinous complexes must have strong σ-components (see Jensen, *Z. anorg. Chem.*, 1935, **225**, 97; 1936, **229**, 225; 1937, **231**, 365; Chatt and Wilkins, *J.*, 1952, 4300). It is to be expected, therefore, that the actual range in electrical asymmetries of co-ordinate σ-bonds in stable platinous complexes will be very much more limited than that theoretically attainable. Nevertheless, it is probably comparable with, or somewhat greater than, that found in organic compounds. On the other hand, the transfer of charge involved in dative π-bonding, which also has a theoretical range from zero to 1 *e* per π-type bond, is not so severely limited in practice. The lower limit of zero is attainable in such bonds as R_3N–Pt where the donor atom (N) has no vacant orbitals in its valency shell for dative π-bond formation. The upper limit is probably attained in such bonds as F_3P=Pt and OC=Pt which are almost non-polar (Chatt and Williams, *J.*, 1951, 3061). In these compounds the donation of electrons in the σ-bond is almost equal to the back donation in forming the π-type bond.

FIG. 1. *Schematic representation of the* R_3P = Pt *bond.*



From such considerations as these it seems fairly certain that the range of magnitudes of inductive effects of donor atoms is not likely to be much greater in most robust complexes than in organic compounds. On the other hand, the range of mesomeric effects arising from the strength of dative π-bonding is probably so great that it may cover all gradations in net charge transfer from zero to 0·5*e* from metal to donor atom. There is thus a great range in the possible magnitude of the electron drift in π-type orbitals from the metal to donor atom. It is this and the rectilinear symmetry of the *d*-orbitals which we consider to be mainly responsible for the directing forces found in square planar and octahedrally co-ordinated complex compounds. The greater the electron drift in π-type orbitals towards the ligand A, the greater the strength of double bonding, A=Pt, and the greater the *trans*-effect of A.

It should be emphasised, however, that, although the above treatment gives some idea of the magnitude of the range of electrical effects associated with co-ordination by double-bonded ligands, it is not intended to imply that the dative σ- and π-bonds are independent. On the contrary, since one tends to neutralise the electrostatic effects of the other they will enhance each other, increasing together without effect on the net charge transfer, but strengthening the double bond.

Transmission of the Directing Forces across the Metal Atom.—As we have shown, ligands in complex compounds should exhibit strong inductive and mesomeric effects; however, the inductive effect, being largely electrostatic in character, should affect all the other ligands (B) attached to the same metal atom in a similar manner. On the other hand, the mesomeric effect would influence almost entirely the *trans*-position, just as in benzene chemistry it affects the *ortho-* and *para*-positions preferentially. Fig. 2 showing the ligand A bound by $p_{\pi} - d_{\pi}$ dative π-bonding illustrates how this occurs. The d_{xz} orbital stretches right across the atom, and so the electron withdrawal into the regions of the dative π-bond *aa'* will reduce the electron density in the antinodes *bb'* in *trans*-positions to *aa'*. If the ligand B in *trans*-position to A has an unfilled π-type orbital capable of dative π-bonding with *bb'* it enters into direct competition with the ligand A for *d*-electrons. Thus the strength of dative π-bonding at B is considerably reduced from what it would be if A were a ligand with little or no double-bonding properties. In this way strong double bonding of the metal to A leads to weak double bonding to B in the *trans*-position. The ligands in *cis*-positions relative to A are, however, only slightly influenced because the d_{xy} and d_{yz} orbitals, at right angles to A–M–B, are affected only by the electrostatic effect of electron withdrawal by A, and this equally affects B.

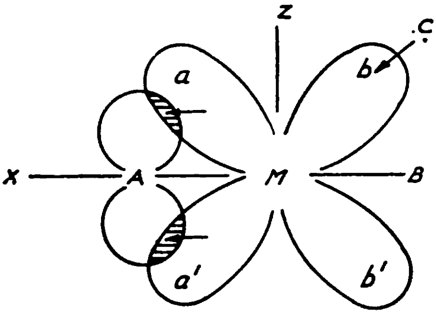


FIG. 2. *Electron withdrawal by the ligand A from a* d-*orbital of the metal* M *on forming a dative π-bond, and proposed mechanism of substitution of* B *by a donor* C *in presence of a ligand* A *of high* trans-*effect.*

Mechanism of the trans-*Effect.*—Current theory assumes that the *trans*-effect operates by the weakening of the bond in *trans*-position to a ligand A of high *trans*-effect. However, the double-bonding hypothesis leads to the deduction that *trans*-bond weakening will only occur if the *trans*-group, B, also has a high *trans*-effect. In fact, a group A of high *trans*-effect facilitates the replacement of the *trans*-group, B, whether it (B) has a low or high *trans*-effect and so the double-bonding hypothesis and assumption of universal bond weakening are incompatible. A mechanism which fits the facts better than that of *trans*-bond weakening is however available.

If all the groups attached to the metal atom have a low *trans*-effect, the withdrawal of *d*-electrons to form dative π-bonds will be small and the electron density in the *d*-orbitals of the metal will be high, thus discouraging nucleophilic attack at the *d*-orbitals. It must be emphasised that all substituting reagents in complex chemistry are nucleophilic. The slow displacement reaction may therefore occur by slow S_N1 dissociative or S_N2 associative mechanism. However, if one of the ligands is replaced by a ligand of high double-bonding capacity the *d*-electron withdrawal from the metal atom will increase its electron affinity. Evidence of this increased electron affinity in the platinous series of complexes is provided by the resistance to oxidation shown by platinous complexes containing groups of high *trans*-effect; *e.g.*, $K[C_2H_4PtCl_3]$ shows the same resistance to oxidation as $K[NH_3PtCl_5]$ (Hel'man and Ryabchikov, *Compt. rend. Acad. Sci., U.R.S.S.*, 1941, 33, 462) and $(CO)_2PtCl_2$ is prepared in presence of chlorine. The increase in electron affinity will facilitate nucleophilic attack and so accelerate an S_N2 reaction. Also, since the electron withdrawal occurs particularly from the regions *bb'*, it facilitates the introduction of groups to the side of the molecule remote from the group A, and near to the *trans*-group B, which may then be eliminated and replaced by the substituting group C (Fig. 2). The greater the double-bonding properties of A the greater the electron affinity of the metal atom, especially in the regions *bb'*, and the faster the rate of substitution. In this way the double-bonding hypothesis predicts that the slow substitutions characteristic of *cis*-substitution may be S_N1 or S_N2 reactions, but the fast substitutions occurring in complex compounds containing a group of high *trans*-effect should be of S_N2 type and the greater speed of *trans*-substitution would be due to a lowering of the activation energy of formation of the transition state, rather than to a weakening of the *trans*-bond.*

The fact that the *trans*-effect was first noticed in platinous complexes rather than in those of other metals is not fortuitous, because electronic conditions in platinous complexes are especially favourable to the development of directing effects by the mechanism just outlined. These favourable conditions are that : (1) Double bonding is facilitated in the last transition series where the 5*d*-orbitals have energy levels close to the 6*s* and 6*p* (distinction from palladium and nickel). (2) The vacant $6p_z$-orbital of the platinum atom, by hybridisation with the $5d_{xz}$-orbital, produces π-type orbitals especially favourable for dative π-bond formation (see Fig. 1) (Craig *et al., loc. cit.*). When one of these is involved in dative π-bond formation, the other, in much the same place as the antinodes *bb'* of the pure *d*-orbital (Fig. 2), is available to receive the lone electron pair of the attacking nucleophilic reagent. (3) Platinum(II) forms a unique series of configurationally stable complex compounds with a greater variety of ligands than any other acceptor atom. (4) The square planar dsp^2 arrangement of bonds brings the substituting ligand entering in the regions *b* or *b'* uniquely close to the *trans*-ligand B, causing 100% *trans*-substitution when A has a high *trans*-effect (Fig. 2).

It seems doubtful whether any metal in a common valency state, except gold(III), will show the *trans*-effect so strongly as platinum(II). The double-bonding hypothesis is simple and explains the known facts; it also allows the prediction of effects undiscovered. These are at present under investigation and will be described in subsequent communications; preliminary results indicate general accord with the double bonding hypothesis of the *trans*-effect.

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* *Note added* 24*th June*, 1955.—Zvyagintsev and Karandasheva (*Doklady Akad. Nauk S.S.S.R.*, 1955, **101**, 93) have just published the results of a kinetic study of the reaction of pyridine with a series of compounds of the type K[NH_3PtXYZ], where X, Y, and Z are halogens or nitro-groups; X is the group replaced under the *trans*-influence of Z, and both of these groups are in *cis*-positions relative to NH_3. They find that the reaction has second-order kinetics. As the rate constant increases, indicating increasing *trans*-effect of Z, the activation energy of the substitution decreases; this is in accord with our hypothesis.