Coordination Chemistry Reviews, 17 (1975) 1—98

THE MUTUAL INFLUENCE OF LIGANDS IN TRANSITION METAL COORDINATION COMPOUNDS WITH MULTIPLE METAL—LIGAND BONDS

E.M. SHUSTOROVICH, M.A. PORAI-KOSHITS and Yu.A. BUSLAEV

The N.S. Kurnakov Institute of General and Inorganic Chemistry,
Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

(Received July 12th, 1974)

CONTENTS

A. INTRODUCTION

The mutual influence of ligands in complexes is one of the fundamental problems in coordination chemistry as it determines the relative changes in properties of the complex that occur upon replacement of one ligand by another. The variety of known coordination compounds is so large that general regularities in the mutual influence of ligands can be established only for some series of related compounds.

In view of this the quasi-square MXL_3 and quasi-octahedral MXL_5 transition metal complexes are most favourable. In such complexes a direct influence of the ligand X upon the *trans* ligand L (in the linear $X—M—L_{trans}$ fragment) is usually stronger than that on the *cis* ligand L (in the triangular $X—M—L_{cis}$ fragment). I.I. Chernyaev was the first [1] to reveal such a regularity in 1926 in substitution reactions of $Pt^{II}XL_3$ complexes. These investigations lead to the conclusion that although the aforementioned regularity of *trans*-influence is of rather general character, there are no (and cannot be) universal series of *trans*-influence since such series would depend not only on the ligands X and L and the metal atom M, but also on the properties of the complex. In particular, it is reasonable to distinguish the equilibrium properties of the M—L bond (e.g., the internuclear distance R_{ML}, the spin-spin coupling constant J_{ML}, the force constant K_{ML}) from those appearing in kinetics of substitution reactions of the L ligand. The first group of properties is determined by the structure of the MXL_n complex itself (in the ground and excited states), while the second group is determined by the reaction transition state and thus depends on the reaction mechanism and in principle upon all reactants. Therefore, it is convenient to introduce different terms: the *trans*-influence of ligand X on the equilibrium properties of the $M—L_{trans}$ bond and the *trans*-effect of ligand X on the rate of L_{trans} ligand substitution by some nucleophile. We shall use this terminology in the ensuing discussion*.

Since the reactivity of complexes has drawn the attention of chemists for a long time whilst precise measurements of various properties of the metal—ligand bond (and especially their interpretation) have been published much later, we find the *trans*-effect series more often in the literature than the *trans*-influence.

The *trans*-effect series should, in principle, be more characteristic, and this appears to be true [5—7]. For example, such a series depends not only on the nature of the metal [8], but on the strength of the nucleophile [9]. The *trans*-influence series, however, is not very characteristic. Other conditions being equal, it depends on what property of the $M—L_{trans}$ bond is being used as an indicator, since different properties are determined by different features of the electronic structure of the complex, among which an unequivocal correlation does not always exist [3,5].

One can think that the relative weakening of some bonds and the

---

* We accept the terminology of the papers [2,3], but we consider the *trans*-influence in both the ground and excited states of the complex (the latter is important, e.g., when considering its photochemical excitation). In general, however, this terminology is not generally accepted. Some authors make no difference between *trans*-influence and *trans*-effect [4], or consider the *trans*-effect to be of broader concept than the *trans*-influence [5].

strengthening of other bonds is the most general evidence of mutual ligand influence. Therefore, it would be most convenient to adopt *trans*-lengthening (shortening) of the $M—L_{trans}$ bond caused by its *trans*-weakening (strengthening) as a measure of the *trans*-influence of the ligand X. In fact the internuclear distances are the only bond characteristics directly observed. Thus, the internuclear M—X and M—L distances give a basis for establishing the *trans*-influence series experimentally. Mason and co-workers have proposed such a series for some square [10] and octahedral [11] complexes. A theoretical interpretation of the series described [10,11] will be discussed in section B (iii). Now we note only that such a series of *trans*-influence has been suggested for ligands which form no more than one covalent σ-bond with the metal atom (e.g., for acidogroups CO_3^{2-}, SO_3^{2-}, Hal^-, NO_2^-, NCS^-, CN^- and for CO, C_2H_4, PR_3, H_2O, NH_3, H, CR_3, SiR_3 etc.). Even if some multiple metal—ligand bonds occur, then their π-components are of the donor-acceptor or dative character*. Experiments show that for such ligands the maximum *trans*-lengthening (Δ_{trans}) is no more than 0.2 Å and for some members of the series the difference in Δ_{trans} may become 0.01—0.02 Å. It is rather hard to separate such small differences from the effects of purely steric factors (and from the experimental errors). All this complicates the theoretical interpretation of the nature of the *trans*-influence.

The effects of *trans*-lengthening are much more explicit in complexes with covalent multiple metal—ligand bonds. First of all they include the nitrido-, oxo- and imino-transition metal complexes MXL_5 (X = N, O, NR) and the binuclear clusters with a multiple metal—metal bond. The *trans*-lengthening caused by multiple bonds has been established for a great number of compounds: both in various mono- and polynuclear complexes and in the infinite coordination structures of the double oxide type and their analogues. The stereochemistry of these compounds, including the empirical regularities of *trans*-lengthening and mutual location of the multiple bonds in the complexes and coordination polyhedra, has been widely covered [12—17] in the annual "Advances in Crystallochemistry of Complex Compounds" since 1966. However, only recently did the possibility arise of considering and classifying this vast and rapidly growing experimental material on a general theoretical basis.

---

* It is true that the terms "donor-acceptor" and "dative" mean the same thing as they describe bonding between a lone pair of the donor and a vacant orbital of the acceptor. However, in such a bond AB, if we wish to distinguish between A:→B and A←:B, we have to use two different terms. The term "donor-acceptor bond AB" is preserved only for the case A←:B (where A is an acceptor), whilst for the case A:→B (where A is a donor) the term "dative (back-donation) bond AB" is introduced. In particular, if we speak about metal—ligand bonds, the term "donor-acceptor" always corresponds to the M←L bond (where the ligand is a donor) and "dative" corresponds to M→L (where the metal atom is a donor). So, throughout the manuscript the term "dative" always means "back-donation", but the term "donor-acceptor" will be used indiscriminately.

The present review contains the results of this analysis. Part B gives the general theoretical approach to the structure of complexes with multiple metal—ligand bonds in terms of the model of *trans*-influence based on the nodal pattern of molecular orbitals (both σ- and π-types). The analytical form of this model is more advantageous than other existing versions of the theory of *trans*-influence (it will be demonstrated in section B (iii)). Parts C, D and E deal with various stereochemical peculiarities of the compounds with multiple bonds. Parts F, G, H and "Note added in proof" give some related material and concluding remarks on the problem of the mutual influence of ligands.

B. THEORY

(i) General considerations

We have mentioned already that we are interested in systems where the mutual influence of ligands is predominantly the *trans*-influence. The theory of *trans*-influence should give answers to at least two questions: 1) why (other conditions being equal) the directed influence of ligand X affects the *trans*-position more than the *cis*, 2) how the properties of the X—M and M—L bonds in the linear X—M—L fragment depend on the nature of X, M and L.

Until recently an answer to the first question was that the spatial properties of *p* and *d* orbitals favour the transmittance of influence in the *trans*-position. As there is a greater number of *cis*-ligands (twice the number in square and four times in octahedral complexes), the relative influence on the *cis*-ligands is weaker (see, e.g. ref. 4). However, in such a general form this supposition should be valid for both transition and non-transition element complexes. A lot of experimental material is available for the transition elements that confirms the regularity of *trans*-influence. However in the case of non-transition elements this problem has not been adequately studied experimentally due to the lack of relevant data. Meanwhile, a model [18] has recently been suggested according to which the *trans*-influence should take place only in transition metal complexes while for non-transition element compounds the *cis*-influence should be observed*.

In any event, the answer to the first question for transition metal complexes seems, if not sufficiently clear, then at least non-contradictory. We may consider the *trans*-influence as a fundamental experimental regularity and thus deal with the analysis of linear X—M—L fragments. For a better understanding of our approach and its comparison with the approaches of other authors we note the following.

1. An analytical model of the *trans*-influence is more desirable since in

---

* The model [18] has been developed in terms of the equivalent orbital theory for σ-bonds of the central atom with acidoligands including only one-center matrix elements (for the central atom). The model does not take into account the donor-acceptor interactions and π-bond formation. The role of these factors will be discussed here. (See also "Note added in proof".)

principle an analytical relationship among different parameters of the ligands and the metal is unequivocal.

2. There is no sense in using a sophisticated computational method for the analysis of such a model since separation of the X—M—L fragment from the actual complex makes any direct quantitative comparison of the results obtained with experimental data impossible (see, e.g. similar discussion in ref. 19). In particular it is reasonable to employ the MO Hückel approach with Coulomb integrals α_A specifying the energy levels and resonance integrals β_{AB} (proportional to the overlap integrals S_{AB}) being the interaction energies of the levels. In terms of such an approximation and in first order perturbation theory, the stabilization (destabilization) energy of the lower (upper) level may be found as (see, e.g. ref. 20)

$$E_{AB} \sim \beta_{AB}^2/|\alpha_A - \alpha_B| \tag{1}$$

3. The parameters of the model (the above mentioned integrals, the MO—LCAO coefficients, etc.) should depend on the nature of the M—X and M—L bonds, i.e. whether their σ- and π-components are bonding or anti-bonding and whether they are covalent, donor-acceptor or dative.

Here and later the term "covalent" will be used for the bond (or its component) formed by the interaction of unpaired electrons. For the purpose of this work it is essential to distinguish such a covalent bond from the donor-acceptor and dative bonds. If we consider a polar covalent bond X—M (where an acidoligand X is more electronegative than a metal atom M) the other representation of this bond will be $\overline{X}{:}\rightarrow\overset{\downarrow}{M}$. In this sense we can compare the structures $\overline{X}{:}\rightarrow\overset{\downarrow}{M}$, $X{:}\rightarrow M$ and $X\leftarrow{:}M$ for covalent, donor-acceptor and dative bonds MX, respectively. Then in the first case the increase of overlap population (which is a measure of mixing and overlapping of interacting levels) leads to a decrease of bond polarity, while in the last two cases the bond polarity increases. Consequently only such a "covalent" bond can be distinguished from an "ionic" bond while the distinction between the covalent and ionic character of donor-acceptor or dative bonds is meaningless*.

From general quantum mechanical considerations it follows that the mixing of interacting levels (χ_A and χ_B) is greater when their energies (α_A and α_B) are closer and their interaction is stronger ($\beta_{AB} \sim S_{AB}$) which is partially described by eqn. (1)**. Since the bond formation results in an electron density redistribution with the change of initial energy levels, the nature of this bonding directly affects the bond strength and the MO—LCAO structure corresponding to this bond.

---

* Only with the simultaneous formation of donor-acceptor and dative bonds due to opposite shifts of charges (the synergistic effect) may the high overlap population take place with low polarity of the resulting multiple bond as in the case of a covalent (ordinary or multiple) bond.

** In general [21] for MO—LCAO $\varphi = c_A\chi_A + c_B\chi_B$ the relation is valid $(c_B/c_A)^2 = [\frac{1}{2}(q - (q^2+4)^{1/2})]^2$ where $q = (\alpha_A - \alpha_B)/\beta_{AB}$.

(ii) Trans-influence and the nodal structure of molecular orbitals

Let us consider the linear X—M—L fragment. Since the *trans*-influence of the ligands X and L is mutual, X alters the equilibrium properties of the M—L bond and vice versa. If, however, the M—X bond is essentially stronger than the M—L bond then the influence of ligand X would be more pronounced, i.e. the changes in properties of the M—L bond would be the more sensible indicator. In this case we are able to distinguish the true "influencing" ligand X and the "influenced" ligand L. This case is the subject of the present paper.

In view of symmetry in the linear X—M—L fragment both σ- and π-three-center MO's are formed. Let us consider how *trans*-influence modifies the structure of these MO's. We shall start with the analysis of σ-type orbitals.

I. A nodal structure of σ-MO's [22,23]

Let us accept that the valence σ—MO's of the X—M—L fragment result from an interaction of some hybrid ligand χ_X and χ_L orbitals with hybrid $\chi_M^{(1)}$ and $\chi_M^{(2)}$ orbitals of the metal. The σ-MO's formed (two lower, bonding, (ψ_1 and ψ_2) and two upper, antibonding, (ψ_3 and ψ_4) have the general form:

$$\psi_i = c_{iX}\chi_X + c_{iM}^{(1)}\chi_M^{(1)} + c_{iM}^{(2)}\chi_M^{(2)} + c_{iL}\chi_L \qquad (i = 1, 2, 3, 4) \tag{2}$$

where the c_{iA} coefficients and the composition of hybrid orbitals χ_A's may be found by the variation method (in principle using the conventional SCF—MO—LCAO scheme). When $X \neq L$ the self-consistent orbitals $\chi_M^{(1)}$ and $\chi_M^{(2)}$ are not equivalent. However in the starting approximation we make them equivalent and take into account the differences in M—X and M—L bonds only with $c_{iM}^{(1)}$ and $c_{iM}^{(2)}$ coefficients.

Let us begin with the structure of σ-MO's for the identical ligands X = L. In this case the bonds M—X (M—L) are completely equivalent. The central atom gives at least two orbitals which should have different symmetry, namely, symmetric and anti-symmetric with respect to inversion at the center of the X—M—X fragment. A symmetric orbital $\chi_M^{(S)}$ will be of an *s* or *d* type, an anti-symmetric orbital $\chi_M^{(AS)}$ of *p* type. Both $\chi_M^{(S)}$ and $\chi_M^{(AS)}$ take part in bonding by participating in the formation of bonding MO's. As is obvious from Fig. 1a, if the nodeless LCAO with $\chi_M^{(S)}$ has the form

$$\psi_1 \sim \chi_X + \chi_M^{(S)} + \chi_L \tag{3}$$

then the nodeless LCAO with $\chi_M^{(AS)}$ must have the form

$$\psi_2 \sim \chi_X + \chi_M^{(AS)} - \chi_L \tag{4}$$

The respective antibonding (two-nodal) LCAO—MO's will be

$$\psi_3 \sim \chi_X - \chi_M^{(S)} + \chi_L \tag{5}$$

$$\psi_4 \sim \chi_X - \chi_M^{(AS)} - \chi_L \tag{6}$$

(normalizing coefficients are omitted).

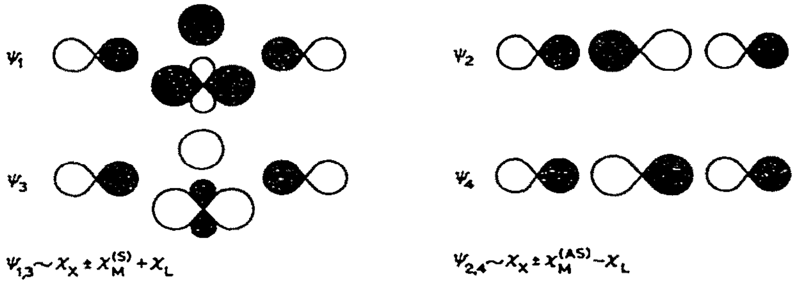


Fig. 1a. The formation of σ-molecular orbitals in the linear fragment X—M—L in the case X=L. The nodal structures of bonding (ψ_1 and ψ_2) and anti-bonding (ψ_3 and ψ_4) molecular orbitals are shown. See text for significance of formulae.

Let us emphasize that the four-orbital MO's of type (2) transform into the three-orbital MO's (3)—(6) only due to the fact that in this case the hybrid metal orbitals

$$\psi_M^{(1)} \sim \chi_M^{(S)} + \chi_M^{(AS)} \tag{7}$$

$$\psi_M^{(2)} \sim \chi_M^{(S)} - \chi_M^{(AS)} \tag{8}$$

are completely equivalent and $c_{iM}^{(1)} \equiv c_{iM}^{(2)}$. At the same time when X $\neq$ L, due to $c_{iM}^{(1)} \neq c_{iM}^{(2)}$, the MO (3) would necessarily contain an admixture of antisymmetric orbital $\delta\chi_M^{(AS)}$ while MO (4) would have an admixture of symmetric orbital $\delta\chi_M^{(S)}$, i.e.

$$\psi_1 \sim \chi_X + \chi_M^{(S)} + \delta\chi_M^{(AS)} + \chi_L \tag{3'}$$

$$\psi_2 \sim \chi_X + \delta\chi_M^{(S)} + \chi_M^{(AS)} - \chi_L \tag{4'}$$

The effect of such admixtures on the properties of M—X and M—L bonds is always opposite: a loop in the region of one bond corresponds to a node in the region of the other bond. In other words, one bond is strengthening at the expense of the weakening of the other bond while the electron density redistribution in the X—M—L fragment (with respect to an "initial" state with X = L) would be more significant with increase of the contribution of such admixtures. Let us estimate this contribution.

If the line X—M—L is chosen as z-axis then the equivalent hybrid metal orbitals will be written in the form

$$\chi_M^{(1)} = a_s s + a_d d_{z^2} + a_p p_z = \chi_M^{(S)} + \chi_M^{(AS)} \tag{7'}$$

$$\chi_M^{(2)} = a_s s + a_d d_{z^2} - a_p p_z = \chi_M^{(S)} - \chi_M^{(AS)} \tag{8'}$$

where, with the slight difference of (3)—(8), the symmetric $\chi_M^{(S)}$ and the antisymmetric $\chi_M^{(AS)}$ components are given in the explicit and normalized form.

Neglecting the overlap integrals the orthonormalized two-center σ-MO's may be given as

$$\varphi_1 = A\chi_M^{(1)} + C\chi_X \tag{9}$$

$$\varphi_2 = B\chi_M^{(2)} + D\chi_L \tag{10}$$

$$\varphi_3 = A\chi_X - C\chi_M^{(1)} \tag{11}$$

$$\varphi_4 = B\chi_L - D\chi_M^{(2)} \tag{12}$$

where $A^2 + C^2 = B^2 + D^2 = 1$, the coefficients A, B, C and D are positive; thus φ_1 and φ_2 are bonding while φ_3 and φ_4 are antibonding MO's.

The bonding (ψ_1 and ψ_2) and antibonding (ψ_3 and ψ_4) three-center canonical σ-MO's may be generated by mixing the respective localized φ_i MO's:

$$\psi_1 = \mu\varphi_1 + \lambda\varphi_2 \tag{13}$$

$$\psi_2 = \lambda\varphi_1 - \mu\varphi_2 \tag{14}$$

$$\psi_3 = \rho\varphi_3 + \tau\varphi_4 \tag{15}$$

$$\psi_4 = \tau\varphi_3 - \rho\varphi_4 \tag{16}$$

where $\mu^2 + \lambda^2 = \rho^2 + \tau^2 = 1$ and the coefficients μ, λ, ρ and τ are positive. Combining (7)—(12) with (13)—(16) we have

$$\psi_1 = \mu C\chi_X + (\mu A + \lambda B)\chi_M^{(S)} + (\mu A - \lambda B)\chi_M^{(AS)} + \lambda D\chi_L \tag{17}$$

$$\psi_2 = \lambda C\chi_X + (\lambda A - \mu B)\chi_M^{(S)} + (\lambda A + \mu B)\chi_M^{(AS)} - \mu D\chi_L \tag{18}$$

$$\psi_3 = \rho A\chi_X - (\tau D + \rho C)\chi_M^{(S)} + (\tau D - \rho C)\chi_M^{(AS)} + \tau B\chi_L \tag{19}$$

$$\psi_4 = \tau A\chi_X + (\rho D - \tau C)\chi_M^{(S)} - (\rho D + \tau C)\chi_M^{(AS)} - \rho B\chi_L \tag{20}$$

The energy level diagram for all the σ-levels mentioned is shown in Fig. 1b.

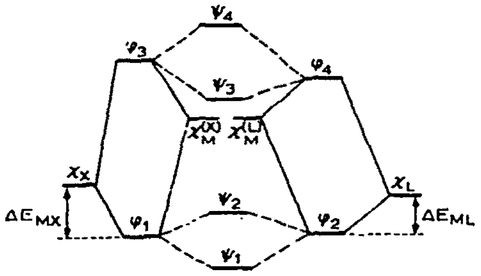


Fig. 1b. Energy level diagram for the X—M—L fragment σ-MO formation (see explanation in the text).

Equation (1) was taken into account while constructing this diagram.

Let us estimate the relative values of the coefficients in MO—LCAO's (9)—(20). Since X and L are more electronegative than M, in equations (9)—(12) $A < C$ and $B < D$. We have already mentioned that it is reasonable to explain the bond strengthening by the increase of overlap population (the degree of mixing and overlapping of interacting levels). For the typical cases discussed here (see part C) $|\alpha_L| > |\alpha_X| > |\alpha_M|$ and $|\beta_{MX}| > |\beta_{ML}|$. Taking into account eqn. (1), we obtain $A > B$ and therefore $D > C$. For the same reason, $\Delta E_{MX} > \Delta E_{ML}$, thus the energies of levels φ_1 and φ_2 tend to become closer, while the level φ_3 should move above φ_4 (see Fig. 1b). Thus in eqns. (13)—(16) $\mu \approx \lambda$ and $\rho < \tau$, hence in MO—LCAO's (17)—(19) all coefficients in brackets are positive and only in eqn. (20) the coefficient $\rho D - \tau C$ may have both positive and negative sign. Thus, the sign distribution in σ-MO—LCAO's (17)—(20) would result in the distribution of nodes in the M—X and M—L bonds shown in Table 1.

The formation of two σ-bonds, M—X and M—L, corresponds to the occupation of the lower (bonding) orbitals ψ_1 and ψ_2 by four electrons. As seen from Table 1 (and relations (3')—(4') for $1 \gg \delta > 0$) the nodes appear only in the region of the M—L bond, thus the M—L bond should be weakened.

So, the proposed model clearly reveals the general mechanism of transmittance of the *trans*-influence through the σ-MO's. Any strengthening of the X—M bond results in an increase in the electron density in the X—M region and in a decrease in the M—L region. The degree of non-equivalence of the X—M and X—L bonds (and their mutual influence) may be estimated from the relevant algebraic coefficients.

It should be pointed out here that in the modern theory of *trans*-influence

TABLE 1

The character of overlap of σ-orbital components in the M—X and M—L bond regions

ψ_i	Symmetry of a central atom component	A bond[a)	
		M—X	M—L
ψ_1	S	+	+
	AS	$\delta+$	$\delta-$
ψ_2	S	$\delta+$	$\delta-$
	AS	+	+
ψ_3	S	—	—
	AS	$\delta+$	$\delta-$
ψ_4	S	$\delta\pm$	$\delta\mp$
	AS	—	—

---

a) The sign + means positive overlap (the absence of node), the sign — means negative overlap (the presence of node).

there still exist two opposite viewpoints where the *trans*-weakening is explained either by the increase of the *sd*- or *p*-contributions in the hybrid metal orbital respectively. The appropriate quantitative estimations are rather ambiguous and sometimes contradictory; in any case the nature of metal (and ligands) may play a significant role [3—8].

In our discussion we combine both extreme viewpoints since from eqns. (17) and (18) it follows that all hybrid components take part in the strengthening (weakening) of the non-equivalent bonds. If the M—X and M—L bond strengths differ slightly, the $\mu A - \lambda B$ and $\lambda A - \mu B$ differences may, in general, have opposite signs, thus the *sd*- and *p*-contributions to the strength of the same M—Y bond would be partly cancelled (see also refs. 340, 341).

Taking into account the values of the coefficients and the nodal structure of antibonding ψ_3 and ψ_4 orbitals it follows that their occupation by electrons should simultaneously weaken both the M—L and M—X bonds with possible change and even reversion of their relative strength. These facts may be responsible for the *trans*-influence in complexes where the number of valence electrons exceeds 18, and in the photochemical excitation of ordinary complexes (with only bonding orbitals occupied in the ground state*). We would like to emphasize here that in principle the features of complex structure mentioned above may be explained only by our model of *trans*-influence that takes into account the peculiarity of both bonding and antibonding MO's through their nodal structure.

Let us come back to the bonding ψ_1 and ψ_2 MO's. We have already mentioned that $\mu \approx \lambda$, hence

$$\psi_1 \sim C\chi_X + (A + B)\chi_M^{(S)} + (A - B)\chi_M^{(AS)} + D\chi_L \tag{17'}$$

$$\psi_2 \sim C\chi_X + (A - B)\chi_M^{(S)} + (A + B)\chi_M^{(AS)} - D\chi_L \tag{18'}$$

Although there is no direct relation between the A and B coefficients, it is reasonable to assume their changes to be opposite (thus, levelling donor and acceptor electron density shifts in the M—X and M—L bonds). In part F we shall see that the effective metal atomic charges in such complexes do not usually change significantly. Thus, one may assume that the sum $A + B$ (or $A^2 + B^2$) changes slightly and the mutual influence of ligands X and L is determined first of all by the $A - B$ difference.

As stated above, the quantity A should increase with the decrease of $|\alpha_X|$ and the increase of $|\beta_{MX}|$. The quantity B decreases with increase of $|\alpha_L|$ and the decrease of $|\beta_{ML}|$**. The changes in these parameters evidently relate to the nature of metal—ligand bonding, namely, the formation of a covalent M—Y bond (with participation of unpaired electrons) results in the decrease

---

* In particular, if the ligand L is more labile in the ground state, then the ligand X could display the higher lability in the excited state [24].

** Naturally one should distinguish the parameters $\beta_{MY}^{(S)}$ and $\beta_{MY}^{(AS)}$ (Y = X, L) in the quantitative calculations.

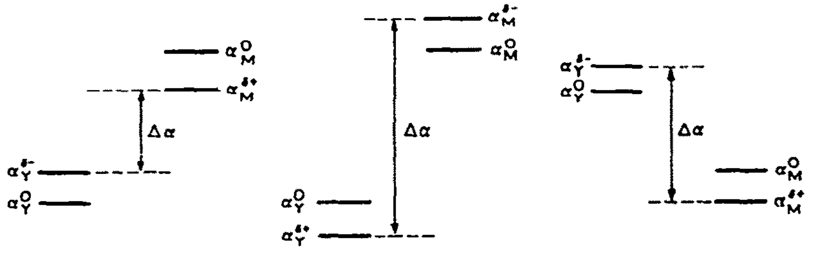


Fig. 2. Energy level diagram for the metal M—ligand interaction: the self-consistent difference $\Delta\alpha = |\alpha_M - \alpha_Y|$ decreases for (a) a covalent bond and increases for (b) donor-acceptor and (c) dative bonds.

of $|\alpha_Y|$ (due to the increase of the electron density on Y). On the other hand, the formation of a donor-acceptor M←Y bond increases $|\alpha_Y|$ (due to the decrease of the electron density on Y). The quantity $|\alpha_M|$ changes in the opposite way. Thus upon the formation of a covalent M—Y bond the initial energies of levels α_M and α_Y become closer, but they grow further apart when the donor-acceptor M←Y bond is formed (Fig. 2). Thus, a self-consistent difference $|\alpha_M - \alpha_Y|$ for a covalent bond is small but for a donor-acceptor bond is large. However, a self-consistent sum $|\alpha_M + \alpha_Y|$ (or any other average value of α_M and α_Y) tends to be approximately constant.

The last point is essential in estimating the value of β_{MY}. Let us remember that most approximations for β_{AB} include the product of an overlap integral and some average value [25] of α_A and α_B*. The tendency towards retention of average values of α_M and α_Y (their self-consistent change) justifies the use of the simplest relation $\beta_{MY} \sim S_{MY}$. One can assume that in typical cases of covalent bonding, the value S_{MY} will be larger than that for the typical donor-acceptor bonds due to two reasons. Firstly, at a given internuclear distance the integral S_{MY} is usually smaller for the donor-acceptor interaction since the vacant orbitals are more diffuse. Secondly, the integral S_{MY} is quite sensitive to an internuclear distance that changes self-consistently depending on the M—Y bond strength. In comparison with a donor-acceptor bond, an internuclear distance in a covalent bond is shorter**. We may add here that the increase in the total M—X multiplicity (of interest to us) results in the strengthening of its σ-component (due to the bond shortening), i.e. in the growth of $\beta_{MX} \sim S_{MX}$. Since ΔE_{MX} versus β_{MX} is quadratic, the *trans*-influence of the ligand X should increase.

Thus, on the basis of eqn. (1) and the arguments given one may state that

---

* The dependence of β_{AB} on α_A and α_B becomes more obscure with more accurate consideration taking into account the two-center kinetic energy [25—27].

** This is easily seen if one compares relevant bonds with the same atoms, e.g. with NCS^- and NH_3 or OH^- and OH_2 ligands (see part C).

a *trans*-weakening of the M—L σ-bond is favoured by the covalent character of M—X and the donor-acceptor character of the M—L bond. From eqns. (17′) and (18′) it is seen that the weakest M—L bond corresponds to the maximum A and minimum B coefficients. Formally $A_{\max} = 1$ and $B_{\min} = 0$. The first condition corresponds to the presence of the metal lone electron pair, the second one corresponds to the vacant metal orbital. However, such formal extrapolation is beyond the model in question.

Actually, our main point is that the bond strength is determined by mixing and overlapping of the interacting levels regarded to be equivalent hybrid orbitals of the metal. The presence of a lone pair at $A = 1$ means the absence of ligand X, but the relative energies of levels, corresponding to the coordinate axis M—X, will change while the coordination number of the complex changes. Thus the starting approximation of equivalent hybrid orbitals could become unsatisfactory, i.e. the wave functions $\chi_M^{(1)}$ and $\chi_M^{(2)}$ would have structure far from that of (7′)—(8′). Then, the relations (17′)—(18′) become meaningless and the value A is no more an indicator of the degree of *trans*-weakening.

In particular, we can judge the rehybridization in tetragonal pyramidal transition metal complexes by the different angular distortions in such complexes and in similar polyhedra of non-transition elements (Fig. 3). In the latter cases the equatorial ligands always diverge towards an apical ligand (the angles L_{eq}—M—$L_{ap} < 90°$), and this fact (along with others) may be quite successfully interpreted in terms of the localized electron pair theory [28] as a result of the interaction between the "bulky" lone pair at the sixth vertex of the octahedron and the electrons of the M—L_{eq} bonds (see, however, criticism of this theory [29]). Transition metal complexes reveal opposite deviation of the equatorial bonds (the angles [30,31] L_{eq}—M—$L_{ap} > 90°$) which is inconsistent with the idea of a metal lone pair localized in the hybrid orbital extending to the sixth vertex of the octahedron.

Since ligand X is not less electronegative than the central atom M, in eqn. (9) we have $A \leqslant C$. Thus, the physically reasonable maximum value of A is $A_{\max} \leqslant 1/\sqrt{2}$, as a further increase in A should result in a decrease of the M—X bond strength.

The value A characterizes a shift of the electron density towards the metal and thus reflects a σ-donor ability of the ligand X. In this sense the *trans*-influence of the ligand is determined by its σ-donor ability. If $A \leqslant 1/\sqrt{2}$, this statement becomes equivalent to the fact that the *trans*-influence of the li-

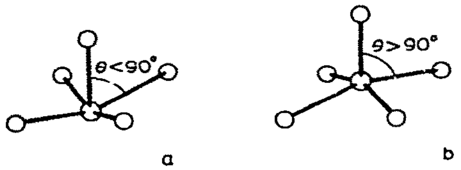


Fig. 3. The stereochemistry of tetragonal pyramidal complexes of (a) non-transition and (b) transition elements. The (a) case is true for 12 σ-electron complexes only.

gand is determined by the strength of its σ-bond with the central atom. However, for $A > 1/\sqrt{2}$ these statements become non-equivalent. The extreme value $A = 1$ (i.e. the presence of a lone pair on the central atom) corresponds to the maximum σ-donor ability of the ligand and to the minimum strength of its σ-bond with the metal atom (due to the absence of such a bond). Such an alternative permits us to check easily what is the most general reason for *trans*-influence. Unfortunately an experimental check of the influence of a lone pair is obscured by the fact that, for symmetry considerations, pure lone pairs do not usually occur. The real pairs occupy various MO—LCAO's with the orbital composition and with the bonding character determined by a minimum of the total energy of a complex.

Rossi and Hoffmann [32] have shown that in C_{4v}-complexes ML_5 the relative strength of the $M—L_{ap}$ and $M—L_{eq}$ bonds must depend on electronic $(n-1)d^m$ configuration of the metal atom. Namely, the $M—L_{ap}$ σ-bond may be both stronger (in the case of d^0—d^6 and d^{10}) and weaker (in the case of d^8) than the $M—L_{eq}$ bond. Really, in the known C_{4v}-complexes ML_5 one observes both possibilities while all these complexes have geometry shown in Fig. 3b [32].

The analysis of the influence of a "vacant orbital" is connected with similar difficulties. Formally, the presence of a vacant metal orbital for $B = 0$ means the absence of ligand L. More precisely, two cases may occur:

1) the σ-donor ligand L forms an infinitely weak donor-acceptor bond with the metal atom; such a case of the "infinitely large" *trans*-influence is trivial;

2) the covalent M—L bond becomes extremely ionic; in terms of the "covalent" model the energy of such a bond is equal to zero. The latter is certainly incorrect (due to the electrostatic interaction).

In general, however, there exist certain relations between the metal—ligand bond strength and the value of negative charge on the ligand (see part F). They could be understood only if we also take into account π-bond formation, which we now discuss.

II. A nodal structure of π-MO's [23,33]

Let us consider the formation of valence π-MO's in the linear X—M—L fragment. Unlike the four-orbital σ-MO basis set, the π-MO basis set is three-orbital. Let this basis include the initial π-orbitals ζ_X, ζ_M and ζ_L which give three π-MO's:

$$\eta_i = m_{iX}\zeta_X + m_{iM}\zeta_M + m_{iL}\zeta_L \qquad (i = 1, 2, 3) \tag{21}$$

where the coefficients m_{iA} are determined by the variation method (the same is true for ζ_A's which, in principle, are the hybrid orbitals, but their composition is insignificant for the discussion).

Taking into account only the signs of the m_{iA} coefficients we adopt, by definition, that the MO

$$\eta_1 \sim \zeta_X + \zeta_M + \zeta_L \tag{22}$$

is nodeless and bonding, while the MO

$$\eta_3 \sim \zeta_X - \zeta_M + \zeta_L \tag{23}$$

having two nodes (between each nuclear pair M—X and M—L) is anti-bonding. The third MO η_2 should have one node (from the orthogonality condition), namely

$$\eta_2^{(1)} \sim \zeta_X + \zeta_M - \zeta_L \quad \text{or} \tag{24}$$

$$\eta_2^{(2)} \sim \zeta_X - \zeta_M - \zeta_L \tag{25}$$

The MO η_2 will be occupied (after MOη_1) if four electrons are located in the starting orbitals ζ_X, ζ_M and ζ_L.

Let the bond M—X be multiple while to a first approximation the M—L bond is single. In such a case one may start from a strong M—X π-bond perturbed by the ligand L. Assume that an initial energy difference for the bonding ($\zeta_X + \zeta_M$) and antibonding ($\zeta_X - \zeta_M$) combinations would be larger than energy splittings due to their interaction with the ζ_L orbital (Fig. 4a). Therefore the form $\eta_2^{(1)}$ should be adopted for MO η_2. In other words, for AO's of η_2 it is more favourable energetically to have a node (negative overlap) in the region of the weaker M—L bond (with the larger internuclear distance) rather than of the stronger M—X bond (with the smaller internuclear distance). The occupation of MO $\eta_2^{(1)}$ by electrons should result in the weakening of the M—L bond and in the strengthening of the M—X bond (with respect to the state when only MO η_1 is occupied).

In principle it is not excluded that if due to some factors the M—X bond is weakened (elongated) and the M—L interaction is large, then the MO $\eta_2^{(2)}$ energy would become lower than that of $\eta_2^{(1)}$ (see Fig. 4b). In such a case the M—X bond would become weaker while the M—L bond gets stronger.

One should remember however that regardless of the MO η_2 type ((24) or (25)) the order of the M—L π-bond is always positive. Actually, using the general relation

$$\sum_i^{\text{occ}} m_{iA} m_{iB} = -\sum_j^{\text{vac}} m_{jA} m_{jB} \tag{26}$$

(where the indices *i* and *j* refer to the occupied and vacant MO's respectively) and the form of the vacant MO η_3 (23) we immediately obtain

$$P^{\pi}_{ML} = 2(m_{1M} m_{1L} + m_{2M} m_{2L}) = -2m_{3M} m_{3L} > 0 \tag{27}$$

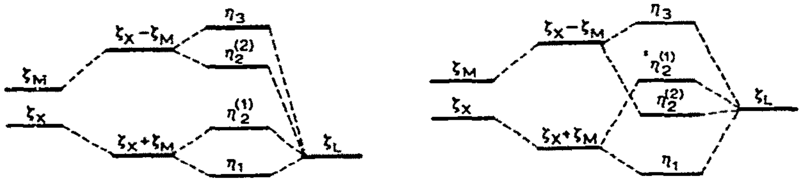


Fig. 4. The X—M—L fragment π-MO formation as a result of the perturbation ((a) weak or (b) strong) of the X—M bond by ligand L (designations are given in the text).

This implies that the π-interaction may only strengthen the initial ordinary M—L bond (whose π-order is equal to zero) at the expense of the decrease of the π-order of the initial multiple M—X bond. In such a case the *trans*-influence through σ- and π-orbitals gives opposite results.

In general if both X and L ligands have π-orbitals, then the M—X and M—L π-bonds formed are competing, i.e. one is becoming stronger at the expense of the other. In this sense the pattern of π-interaction is similar to that of σ-interactions. The orders of both σ- and π-bonds M—L, as it is easy to show, depend in a similar manner on the parameters α_Y and β_{MY}. Namely, the value of P_{ML} decreases (increases) with increase (decrease) of $|\alpha_L|$ and $|\beta_{MX}|$ and with decrease (increase) of $|\alpha_X|$ and $|\beta_{ML}|$ (for P_{MX} the corresponding permutation of the indices is quite obvious)*.

However although the covalent and donor acceptor origin appears in the strength of both σ- and π-components of the M—Y bonds in the same qualitative manner, a quantitative contribution of σ-interactions to the strength of the M—L bond should usually be decisive (since the M—L π-bond is the result of minor perturbation of the M—X π-bond). Thus for typical multiple M—X bonds the weakening influence of σ-interactions should be more significant than the strengthening influence of π-interactions. In general the resulting *trans*-weakening of the "multiple" M—L bond would increase with the decrease of both P^{σ}_{ML} (more weakening of the σ-bond) and P^{π}_{ML} (less strenthening of the π-bond). Therefore, in particular, if the ligand L has no π-orbitals, then $P^{\pi}_{ML} = 0$ and (other conditions being equal) the *trans*-weakening of such a M—L bond should be more significant than that for the ligand L', having π-orbitals (whether occupied or vacant).

The metal—ligand σ-bonds are almost always covalent or donor-acceptor, while the π-bonds are dative as well. Let us consider a dative M→X bond and its influence on the *trans*-weakening of the M—L bond. In typical cases, e.g. for X = CO, C_2H_4, PR_3, the vacant π-orbital ζ_X is essentially higher than the occupied one ζ_M. Therefore, a self-consistent energy difference $|\alpha_X - \alpha_M|$ becomes still larger (as in the case of donor-acceptor interaction, but with an opposite sign of $\alpha_X - \alpha_M$) and the π-bond is relatively weak. Since here the σ-bond is donor-acceptor, then the actual multiplicity and the strength of the M—X bond are rather small. Thus its *trans*-influence should be insignificant.

From ESCA data [34] it can be seen that as a whole the ligand PR_3 behaves as an electron donor while CO and C_2H_4 behave as acceptors. The latter means that the metal—ligand π-back-donation prevails over the donor σ-interaction. This explains the noticeable *trans*-effect of CO and C_2H_4 (which is larger than that of PR_3) in tetracoordinated Pt^{II} compounds. Let us remember that in this case substitution reactions occur most likely via the tetragonal pyramid transition state and the d_π-density concentration in the

---

* This conclusion comes from analysis of a relevant secular equation [33] as well as from our quantitative calculations for a wide range of these parameters (the results may be communicated by request).

M—X region facilitates an attack [6,7] of the *trans*-ligand L by a nucleophile A^-. At the same time the *trans*-influence of CO and C_2H_4 (i.e. their $M—L_{trans}$ bond weakening) is insignificant since the M—CO or $M—C_2H_4$ bonds themselves are generally weak. This is especially true of their σ-components which play the dominant role in the *trans*-weakening mechanism. Of these ligands, only the *trans*-influence of NO is of interest to us (see section C (ii)).

Thus, the behaviour of a dative bond is similar to that of a donor-acceptor bond. Therefore, summing up, we come to the following conclusion.

The M—L bond weakening becomes more important, i) the higher the total M—X bond multiplicity and the larger its covalent (the smaller donor-acceptor and dative) character and, ii) the lower the total M—L bond multiplicity and the larger its donor-acceptor and dative (the smaller covalent) character.

(iii) Comparison with other versions of the trans-influence theory

The modern theory of *trans*-influence is not monolithic. The existing approaches differ in both the initial points and the conclusions obtained. Now we shall discuss how the concepts, described in the previous section, relate to other authors' viewpoints concerning the nature of *trans*-influence*.

Mason and co-workers [10,11] have developed the most detailed model. These authors have suggested that the *trans*-influence is most distinct in systems in which the "influencing" ligand (X) is essentially electroneutral with substantial inductive σ-donor and weak mesomeric π-acceptor properties, while the "influenced" ligand (L) is invariably highly electronegative and is a poor σ-donor and π-acceptor. In such systems, on the basis of simple MO theory, the electron density of the X—M—L σ-molecular orbital will lie principally between the ligand X and the metal M (leading to a strongly covalent X—M bond) and on the ligand L (conferring an increased degree of ionicity to the M—L bond) (ref. 11, p. 1611)**.

These authors were the first to propose a relation of the type (1) as a measure of the metal—ligand σ-bond strength in the form $S^2/|\Delta\epsilon|$, where S is an overlap integral for orbitals with the energy gap $|\Delta\epsilon|$. In this case the relevant sp^3, sp^2 or sp hybrid atomic orbital (of the terminal atom) has been adopted for the ligand σ-orbital, while the pure np_σ-AO serves as the metal σ-orbital. The values $|\Delta\epsilon|$ have been estimated as differences of the relevant valence state ionization potentials (cf. p. 21, however).

---

* We do not consider these viewpoints here as they have recently been reviewed in detail [3,5]. We would like to note only the pioneering work of Langford and Gray [6] (though it concerns *trans*-effect rather than *trans*-influence). These authors were the first to pay attention to the correlation of the bond *trans*-weakening with relevant overlap integrals and to non-coincidence of the σ- and π-effects.

** For the sake of convenience we use our designations for the "influencing" and "influenced" ligands (cf. p. 6) although reverse designations (L and X) are used elsewhere [11].

The authors themselves agree that their model "usually predicts a higher relative *trans*-influencing ability for ligands which possess good π-acceptor properties, e.g., PR_3, CO and C=C. This may be explained by assuming that, in such ligands, the π-acceptor orbitals compete, by a back-donation process, with the ligand L for the excess of charge on the metal, thereby detracting from the effect caused by any inductive σ-donor ability" (ref. 11, p. 1611). The authors have concluded that in both square and octahedral complexes "the *trans*-influence of a ligand arises principally from its inductive σ-donor ability, transmitted to the *trans*-ligand by the appropriate metal p_σ-orbital" (ref. 11, p. 1613).

Our ideas agree with these to a certain extent if an increase of σ-donor ability of the ligand X is understood as an increase in the coefficient A (cf. p. 12, 13). Further, we also come to the conclusion that there is a competition of σ- and π-interactions.

Meanwhile there are a number of points where we disagree. Firstly, it is useful to distinguish covalent and ionic bonds only for the interaction of unpaired electrons (see p. 5). Therefore one cannot consider the statement "the M—L bond ionicity increases as the M—L bond weakens" to be general. Moreover, the purely donor ligands, such as NH_3 or H_2O, and also bridging halogen atoms show considerably higher *trans*-weakening than the most electronegative ligands — terminal halogen atoms with the more polar bonds (cf. experimental data in part C). Secondly, in transmittance of the *trans*-influence our model is not limited to the metal p_σ-orbital, but also takes into account the s- and d-orbitals, the contribution of which may be even more significant (see lower). Thirdly, the role of π-interaction is more complicated than the simple π-donor or π-acceptor charge transfer.

We would like to emphasize that one of the main differences of our model from that of Mason and co-workers is the use of a charge distribution pattern determined not only by the absolute values of MO—LCAO coefficients but also by the nodal structure of molecular orbitals defined by the signs of these coefficients (giving important additional information).

It has been mentioned already that in the Mason and co-workers model the *trans*-influence is transmitted through the central atom p_σ-orbital (which agrees with Langford and Gray's suggestion [6]). However in transition metal atoms the s- and d-orbitals lie below the p-orbital and most likely make the major contribution to bond formation. This leads to the idea (first proposed by Syrkin [35] as early as 1948) that in the formation of non-equivalent M—X and M—L σ-bonds, the bond strengthening (weakening) is a result of the increase (decrease) of s and d character of the hybrid metal orbital.

One has to bear in mind, however, that although an increase of χ-character (s, p or d) in the hybrid $\chi_M^{(X)}$ means a decrease of this character in the hybrid $\chi_M^{(L)}$ (due to normalization), such a relation is not necessarily valid for relevant canonical MO—LCAO coefficients (see eqn. (2)). In other words, there is no direct correlation between χ-characters of the bonds M—X and M—L since the χ-component population (determined by the variation method within the total SCF—MO—LCAO scheme) is not constant, but depends on the nature of ligands and the metal.

The approximate character of the calculations and ambiguity in the population analysis procedure results in rather contradictory statements on the relative role of various components in the basis set (e.g. see the reviews [25,36]). However, the fact that the Sidgwick 18-electron rule suits the transition metal complexes, shows clearly that not only the *ns*- and (*n*—1)*d*- but also *np*-orbitals of the central atom participate in the formation of chemical bonds. This can be easily understood since their energies do not usually differ very much (no more than 5—6 eV, e.g., for elements of the first transition series [37]). On the other hand, this (or a similar) rule is not valid for non-transition element compounds and contributions of *s*, *p* and *d* orbitals are quite different. This phenomenon can be easily understood since here *np*-orbitals are considerably above *ns*- and far below *nd*-orbitals. The appropriate energy differences for elements of group IV and the following groups may exceed [36—39] 10 eV; thus *np*-orbitals should play a decisive role in bond formation. Thus the $sp^m d^n$ hybridization scheme of the central atom may prove to be adequate only in transition metal coordination compounds and not acceptable even as a starting approximation in non-transition element compounds*. (See p. 85 and refs. 320—323.)

Let us discuss again rehybridization as the reason for *trans*-influence. Unfortunately, only one systematic theoretical study devoted to rehybridization in the series of *trans*-$PtCl_2(L)(NH_3)$ complexes (where L = NH_3, H_2O, H_2S, CH_3^-, H^-) has been published [40]. The calculation has been carried out in the framework of the extended Hückel method for the fixed geometry of complexes and with the incomplete iterative procedure (which certainly is not very accurate). The results reported demonstrate that the *trans*-weakening of the Pt-NH_3 bond is associated with a lower overlap population at the expense of the contribution of the *s*- and *d*-platinum orbitals. On the other hand, the *trans*- and *cis*-weakening proved to be very close. It would be wrong to accept this as a general statement. As for the compounds in question, it is rather hard to check these conclusions due to the indirect character of the experimental data (IR spectra)**.

Therefore, up to now a decrease of nuclear spin-spin coupling constants J_{ML} in the NMR spectra serves as the only experimental evidence of the decrease of *s*-character with the weakening of the *trans*-bond M—L, though the relevant experimental material is limited and its interpretation is based on

---

* For example, the concept of almost pure *p*-character of the (three-center) bonds in polyhalides and in the noble gas compounds is already widely adopted. It is rather novel and unexpected that the 2*s*-carbon electron pair in CH_4 is practically lone, thus the tetrahedral structure of CH_4 is by no means determined by sp^3 hybridization [29].

** See also the theoretical analysis of *trans*- and *cis*-influence in Pt^{II} complexes in the series of papers by Baranovskii et al. [41].

rather approximate theory (see the reviews [3,5])*.

In conclusion it is worth mentioning the Pearson approach [43] to the problem of *trans*-influence (and *trans*-effect) in terms of the concept of hard and soft acids and bases (HSAB). It is easy to show that the regularities discussed by Pearson (in particular, the ligand competition for *cis*- and *trans*-positions) are explained quite naturally in terms of our model. This is important as the HSAB concept itself reveals a number of vulnerable points [44].

(iv) The trans-weakening series in MXL_5 complexes with multiple M—X bonds

By definition, in an isolated linear X—M—L fragment the mutual influence of the X and L ligands is *trans*-: both concepts are identical here. However in any real quasi-square or quasi-octahedral complex (MXL_n, MX_2L_n etc.) the *trans*-influence is a result of the mutual influence of all ligands. Hence for a non-contradictory discussion one should bear in mind the following.

The *trans*-influence (the change of properties of the $M—L_{trans}$ bond) appears only as a relative characteristic, namely by comparison with properties of the $M—L_{cis}$ bond** or with those of some conventional "standard" ordinary M—L bond. This complicates the choice of any unequivocal criterion for the estimation of the *trans*-influence and requires special care when comparing compounds which differ by more than one component (X, M and L).

In particular, various steric factors may prove to be of importance, namely non-valence interactions of atoms (groups) to which certain covalent, Van der Waals' and other radii are assigned. Undoubtedly the role of steric factors increases with an increase in the total asymmetry of the complexes. In part C it will be shown, however, that steric factors (in such a sense) are not predominant and do not explain the regularities observed.

Let us consider the structure of quasi-octahedral MXL_5 complexes where the X—M bond is multiple covalent and the ligands L (the same or different) are coordinated (in the first approximation) to the atom M by essentially ordinary σ-bonds. The latter means that the ligand L has either one unpaired electron (e.g. halogens, OH or CN) or no such electron at all (e.g. NH_3, H_2O or PR_3).

In the nitrido-, oxo- and iminocomplexes (X = N, O, NR respectively) the M—X bond has one σ- and two π-components ($\pi\bar{\pi}$) and thus is triple. In nitridocomplexes all three components are covalent ($M\equiv N$), in the oxo- and iminocomplexes one of the components is donor-acceptor ($M\overset{+}{\equiv}O$ and $M\overset{+}{\equiv}NR$). In such complexes a transition metal atom forms eight two-center bonds

---

* Let us remember that this interpretation takes into account only the contact (Fermi) contribution to J_{AB} within the approximation of average excitation energy, which at present causes a lot of doubt (see, e.g., ref. 42).

** In this sense one can speak of the *cis*-influence of the ligand X. However, we shall not consider this problem since it is insufficiently developed and the arguments are often contradictory (see the reviews [3,5]).

with one valence orbital, namely d_{xy}, unused if the molecule has a four-fold z symmetry axis [45]. This d_{xy} orbital may take part in a π-interaction with the equatorial ligands. This fact should be added to the mutual ligand influence scheme described above.

In some transition metal dimeric compounds $M_2L'_8L_2$ with a linear L—M—M—L fragment the d_{xy} orbital participates in M—X bonding (in this case X is M as well) thus this bond becomes [46] quadruple covalent M≣M. Since, however, the fourth bond component is of δ-symmetry it has no analogue at the ligand L and therefore does not directly influence the M—L bond. This influence is only indirect: through the strengthening of the σ- and π-components of the metal—metal bond.

We have pointed out at the beginning of this paper that there exists no universal series of *trans*-influence and comparisons can be reliable only if all other conditions are equal. Bearing in mind both this and the last conclusion of section B(ii) (which summarizes the dependence of *trans*-weakening on the bond multiplicity and covalency) we may generate a series of *trans*-weakening of the M—L bond depending on all three conceivable components X, M and L.

Let us choose a number of ligands that form bonds of formally equal multiplicity (say, triple) with the metal atom. To obtain unequivocal results we shall consider the elements X of the same period (e.g. the second one as the most typical). Then one may predict that $M—L_{trans}$ bond weakening would increase according to X in the sequence:

$$\mathrm{OC}\overset{\leftarrow}{\underset{\leftarrow}{\rightarrow}}, \quad \mathrm{N_2}\overset{\leftarrow}{\underset{\leftarrow}{\overset{\rightarrow}{-}}} < \mathrm{ON}\overset{-}{\rightleftarrows} < \mathrm{RN}\underset{\rightarrow}{=} < \mathrm{O}\overset{-}{\rightrightarrows} < \mathrm{N}\equiv \tag{28}$$

which corresponds to the increase of the M—X bond covalency. However, there are complexes where the *trans*-influence of the NO group is abnormally high. However this happens only in 20 electron compounds where (see p. 43) the destabilization is due to the influence of the last "antibonding" electron pair and the nature of X is less important. Thus to maintain "other equal conditions" it is generally only necessary to compare isoelectronic complexes.

If atoms O and N are bridging, they form quasi-double bonds with the metal atom ($\mathrm{M}\overset{\leftarrow}{-}\mathrm{O}\overset{\rightarrow}{-}\mathrm{M}$ and $\mathrm{M} = \mathrm{N}\overset{\rightarrow}{-}\mathrm{M}$). Therefore their *trans*-influence should become somewhat lower while the larger influence of a nitrogen bridge is retained (due to the same reasons that $\mathrm{N}\equiv$ has a stronger influence than $\mathrm{O}\overset{-}{\rightrightarrows}$).

The *trans*-influence of a metal—metal bond (X = M) has a special place. In typical cases when both M atoms have the same ligand environment we may take $\alpha_X = \alpha_M$; then in eqn. (9), $A = A_{max} = 1/\sqrt{2}$. In principle, one may immediately foresee a strong *trans*-influence of any homonuclear M—M bond (see also ref. 18) with, however, a special peculiarity. Namely, if the M—M σ-bond is not very strong, i.e. ΔE_{MM} is relatively small, then due to $|\alpha_X| = |\alpha_M| \ll |\alpha_L|$ the level φ_1 would be considerably above level φ_2 (cf. Fig. 1b). But in this case in eqns. (13), (14), (17) and (18) $\mu < \lambda$ and it is possible that $\mu A - \lambda B < 0$, thus the M—L σ-bond would be weakened due to the *sd*-metal component but would be strengthened due to the p component*. Therefore, noticeable *trans*-weakening should be expected only for strong (multiple) metal—metal bonds. Experiment readily proves these theoretical predictions (see part C).

Consider the dependence of M—L bond weakening on the nature of L. For example, the σ-component of the metal—halogen bond is covalent and the bond as a whole can be partially multiple. At the same time the metal—NH_3 bond is only ordinary and donor-acceptor. Therefore, *trans*-weakening for halogens (or OH) should always be lower than that for NH_3 (or H_2O, CH_3CN, dioxan etc.). For the same reason, M—L bond lengthening for the terminal ligand L should be less than that for the same bridging ligand. In general, the weaker M—L bond should show the greater lengthening due to the smoother slope of its potential curve.

Finally, let us consider the influence of the nature of metal atom M. We may make the general statement that the greatest *trans*-influence would be displayed by such a metal atom whose orbitals (of appropriate energy, symmetry and occupancy) provide maximum M—X bond strength and minimum M—L bond strength. Therefore the effect of M upon the M—L bond *trans*-weakening should depend on the α_M, β_{MX} and β_{ML} parameters although we used them only for the estimation of the mutual influence of X and L. In principle, the values α_M are most characteristic of the metal atom but it is rather difficult to establish even their relative magnitudes (for different M's). Let us remember that a diagonal matrix element α_M includes both one- and two-center integrals, the latter corresponding to the Madelung ligand field corrections. They are not at all small, so almost all purely atomic (one-center) approximations of α_M have a number of disadvantages [25,26]**.

Hence for the estimation of α_M the average ionization energies of valence orbitals are more often used (moreover, due to a lack of spectroscopic data for heavy elements these energies are systematically calculated only for the first transition series [37]). It is well known, however, (e.g. refs. 27, 48) that a diagonal element in the one-electron model correlates with Mulliken's electronegativity $\frac{1}{2}(I+A)$ (A is electron affinity) rather than with ionization energy I. But even if one of these quantities is identified with the α_M parameter, such information can rarely be used even when comparing entirely similar XML_n polyhedra where the metal atoms M are analogues of the same group. In particular, the widespread assumption that the *trans*-influence (and *trans*-effect) increases from top to bottom within a group should be clarified (see part F). As far as comparing metal atoms along a period (say, W and Pt), is concerned, this makes little sense.

---

[*] Moreover, taking into account π-strengthening, the M—L_{trans} bond could be even stronger (shorter) than M—L_{cis} bonds.

[**] Moreover, for essentially heteropolar molecules (which, by the way, include many complexes with acidoligands) a better approximation may be reached by neglect of covalent bonding and by estimation of the total energy from imposition of the Madelung potentials of fractional atomic charges [47].

The fact is that if the complexes MXL_n have the same charge, then they are not isoelectronic, and this difference always affects bond properties due to different occupancy of the bonding and anti-bonding orbitals (see, e.g. p. 43). If MXL_n complexes are isoelectronic, then the metal atoms exist in different oxidation states. Hence the complicated iterative dependence of α_M on the varied effective charges of all atoms should be taken into account (see e.g. ref. 25).

Finally, one should remember that for metals in the beginning, the middle and the end of the period, the prefered ligands will vary (simply due to different occupancy of the metal valence shell). Therefore, in reality one has to compare rather different complexes where valence states of the metal (and energies of its levels) may vary considerably. Therefore it makes little sense to ascribe certain numerical values to parameters α_M's for a given metal or, as is often done, to assume them monotonously changing along the period (cf. also the discussion in ref. 19). Therefore we shall make no attempt to state quantitative correlations but point out only two qualitative effects.

The first of these concerns the structure of linear X—M—X fragments. From the analysis of the relevant three-orbital secular equation it follows [33] that there may exist some conditions when an asymmetric linear configuration $X^{(1)}$—M—$X^{(2)}$ is more advantageous than a symmetric one (for example, when $\beta_{MX}^{(i)} = \exp(-\xi R_{MX}^{(i)})$ where $R_{MX}^{(1)} = R + \Delta R$ and $R_{MX}^{(2)} = R - \Delta R$). Since the values $R^{(i)}$ and, consequently, $\beta^{(i)}$ depend on the structure of the entire molecule and even on its environment, the molecular X—M—X fragments may be in principle both symmetric and asymmetric.

The simplest example is the linear I_3^- anion which, depending on some subtle effects (mainly on its environment in the crystal), may be symmetric or asymmetric [49]. Another example is the linear FHF^- anion which (along with the well-known symmetric configuration) has the recently discovered asymmetric configuration stabilized by considerable asymmetry of the environment in the crystal [50].

The same group of phenomena may include existence of linear metal—oxygen chains with both equivalent and alternating internuclear distances [51], e.g.,

$$\overset{\leftarrow}{-} O \overset{\rightarrow}{-} M \overset{\leftarrow}{-} O \overset{\rightarrow}{-} M \overset{\leftarrow}{-} \quad \text{and} \quad \leftarrow O \overset{\rightarrow}{\equiv} M \leftarrow O \overset{\rightarrow}{\equiv} M \leftarrow$$

In such cases the difference in the structure is determined by the π-interaction delocalization energy dependent on the nature of the metal. This fact is directly associated with the problem of *trans*-influence, since in our model the larger π-interaction localization in the M—X bond causes the larger *trans*-weakening of the M—L bond. For example in MO_3 oxides and some oxocompounds, rhenium forms equivalent O—M—O bonds, while molybdenum forms alternating bonds. If one assumes that the higher π-bond localization is intrinsic for Mo rather than Re compounds, the *trans*-influence in the Mo complexes should be more clearly expressed than in the Re compounds; this appears to be so (see sections C—E).

The second effect considers the peculiarity of the metal—*cis*-ligand interaction (though this extends somewhat the validity of our model formally limited to the linear X—M—L fragments). This case involves the stereochemical consequences of the d_{xy} orbital population.

If the d_{xy} orbital is vacant (d_{xy}^0), then it would attract the relevant π-electron pairs of the *cis*-ligands (their σ-bonds are directed along the x and y coordinate axes). In such a case the *trans*-weakening of the M—L bond would be great (especially if one compares *trans*- and *cis*-bonds with the same ligands). On the other hand when the d_{xy} orbital is occupied (partially as d_{xy}^1 or completely as d_{xy}^2), then the repulsion of d_{xy} electrons from electron pairs of the equatorial ligands would result in little M—L *trans*-weakening (or none at all). Thus, other conditions being equal, the *trans*-weakening for π-donor ligands should increase in the sequence

$$d_{xy}^2 < d_{xy}^1 < d_{xy}^0 \qquad (29)$$

In part C we shall see that the admittedly incomplete experimental data demonstrate that relation (29) is true but limited. There is, after all, the stereochemical problem — the MO_2 group geometry in dioxocompounds — where the d^n metal configuration is decisive. The d^0 configuration stabilizes the angular (*cis*) geometry, while the linear (*trans*) configuration is preferable for the d^2 configuration.

C. STRUCTURAL DATA ON THE *TRANS*-INFLUENCE OF MULTIPLE BONDS

(i) A comparison of metal—ligand distances. General remarks

1. The "standard" M—ligand distances

Comparison of internuclear distances in various complexes or in different directions in the same complex requires consideration of many factors which are not related directly with the *trans*-influence of multiple bonds. In principle, account should be taken of the fact that bond lengths depend on the metal valence state and nature, size and mutual arrangement of all the (different) ligands in the complex as well as on the nature of outer ions and their location in the structure. Complications caused by such a dependence have been briefly reviewed [52] (see also original references cited therein). To try and avoid such complications comparison should be made only within a limited number of similar compounds; this of course results in a considerable decrease in the amount of data which can be compared.

To extend the number of compounds involved in an analysis of internuclear distances one has to introduce this or that subjective estimation of "ordinary" or "expected" M—ligand bond length in the absence of the *trans*-influence. In the discussion which follows we rely on the following points.

1 The data available on Pd, Pt, Rh and Ir complexes [15—17] demonstrate that mutual bond labilization in the linear Cl—M—Cl fragments is negligible. It is assumed that this situation may be extended to other transition metal

complexes (Re, Mo, W, Nb, V) and to a certain extent to other *trans*-halogenides. It is also suggested that an internuclear M—ligand distance changes negligibly with change of metal oxidation state over one or two units (usually within electronic configurations d^0, d^1, d^2). Structural data on the complexes of the aforementioned metals do not contradict such an assumption [12—14].

On the basis of these assumptions the mean M—Cl, M—F and M—Br distances in *trans*-$[MX(Hal)_4L]^{n-}$ complexes may be used as standards. The averaging omits the data on *trans*-$[MX(Hal)_2L'_2L]^{n-}$ complexes where L′ = PR_3 or a similar ligand which may affect the MO electron distribution while descending from C_{4v} to C_{2v}.

2 The structural data available for Pd and Pt compounds permit us to construct a table of approximate differences in M—Cl and M—L distances for some ligands whose *trans*-influence is relatively small. It is assumed that such differences are more or less the same for other transition metals of groups VI to VIII. Such transfer enables us to extend the number of standard distances and in particular to estimate the "ordinary" M—H_2O and M—NR_3 distances. The respective numerical values with some corrections accounting for the available experimental data are listed in Table 2. Certainly it should be noted that such values are a matter of convention since "ordinary" or "standard" distances cannot be precisely defined.

The standard distances for metals of the first transition period are not included in Table 2. They could be found approximately by subtracting the value 0.1 Å from the respective metal—ligand distances in complexes of metals located lower in the same groups.

2. *The role of steric factors*

Another problem which is also expected to be analysed in advance is the separation or a priori estimation of the comparative role of electronic and purely steric factors in the mutual influence of ligands. For the majority of complexes to be discussed further steric hindrance via contacts of peripheral atoms of polyatomic ligands is absent. Thus we can afford to take into consideration only those atoms which are directly bonded to the central atom. Conventionally

TABLE 2

The standard (expected) M—ligand distances in complexes of transition metals of the Vth and VIth periods (Å)

	F	Cl	Br	OR_2	NR_3	OH
Nb, Ta	1.83	2.41	2.54	2.10		2.02
Mo, W	1.82	2.40	2.53	2.09	2.12	2.01
Re, Tc	1.81	2.39	2.52	2.08	2.11	2.00
Ru, Os	1.78	2.36	2.49	2.05	2.08	1.97
Ir, Rh		2.34	2.47	2.02	2.05	
Pd, Pt		2.31	2.45	2.00	2.03	

such an interaction may be reduced to the M—ligand bond repulsion and to the repulsion of ligand atoms when they approach too closely in the course of formation of the metal—ligand polyhedron*.

Numerous structural data show quite convincingly that in complexes with different ligands, steric hindrance may yield angular distortions in the metallic polyhedron (e.g. refs. 12—17). In particular, in all octahedral mono-nitrido- or mono-oxo-transition metal complexes shortening of the N≡M or O≡M distances always leads to an inclination of the M—L_{eq} bonds towards the *trans*-ligand. As examples we shall cite only the series $[MoOL_5]^{2-}$ where L = F, Cl, Br**, where the mean OMoL_{eq} angles are equal respectively to 93.4, 94.8 and 95.6° (Mo displacement out of the plane of four L_{eq} ligands is 0.11, 0.20 and 0.25 Å respectively). The distortions increase from F to Cl to Br. The first steric factor seems to be prevailing, since electron pair repulsion in the bonds should enhance with decreasing polarity (and increasing order) of the bond. On the other hand repulsion of atomic electronic shells should be more important with increasing differences between the sums of atomic Van der Waals' radii of ligands (O and Hal in this case) and their separation in the complex in the absence of angular distortions. For the series considered these differences are practically equal (nearly 0.15 Å).

A question may arise then whether an interligand interaction noticeably affects not only the angular but also the linear characteristics of the complex. In principle the inclination of all four M—L_{eq} bonds to the *trans*-partner of the multiply-bonded ligand always generates a resultant force along the M—L_{trans} line.

However, the structural data give us no hint of any important difference in M—L_{cis} and M—L_{trans} distances in the complexes MLL'_5, MLL'_4L'' etc. with "ordinary" ligands having different Van der Waals' radii (e.g. chloroammoniates). The same could be said for the binuclear complexes $Cl_5M{=}O{=}MCl_5$ where M = Re, Ru (Table 3). An interligand interaction O...Cl_{eq} increases the OMCl_{eq} angles to 94° and 94.6° in the first and second compounds respectively. However, the bond lengths M—Cl_{eq} and M—Cl_{trans} are equal.

The situation may change only when the bond with the *trans*-partner is already considerably loosened by electron redistribution over the bonds (the case of a strong *trans*-influence). Then the dynamic equilibrium in the system would be different: the interligand "repulsion" forces acting along the line of the least resistance lead to a greater increase in the M—L_{trans} distance than in M—L_{eq}.

In other words an electron redistribution over the bonds in the presence of a strongly "influencing" ligand results in changing the energy curve characteristics of the metal—L_{trans} interaction: the depth of the minimum di-

---

* Naturally both these factors are taken into account automatically in an accurate quantum chemical computation of an equilibrium geometry of the complex, but in the model developed here they act as additional steric effects.

** Original structural studies are referenced in Tables 3—17.

minishes, the curvature decreases and the minimum position is shifted somewhat towards higher values of $R_{\mathrm{M}\text{-}trans}$. A decrease in the curvature (bond force constant) facilitates an additional M—L$_{trans}$ elongation owing to interligand interaction.

In spite of the fact that such an approach artificially separates the factors responsible for the equilibrium configuration of a complex, it is nevertheless convenient to allow us to understand one of the possible (and probably most significant) reasons for the large scattering in *trans*-elongation in complexes of similar structure and electronic configuration.

The above implies that one may not expect any unequivocal dependence of the *trans*-elongation on the nature of the X, M and L$_{trans}$ components (forming a linear fragment) independently of the composition of the equatorial ligands not only because of their influence on the electron density distribution along the bonds but also due to the different steric conditions. Thus such dependences should only be discussed qualitatively and include statistics of a sufficiently large number of compounds.

The situation is simplified by the fact that in nitrido- and oxo-complexes and some other classes of compounds *trans*-elongation is so clearly expressed that some weak additional effects would not spoil the general pattern.

For the same reason we pay no special attention to the accuracy of the distances obtained and their objective estimation in the original papers. The principle differences in M—L$_{trans}$ and M—L$_{eq}$ considerably exceed their standard deviations. On the other hand we are not going, as a rule, to dwell on the tiniest details *. It is important to outline that steric interaction along the line L$_{eq}$...L$_{trans}$ may in general only increase the effect of *trans*-elongation, since the weaker the metal—L$_{trans}$ bonds the more their energy curve slopes and thus the greater is the L$_{trans}$ shift from the point of minimum under the action of equatorial ligands.

3. *Experimental data*

The complexes which are of interest to us have been investigated rather irregularly. Few data are available on interatomic distances in the nitrido- and imino-complexes and in binuclear complexes with symmetric linear (oxygen or nitrogen) bridges. The situation is somewhat better for nitrosyl compounds and binuclear complexes with multiple metal—metal bonds although their structural data are rather irregular for different metals (ruthenium compounds occur more often among nitrosyls, while complexes with multiple M—M bonds more often involve rhenium compounds). Most structural data deal with oxocomplexes: oxohalides, oxocomplexes with donor ligands, oxoperoxocomplexes, oxooxalate complexes, oxocomplexes with polydentate organic ligands etc. Molybdenum oxocompounds have been stu-

---

* Standard deviations are not shown in the tables which follow. A possible round off error in the distances does not usually exceed 5 units in the last significant figure.

died most intensively, with tungsten, rhenium and niobium (in that order) having been less studied.

The monooxo- and dioxocomplexes of Mo have been widely investigated. Structural data are also avaliable on trioxocomplexes. With these compounds there arises the problem of how the arrangement of multiple metal—ligand bonds is regulated. This problem is specially considered in one of the following sections.

Considerable structural data have been published recently on Mo and W (as well as Nb and V) oxygen-containing compounds: complex oxides, binary and ternary salts including those of iso- and heteropolyacids. The crystals of such compounds may have both island structures with finite anionic polynuclear complexes and polymeric structures with infinite metal—oxygen chains, layers or three dimensional frameworks.

Although the model discussed in the previous section is strictly valid only for mononuclear complexes we do not abandon the fact that the same dependences govern equally interatomic distances in mononuclear complexes and polynuclear formations as a consequence of the localization of π-interaction over certain M—O bonds. With this in mind the last part of the review will concern the stereochemistry of oxygen-containing compounds, generally those of molybdenum and tungsten. A more detailed description of crystal structures in Mo and W coordination compounds and analysis of their structural and stereochemical dependences (including the distribution of multiple bonds in the coordination polyhedra and the *trans*-influence of multiple bonds) may be found elsewhere [53].

(ii) The role of the multiply bonded ligand X

1. The general series of trans-influence

To reveal the dependence of the M—L_{trans} bond length on the various factors which affect the electronic structure of the complex, it is important to compare only those complexes in which the equivalence of the action of other factors is ensured. This requirement effectively limits use of the experimental data available. Nevertheless, the role of ligand X (the number and character of its π-bonds with the metal atom) is sufficiently explicit. Table 3 lists the X—M, M—L_{trans} and M—L_{eq} distances for 27 compounds. The first 23 compounds are subdivided into three groups. In each of them: 1 ligand L_{trans} is the same (Cl in the first two groups, H_2O in the third), 2 the *cis*-environment is kept constant wherever possible (halogen and carboxylato-halogen in the first and third groups and halogen phosphine in the second), 3 the number of valence electrons is kept constant wherever possible. In most complexes a non-bonding orbital (generally metal d_{xy}) is occupied by an electron pair. Compounds 20 (d_{xy}^1) and 1, 16, 17 are exceptions (the last three contain an M≡M bond, i.e. an electron pair in the bonding δ-orbital instead of a lone pair d_{xy}^2).

In the table the *trans*-elongation is specified by the differences Δ and Δ'.

TABLE 3

The influence of ligand X on *trans*-elongation

Nos	Compound	d^n_{xy}	Bond X—M	Distances, Å			Δ	Δ′	Ref., fig.
				X—M	M—L_{trans}	M—L_{equ}			
1	$(NH_4)_2[Re_2Cl_4(HCOO)_2Cl_2]$ a)	δ^2	M≣M	2.260	2.71 Cl	av. 2.32 Cl	0.39	0.32	[54], 10c
2	$K_2[OsNCl_5]$	d^2_{xy}	N≡M	1.75 1.614	2.60 2.605 Cl	av. 2.36 av. 2.362 Cl	0.24 0.24	0.24 0.24	[55a] [55b]
3	$K_2[ReOCl_5]$	d^2_{xy}	O⇶M	1.66	2.47 Cl	av. 2.39 Cl	0.08	0.08	[56]
4	$Cs_4[Os_2OCl_{10}]$ a)	d^2_{xy}	⇇O⇶M	1.778	2.433 Cl	av. 2.370 Cl	0.06	0.07	[57]
5	$K_4[Ru_2OCl_{10}].H_2O$ a)	d^2_{xy}	⇇O⇶M	1.80	2.36 Cl	av. 2.36 Cl	0	0	[58]
6	$K_4[Re_2OCl_{10}].H_2O$ a)	d^2_{xy}	⇇O⇶M	1.86	2.38 Cl	av. 2.38 Cl	0	−0.01	[59]
7	$(NH_4)[RuNOCl_5]$ a)	d^2_{xy}	ON⇆M	1.74	2.357 Cl	av. 2.376 Cl	−0.02	0	[60]
8	$K_2[RuNOCl_5]$ a)	d^2_{xy}	ON⇆M	1.747 1.799	2.359 2.369 Cl	av. 2.372 av. 2.357 Cl	−0.01 0.01	0 0.01	[61a] [61b]
9	$ReNCl_2(PEt_2Ph)_3$	d^2_{xy}	N≡M	1.788	2.56 Cl	2.45 Cl	0.11	0.17	[62]
10	$ReOCl_3(PEt_2Ph)_2$	d^2_{xy}	O⇶M	1.60	2.47 Cl	av. 2.42 Cl	0.05	0.08	[63]
11	$MoOCl_2(PMe_2Ph)_3$(blue)	d^2_{xy}	O⇶M	1.676	2.551 Cl	2.464 Cl	0.09	0.15	[64]
12	$MoOCl_2(PEt_2Ph)_3$(green)	d^2_{xy}	O⇶M	1.803	2.426 Cl	2.479 Cl	−0.05	0.03	[65]
13	$Re(NMe)Cl_3(PEtPh_2)_2$	d^2_{xy}	RN⇶M	1.685	2.411 Cl	av. 2.418 Cl	−0.01	0.02	[66]
14	$Re(NC_6H_4COCH_3)Cl_3(PEt_2Ph)_2$	d^2_{xy}	RN⇶M	1.690	2.410 Cl	av. 2.416 Cl	−0.01	0.02	[67]
15	$Re(NC_6H_4OCH_3)Cl_3(PEt_2Ph)_2$	d^2_{xy}	RN⇶M	1.709	2.432 Cl	av. 2.421 Cl	0.01	0.04	[67]
16	$Cs_2Re_2Cl_8(H_2O)$ a,b)	δ^2	M≣M	2.211	2.44 H_2O	av. 2.289 Cl		0.35	[68], 10b
17	$Re_2Cl_4(CH_3COO)_2(H_2O)_2$ a)	δ^2	M≣M	2.224	av. 2.507 H_2O	av. 1.1995 O_L av. 2.300 Cl		0.43	[69], 10c
18	$K[OsNCl_4H_2O]$	d^2_{xy}	N≡M	1.74	2.50 H_2O	av. 2.345 Cl		0.45	[70]
19	$K[OsNBr_4H_2O]$	d^2_{xy}	N≡M	1.67	2.42 H_2O	av. 2.48 Br		0.37	[71]
20	$ReOCl_4H_2O$	d^1_{xy}	O⇶M	1.63	2.27 H_2O	av. 2.29 Cl		0.19	[72]
21	$(Et_4N)[ReOBr_4H_2O]$	d^2_{xy}	O⇶M	1.71	2.32 H_2O	av. 2.51 Br		0.24	[73]
22	$K_3[Ru_2NCl_8(H_2O)_2]$ a)	d^2_{xy}	⇇N=M	1.72	2.18 H_2O	av. 2.36 Cl		0.13	[74]
23	$(NH_4)_2[RuNOCl_4H_2O]Cl.H_2O$ a)	d^2_{xy}	ON⇆M	1.67	2.06 H_2O	av. 2.35 Cl		0.01	[75]

TABLE 3 (continued)

Nos	Compound	d_{xy}^n	Bond X–M	Distances, A			Δ	Δ′	Ref., fig.
				X–M	M–L_{trans}	M–L_{equ}			
24	$(ReOCl_4)_2$	d_{xy}^1	$O \Rrightarrow M$	av. 1.63	av. 3.60 Cl_b	av. 2.255 Cl_t av. 2.275 Cl_b	1.32		[76], 5b
25	$(MoOCl_3)_\infty$	d_{xy}^1	$O \Rrightarrow M$	1.60	2.81 Cl_b	av. 2.28 Cl_t av. 2.43 Cl_b	(0.53) 0.38		[77], 5a
26	$(WSCl_4)_2$	d_{xy}^0	$S \Rrightarrow M$	av. 2.084	av. 3.05 Cl_b	2.277 Cl_t 2.37 Cl_b	(0.77) 0.32		[78], 5b
27	$[W(NC_2Cl_5)Cl_4]_2$	d_{xy}^0	$RN \Rrightarrow M$	1.71	2.70 Cl_b	av. 2.27 Cl_t 2.44 Cl_b	(0.43) 0.26		[79], 5b

---

[a] The formal metal electronic configuration is d^4 (d^3 in compound 6).

[b] The crystals are composed of two types of complexes: $[Re_2Cl_8]^{2-}$ and $[Re_2Cl_8(H_2O)_2]^{2-}$ and Cs^+ cations. Suffix b = bridging, suffix t = terminal, suffix L = atom of organic ligand. Similar abbreviations used in the following tables.

Column Δ shows the differences of M—ligand distances for the same type of ligands in *trans*- and *cis*-positions, column Δ′ shows the $\mathrm{M—L}_{trans}$ bond elongation with respect to a standard taken from Table 2. Both characteristics have certain disadvantages, each being in its way (more or less) a matter of convention. However, the relevant differences are rather small and thus the use of both measures should not yield inconsistency.

It can be seen from these data that *trans*-elongation undoubtedly decreases in the series:

$$\mathrm{M} \equiv\!\!\!\!= \mathrm{M}\,,\;\; \mathrm{N} \equiv \mathrm{M} > \mathrm{O} \underset{\rightarrow}{=} \mathrm{M} > \mathrm{RN} \underset{\rightarrow}{=} \mathrm{M}\,,\;\; \leftrightarrows \mathrm{O} \underset{\rightarrow}{-} \mathrm{M} > \mathrm{ON} \overset{\rightarrow}{\underset{\leftarrow}{-}} \mathrm{M}$$

According to the data listed in Table 3 the quadruple $\mathrm{M} \equiv\!\!\!\!= \mathrm{M}$ bond causes nearly the same elongation as does a nitride ligand. This is in agreement with the fact that the δ-component of the quadruple $\mathrm{M} \equiv\!\!\!\!= \mathrm{M}$ bond has no bonding analog in the $\mathrm{M—L}_{trans}$ bond and thus produces no direct influence upon such a bond.

Table 3 includes data on two similar oxomolybdenum complexes (compounds 11 and 12). In 1970 two forms were found for $\mathrm{MoOCl_2(PMe_2Ph)_3}$ crystals which are of different stability, colour and spectra [80]. The blue, more stable complexes show the band $\nu_{\mathrm{Mo—O}}$ at 954 $\mathrm{cm^{-1}}$ in the IR spectrum while the less stable green compounds exhibit absorption at 943 $\mathrm{cm^{-1}}$; on heating, the green form converts to the blue one. The crystals $\mathrm{MoOCl_2}$-$\mathrm{(PEt_2Ph)_3}$ containing ethyl groups instead of methyl groups are analogous to the green form of the former compound (also green [65], $\nu_{\mathrm{Mo—O}}$ = 940 $\mathrm{cm^{-1}}$). Investigation of the structure demonstrates that the arrangement of ligands in complexes 11 and 12 is identical but the Mo—O bond lengths are different: 1.676 (7) Å and 1.803 (11) Å in the first and second complexes respectively. The difference exceeds 11-times the standard deviations. The weakening of the O—M bond on going from the blue to the green isomer causes a noticeable decrease in *trans*-elongation (by 0.12 Å), while the $\mathrm{M—L}_{cis}$ bonds are practically the same (only one Mo—P bond becomes 0.04 Å longer).

It is hardly possible to overestimate the importance of this result; two isomeric forms were discovered which have the same ligand arrangement in the complex but completely different equilibrium internuclear distances and thus different spectroscopic properties, as evidence of the change in electronic structure in passing from one form to the other. It is surprising however that the difference in $\nu_{\mathrm{Mo—O}}$ is so small. It is also worth mentioning that the electronic structure of the second (green) form causes a *trans*-elongation in the $\mathrm{O} \underset{\rightarrow}{=} \mathrm{M—Cl}$ fragment close to that in the $\mathrm{RN} \underset{\rightarrow}{=} \mathrm{Re—Cl}$ fragment (compounds 13—15).

Table 3 also presents data on nitrosyl complexes and those with oxygen and nitrogen bridges. In the three nitrosyl complexes (7, 8 and 23) and in two oxygen bridge complexes (5 and 6) virtually no *trans*-elongation was observed. The last fact is specific for all nitrosocomplexes with a linear ON—M fragment (see section 4) while *trans*-elongation is clearly expressed in at least one oxygen bridge complex (4) and one nitrogen bridge compound (22).

Hence one may conclude that in general the N and O atoms participating in the formation of symmetric linear bridges cause a somewhat greater perturbation in an octahedral electronic structure than does the "linear" nitroso group.

The last part of Table 3 contains data on two groups of compounds separated from the rest. The structure of these complexes is shown schematically in Fig. 5a and b. Tungsten sulfotetrachloride dimer is as yet the only structure studied with multiply bonded sulfur. Considering the M—Cl bridge distances in the position *trans* to the multiple bond in this complex and in oxo-complexes of similar composition (but unfortunately with different electronic configuration) one is likely to conclude that sulfur leads to a greater elongation than does oxygen.

The data on the *trans*-influence of the imino-group RN⇛ are specific. This

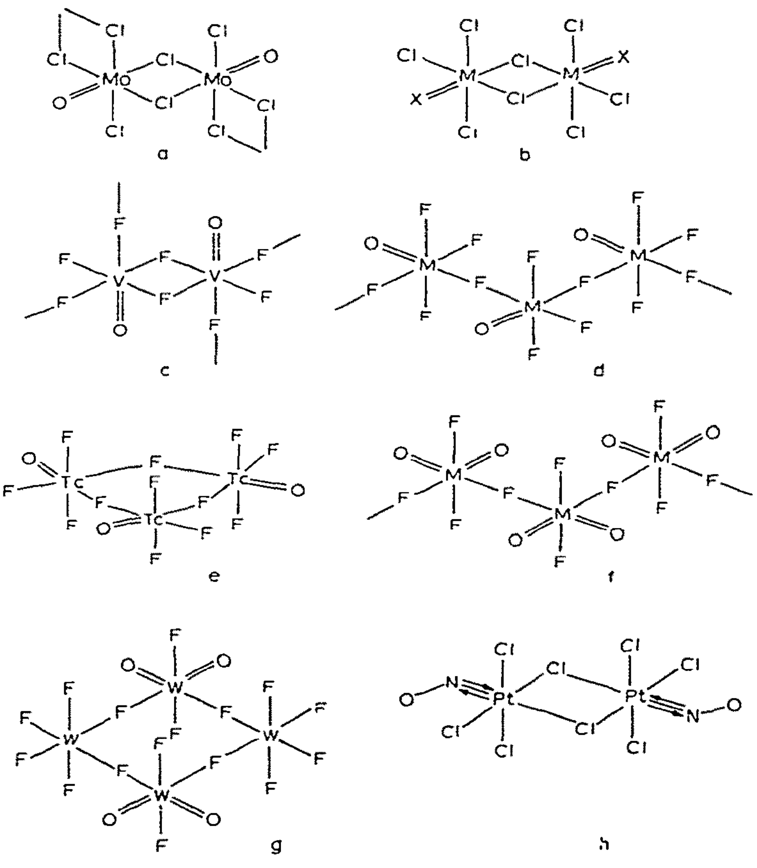


Fig. 5. The structures of polynuclear complexes with halogen bridges: a, $[MoOCl_3]_\infty$; b, $[MXCl_4]_2$; c, $[VOF_3]_\infty$; d, $[MOF_4]_\infty$, M = Mo, Re; e, $[TcOF_4]_3$; f, $\{[MO_2F_3]^-\}_\infty$; g, $[WOF_4]_4$; h, $[PtNOCl_4]_2^{2-}$.

TABLE 4

Trans-elongation in mono- and dioxo-complexes

Nos	Compound	d_{xy}^n	MO_n
28	$K_2[NbOF_5]$	d^0	NbO
29	$K_2[MoOF_5].H_2O$	d^1	MoO
30	$K_2[MoO(O_2)F_4].H_2O$ a)	d^0	MoO
31	$(NH_4)_3F[MoO(O_2)F_4]$ a)	d^0	MoO
32	$K_2MoO_2F_4$ b)	d^0	MoO_2
33	$K_2MoO_2F_4.H_2O$	d^0	MoO_2
34	$(VOF_3)_\infty$	d^0	VO
35	$(ReOF_4)_\infty$	d^1	ReO
36	$(TcOF_4)_3$	d^1	TcO
37	$(MoOF_4)_\infty$	d^0	MoO
38	$K_2[VO_2F_3]$	d^0	VO_2
39	$NH_4[MoO_2F_3]$	d^0	MoO_2
40	$(WOF_4)_4$ c)	d^0	WO_2
(20)	$ReOCl_4H_2O$	d^1	ReO
(21)	$(Et_4N)[ReOBr_4H_2O]$	d^2	ReO
41	$K[MoOCl_4H_2O]$	d^1	MoO
42	$(Ph_4As)[MoOBr_4H_2O]$	d^1	MoO
43	$(MoO_2Cl_2H_2O)_\infty$	d^0	MoO_2
44	$MoO_2Cl_2H_2O.KCl$	d^0	MoO_2
45	$MoO_2Cl_2(H_2O)_2.2KCl$	d^0	MoO_2
46	$MoO_2Cl_2(DMF)_2$	d^0	MoO_2
47	$\{MoO_2Cl(DMF)_2\}_2O$	d^0	MoO_2
48	$Cs[NbO(C_2O_4)_2(H_2O)_2].2H_2O$ a)	d^0	NbO
49	$K_2[\{MoO_2(C_2O_4)H_2O\}_2O]$	d^0	MoO_2
50	$RbNbO(SO_4)_2$	d^0	NbO
51	$CsNbO(SO_4)_2$	d^0	NbO
52	$Mo_4Cl_4O_6(OPr)_6$	d^0, d^I	MoO
53	$HgMoO_4$	d^0	MoO_2
54	$Na_6[Mo_5P_2O_{23}].13H_2O$	d^0	MoO_2

Nos	Distances, A			Δ	Δ′	Ref., fig.
	O—M	M—L_{trans}	M—L_{equ}			
28	1.68	2.06 F	1.84 F	0.22	0.23	[82]
29	1.66	2.03 F	av. 1.86 F	0.17	0.20	[83]
30	1.64	2.01 F	av. 1.997 F av. 1.935 O_2		0.18	[84]
31	1.67	2.03 F	av. 1.96 F 1.91 O_2		0.20	[85]
32	1.67	1.99 (F)	1.87 (F)	0.12	0.16	[86]
33	av. 1.71	av. 1.97 F	av. 1.925 F	0.05	0.14	[87]
34	1.57	2.34 F_b	1.70 F_t 1.81 F_b av. 1.94 F_b	0.40	0.40	[88], 5c
35	av. 1.645	av. 2.295 F_b	av. 1.86 F_t av. 1.99 F_b	0.30	0.35	[89], 5d
36	1.66	2.26 F_b	av. 1.81 F_t 1.89 F_b	0.37	0.32	[90], 5e
37	av. 1.635	av. 2.29 F_b	av. 1.83 F_t av. 1.945 F_b	0.34	0.35	[91], 5d
38	1.636	2.187 F_b	av. 1.89 F_t		0.25	[92], 5f
39	av. 1.68	2.14 F_b	av. 1.92 F_t		0.20	[93], 5f
40	1.63	2.10 F_b	av. 1.845 F_t		0.16	[94], 5g
(20)	1.63	2.27 H_2O	av. 2.29 Cl		0.19	[72]
(21)	1.71	2.32 H_2O	av. 2.51 Br		0.24	[73]
41	1.72	2.27 H_2O	av. 2.37 Cl		0.18	[56]
42	1.78	2.39 H_2O	2.516 Br		0.30	[95]
43	1.65 O_t 1.77 O_b	2.26 H_2O 2.20 O_b	av. 2.34 Cl		0.17	[96], 8a
44	1.68 O_t 1.83 O_b	2.30 O_b 2.25 H_2O	av. 2.38 Cl		0.16	[97], 8b
45	av. 1.715	av. 2.25 H_2O	av. 2.40 Cl		0.16	[98]
46	1.68	2.20 O_{DMF}	2.341 Cl		0.11	[99]
47	1.68	2.27 O_{DMF}	1.90 O_b 2.464 Cl		0.18	[100]
48	1.691	2.328 H_2O	av. 2.114 O_{ox} 2.169 H_2O		0.22	[101]
49	av. 1.69	2.330 H_2O	1.88 O_b		0.24	[102]
		2.19 O_{ox}	2.09_{ox}	0.10	~0.18	
50	1.73	$2.26 \leftarrow O_{SO_4}$	av. 2.00 O_{SO_4}	0.26	~0.20	[103], 6a
51	1.56	$2.35 \leftarrow O_{SO_4}$	av. 2.03 O_{SO_4}	0.32	~0.30	[104], 6a
52	av. 1.626	av. $2.21 \leftarrow O\!<$	av. 1.978 $O_b$$^{d)}$	0.23	~0.16	[105]
53	1.72	$2.23 \leftarrow O\!<$	1.94 O_b	0.29	~0.18	[106], 6b
54	1.72	$2.28 \leftarrow O_{PO_4}$	1.94 O_b	0.34	~0.23	[107]
	av. 1.725	av. $2.201 \leftarrow O_{PO_4}$	av. 1.917 O_b	0.28	~0.15	
	av. 1.725	av. $2.309 \leftarrow O_{PO_4}$	1.917 O_b	0.39	~0.26	

TABLE 4 (continued)

Nos	Compound	d^n_{xy}	MO_n
55	$[(MoO)_2(\mu\text{-}S)_2EDTA].2H_2O$	d^0	MoO
56	$H[MoO_2N(CH_2CH_2O)_3]$	d^0	MoO_2
57	$Na_4[(MoO_3)_2EDTA].8H_2O$	d^0	MoO_3
58	$MoO_3NH(CH_2CH_2NH_2)_2$	d^0	MoO_3
59	$(NH_4)[VO(O_2)\{C_5H_3N(COO)_2\}H_2O].1.3H_2O$ [a]	d^0	VO
60	$[MoO(O_2)_2\{OP(NMe_2)_3\}H_2O]$ [a]	d^0	MoO
61	$K_2[\{MoO(O_2)_2H_2O\}_2O].2H_2O$ [a]	d^0	MoO
62	$(PyH)[\{MoO(O_2)_2H_2O\}_2O]$ [a]	d^0	MoO
63	$K_2[\{WO(O_2)_2H_2O\}_2O]$ [a]	d^0	WO
64	$(PyH)_2[\{MoO(O_2)_2\}_2(OOH)_2]$ [a]	d^0	MoO
65	$(NH_4)_4[\{VO(O_2)_2\}_2O]$ [a]	d^0	VO
66	$[CrO(O_2)_2Phen]$ [a]	d^0	CrO
67	$[MoO(O_2)_2\{OP(NMe_2)_3\}Py]$ [a]	d^0	MoO
68	$K_2[MoO(O_2)_2(C_2O_4)]$ [a]	d^0	MoO

a) Pentagonal bipyramid coordination with X—M—L_{trans} fragment along the axis of bipyramid.
b) Probably L_{trans} is F and L_{equ} are ¼O + ¾F.
c) By assuming the alternation MoO_2F_4—MoF_6—MoO_2F_4—MoF_6 in the cluster with some mixing of terminal O and F.
d) The distances from metal to other *cis*-ligands: to Cl 2.382 (av.), OPr 2.165 (av.) and 1.983 (av.), Mo 2.669 Å.

group causes virtually no elongation of the *trans*-partner in the case of terminal chlorine and the metal with d^2 configuration (compounds 13—15), but it causes a considerable elongation if a bridging chlorine occupies the same position and the metal electronic configuration is d^0 (27). Here the effect of other partners in the X—M—L_{trans} fragment is quite clear (see below). In any event the difference in the action of the O≡ and RN≡ groups is quite evident:

Nos	Distances, A			Δ	Δ'	Ref., fig.
	O—M	M—L_{trans}	M—L_{equ}			
55	1.683	2.448 N_L	av. 2.111 O_{EDTA} av. 2.293 S		0.33	[108], 6c
56	1.815 1.76	2.43 N_L 2.34 O_L	av. 1.94 O_L	(0.38)	0.32	[109]
57	av. 1.74	2.40 N_L av. 2.19 O_L	—		0.28	[110], 6d
58	av. 1.737	av. 2.323 N_L	—		0.20	[111]
59	1.579	2.211 H_2O	av. 1.871 O_2 2.058 O_L 2.088 N_L		$\sim$0.2	[112]
60	1.662	2.347 H_2O	av. 1.942 O_2 av. 2.057 O_L		0.26	[113], 7a
61	av. 1.663	av. 2.445 H_2O	av. 1.963 O_2 av. 1.917 O_b		0.35	[114], 7b
62	1.674	2.43 H_2O	av. 1.967 O_2 1.927 O_b		0.34	[115], 7b
63	av. 1.70	av. 2.355 H_2O	av. 1.927 O_2 av. 1.925 O_b		0.26	[116], 7b
64	1.669	2.391 OOH_b	av. 1.937 O_2 2.047 OOH_b	0.34	0.30	[115], 7c
65	av. 1.61	av. 2.505 $(O_2)_b$	av. 1.863 $(O_2)_t$ av. 1.875 $(O_2)_b$ av. 2.005 O_b	0.63	$\sim$0.40	[117], 7d
66	1.57	2.26 N_{Phen}	av. 1.835 O_2 2.11 N	0.15	$\sim$0.25	[118], 7a
67	1.658	2.450 N_{Py}	av. 1.926 O_2 2.035 O_L		0.35	[113], 7a
68	1.68	2.26 O_{Ox}	av. 1.945 O_2 2.08 O_{Ox}	0.18	$\sim$0.26	[119], 7a

the former group causes *trans*-elongation almost always and with any *trans*-partner, while certain conditions are required for elongation in the case of the second group.

2. *Mono- and dioxocompounds*

The oxocomplexes form the largest group of those compounds structurally studied with multiple M—ligand bonds in mono- and binuclear complexes. Structural data include nearly 45 mono- and 40 dioxocomplexes. Trioxocompounds are less well known: only the structures of the crystals $MoO_3NH(CH_2CH_2NH_2)_2$ (compound 58, Table 4) and $Na_4[(MoO_3)_2EDTA].8H_2O$ (57) have been determined. One may also include here polynuclear complexes with one or two (of the three) oxygen atoms per metal atom acting as asymmetric bridges $M \leftarrow O = M$, e.g. $NH_4Na[MoO_2(\mu\text{-}O)C_2O_4].2H_2O$ (76, Table 5).

TABLE 5

Trans-elongation in complexes with oxygen bridges

Nos	Compound	d^n_{xy}	Bond [e)] X—M
69	β-$TeVO_4$	d^1	←O⇛
70	V_4O_9	d^0—d^1	←O⇛
71	VO(Salpn) [a)]	d^1	←O⇛
72	$MoOBr_3$	d^1	←O⇛
73	$WOCl_4$	d^0	←O⇛
74	[VO(μ—O)FBipy$]_2$	d^0	{ O⇛ ←O=
75	WO_2Cl_2	d^0	{ ←O⇛ ←O⇚ }
(43)	$(MoO_2Cl_2H_2O)_\infty$	d^0	{ O⇛ ←O⇚
(44)	$[(MoO_2Cl_2H_2O)_3]$.KCl	d^0	{ O⇛ ←O⇚
76	$NH_4Na[MoO_2(\mu—O)C_2O_4].2H_2O$	d^0	O= O= ←O=
77	$K_6[Mo_7O_{22}(O_2)_2].8H_2O$ [b)]	d^0	{ ←O= ←O=
78	$(NH_4)_{10}[H_2W_{12}O_{42}].4H_2O$ [c)]	d^0	O⇛ ←O= O⇛ ←O=
(6)	$K_4[(ReCl_5)_2O]$[f)]	d^2_{xy}	⇐O⇒
(5)	$K_4[(RuCl_5)_2O]$[f)]	d^2_{xy}	⇐O⇒
(4)	$Cs_4[(OsCl_5)_2O]$[f)]	d^2_{xy}	⇐O⇒
(47)	$\{MoO_2Cl(DMF)_2\}_2O$	d^0	O⇛ O⇚ ⇐O⇒
(49)	$K_2[\{MoO_2(C_2O_4)H_2O\}_2O]$	d^0	O⇛ O⇚ ⇐O⇒
79	$\{MoO(S_2COEt)_2\}_2O$	d^1	{ O⇛ ⇐O⇒
80	$\{MoO[S_2P(OEt)_2]_2\}_2O$	d^1	{ O⇛ ⇐O⇒
(22)	$K_3[\{RuCl_4(H_2O)\}_2N]$[f)]	d^2_{xy}	⇐N=
81	$K_2[\{Ti(O_2)NC_5H_3(COO)_2(H_2O)\}_2O].3H_2O$ [d)]	d^0	⇐O⇒
82	$[\{Cr(NH_3)_5\}_2O]Cl_4.H_2O$[f)]	d^2_{xy}	⇐O⇒
83	$[\{MnPcPy\}_2O].2Py$[f)]	d^2_{xy}	⇐O⇒

Nos	Distances, A			Δ	Δ'	Ref., fig.
	X—M	M—L_{trans}	M—L_{equ}			
69	1.61	2.77 O_b	av. 1.99 O_b	0.78	~0.8	[120], 8c
70	1.63	2.23 O_b	av. 1.940 O_b	0.29	~0.25	[121]
71	1.63	2.21 O_b	av. 1.945 O_{sal} av. 2.053 N_{sal}	0.27	~0.25	[122], 8d
72	1.65	2.31 O_b	2.41 Br_t 2.61 B_b		0.22	[123], 8e
73	~1.8	~2.2 O_b	av. 2.286 Cl		~0.1	[124], 8f
74	1.60 1.68	2.35 O_b 2.19 N	1.81 F 2.14 N	0.05	~0.2	[125], 8g
75	1.63	2.34 O_b	av. 2.31 Cl		0.25	[126], 8h
(43)	1.65 1.77	2.26 H_2O 2.20 O_b	av. 2.34 Cl		0.11	[96], 8a
(44)	1.68 1.83	2.30 O_b 2.25 H_2O	av. 2.38 Cl		0.16	[97], 8b
76	av. 1.83 1.88	av. 2.238 O_{ox} 2.230 O_b	—		0.14	[127], 9a
77	1.76 1.76	2.33 2.33 O_b	av. 1.895 O_b	0.44	0.24	[128], 14d
78	1.75 1.79	2.19 2.16 O_b	av. 1.96 O_b	0.20	0.07	[129], 14e
	1.72 1.81	2.30 2.02 O_b	av. 1.89 O_b	0.13	—0.05	
(6)	1.86	2.38 Cl	av. 2.38 Cl	0	—0.01	[59]
(5)	1.80	2.36 Cl	av. 2.36 Cl	0	0	[58]
(4)	1.778	2.433 Cl	av. 2.370 Cl	0.06	0.07	[57]
(47)	1.68 1.68 1.90	2.27 O_{DMF} 2.27 O_{DMF} 2.464 Cl	—		(0.18) (0.18) 0.06	[100]
(49)	1.680 1.700 1.700	2.330 H_2O 2.187 O_{ox} 2.087 O_{ox}	—		(0.24) (~0.18) ~0.08	[102], 9b
79	av. 1.645 av. 1.861	av. 2.697 S av. 2.535 S	av. 2.486 S	(0.21) 0.05		[130], 9c
80	1.65 1.86	2.801 S 2.547 S	av. 2.470 S	(0.33) 0.08		[131], 9c
(22)	1.72	2.18 H_2O	av. 2.36 Cl		0.13	[74]
81	1.825	2.183 H_2O	av. 1.888 (O_2) av. 2.073 O_L 2.172 N_L		~0.20	[132], 9d
82	1.803	2.14 NH_3	av. 2.10 NH_3	0.04	~0.12	[133]
83	1.71	2.15 N_{Py}	av. 1.96 N_{Pc}		~0.14	[134]

TABLE 5 (continued)

Nos	Compound	d^n_{xy}	Bond [e)] X—M
84	$[\{Fe(C_{15}H_{23}N_5)H_2O\}_2O](ClO_4)_4$ d,f)		$\rightleftarrows O \leftrightarrows$
85	$(enH_2)_2[\{Fe(HEDTA)\}_2O].6H_2O$ f)	d^2_{xy}	$\rightleftarrows O \leftrightarrows$

a) Salpn = *N*, *N'*-propylene-bis(salicylaldiminate).
b) In one of four independent Mo—oxygen polyhedra.
c) In two of six independent Mo—oxygen octahedra

The available data show that multiple O$\underset{\rightarrow}{=}$M or O=M bonds always produce considerable elongation. Only in a few oxofluorides — where some disorder in the O and F location at the vertices of the polyhedron is observed — is this effect less clearly evident. An example [81] is $Rb_2MoO_2F_4$.

Table 4 shows metal—ligand distances in those mono- and dioxocompounds which have similar composition. They include oxofluorides, oxoaquohalogenides and their analogs*, oxoaquooxalates and some other complexes. Unfortunately, the oxocomplexes most often studied structurally contain polydentate ligands or oxygen bridges. Simple comparison of the values of *trans*-elongation in such dissimilar cases is of little value. We have, however, included several such compounds in Table 4 (with related compositions where possible) mainly for a comparison of the *trans*-influence in di- and trioxocomplexes. Table 4 also gives the data on monooxoperoxo complexes. Since no structural data are available for similar dioxocomplexes these data are only a supplement. The structures of polynuclear and some oxoperoxo complexes listed in Table 4 are shown in Figs. 5—8.

In principle one would expect that transfer from mono- to dioxocomplexes of the same metal at constant oxidation state will result in some elongation of the oxygen—metal distances due to a decrease of formal multiplicity of such a bond. However, no such dependence is revealed by the data in Table 4. It is quite probable that the change of bond length is concealed in the errors in determined distances**.

---

* With oxoaquohalides one does not retain the requirement of constant electronic configuration of the metal. However, this does not seem to be important (see section C (iv)).

** The large and hardly interpretable deviations in X—M distances in different compounds observed by many workers lead to the idea that the actual accuracy in the determination of heavy—light atom distances in the region of 1.5—1.8 Å is far below that formally estimated from the reciprocal matrix formulae. The problem arises when fixing the maxima of electron density. The first false maxima that appear as a result of the Fourier series termination are usually located at a distance of 1.5—1.8 Å from the center of the heavy atom. In refinement by least squares, error may be caused by an increase of covariation coefficients in the matrix of normal equations if the distance between the given (light) and neighbouring (heavy) atoms becomes too short.

Nos	Distances, A			Δ	Δ′	Ref., fig.
	X—M	M—L_{trans}	M—L_{equ}			
84	1.8	2.15 H_2O	av. 2.2 N_B		~0.17	[135]
85	1.80	2.27 N_{EDTA} {	2.20 N_{EDTA} av. 2.04 O_{EDTA}	0.07	~0.30 }	[136], 9e

d) Pentagonal bipyramidal coordination

e) The symmetrical oxygen bridges are designated by $\Leftarrow O \Rightarrow$ irrespective of the number of valence electrons in the system.

f) The formal metal electronic configuration is d^n with $n > 2$.

On the other hand a comparison of M—L_{trans} distances in each group of related compounds shown in Table 4 illustrates unequivocally that on passing from mono- to dioxo-complexes there occurs a small but quite definite decrease in the distance to the *trans*-partner (only structures with the oxygen atom of the SO_4, PO_4 or O_{bridge} groups as *trans*-partner are exceptions). As an average the M—F_{trans} distances decrease over 0.05 Å for terminal F and over 0.15 Å for bridged F, while the M—$(H_2O)_{trans}$ bond diminishes over 0.08 Å. One of the obvious reasons for the weakening of the *trans*-influence by oxygen atoms in dioxocomplexes is a decrease in the oxygen—metal bond order (bond strength) because of their competition in p_π-d_π interactions (see also section E). It is rather difficult to judge if a further reduction in M—L_{trans} distances occurs in passing from di- to trioxocomplexes. The data for compounds 55—58 certainly do not provide sufficient proof since in these instances the ligands are polydentate and the number of compounds is rather small.

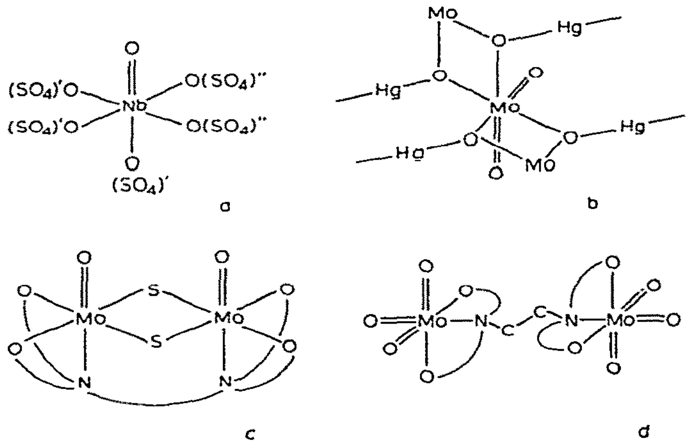


Fig. 6. The structures of polynuclear complexes with polydentate ligand bridges: a, $[NbO(SO_4)_2]^-$; b, $HgMoO_4$; c, $[(MoO)_2(\mu\text{-}S)_2EDTA]$; d, $[(MoO_3)_2EDTA]^{4-}$.

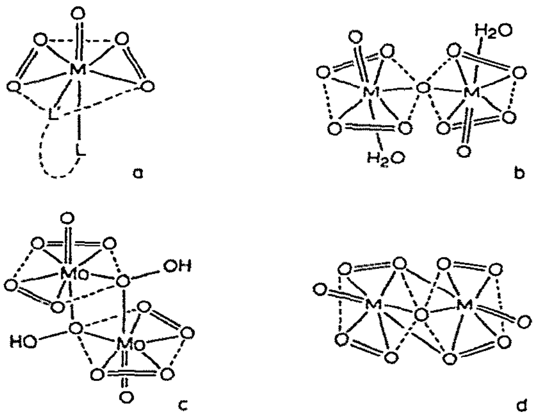


Fig. 7. The structures of oxoperoxocomplexes: a, $[MO(O_2)_2LL']$ and $[MO(O_2)_2L\dot{L}']$; b, $[\{MO(O_2)_2H_2O\}_2O]$; c, $[\{MoO(O_2)_2\}_2(\mu\text{-}OOH)_2]^{2-}$; d, $[\{VO(O_2)_2\}_2O]^{4-}$.

All oxoperoxocomplexes (compounds 59—68) have the structure of a pentagonal bipyramid (PBP), the $O \rightrightarrows M \leftarrow L$ fragment being invariably oriented along a bipyramidal axis. An increase in the number of equatorial ligands from 4 to 5 (or quite possibly, a specificity of these ligands) increases the *trans*-influence. The mean *trans*-elongation of the $M—H_2O$ bond in octahedral monooxocomplexes (for the compounds shown in Table 4) is equal to 0.22 Å, and that observed in the pentagonal bipyramid is 0.31 Å.

3. Complexes with oxygen bridges

Bridge oxygen atoms may play a different function in the structure of crystals. At present we are interested in cases where the oxygen atom connects only two metal atoms forming a multiple bond with one or both of them; the fragments may be described by canonical formulae $M \leftarrow O \rightrightarrows M$ (or $M \leftarrow O{=}M$) and $M \leftleftarrows O \rightrightarrows M$ (or $\overleftrightarrow{M—O—M}$).

The first case is usually realized in polynuclear complexes or in crystals with infinite metal—oxygen structures (chain, layer or three dimensional frameworks). Since such a case includes almost all oxygen-containing compounds of Mo, W, Nb and some other metals, many examples could be given. Table 5 contains only the data on some of the more simple compounds and several oxycompounds of complex composition investigated of late. In sections D and E the specificity of stereochemistry of such compounds is discussed in more detail.

The lower part of Table 5 gives structural data on the binuclear complexes with symmetric linear oxygen bridges (in 22 with a nitrogen bridge). Besides the six compounds mentioned in Tables 3 and 4, this table includes seven new compounds.

As expected, the *trans*-influence of the "multiply bonded" side in an asymmetric oxygen bridge is greater than in the case of a symmetric linear bridge,

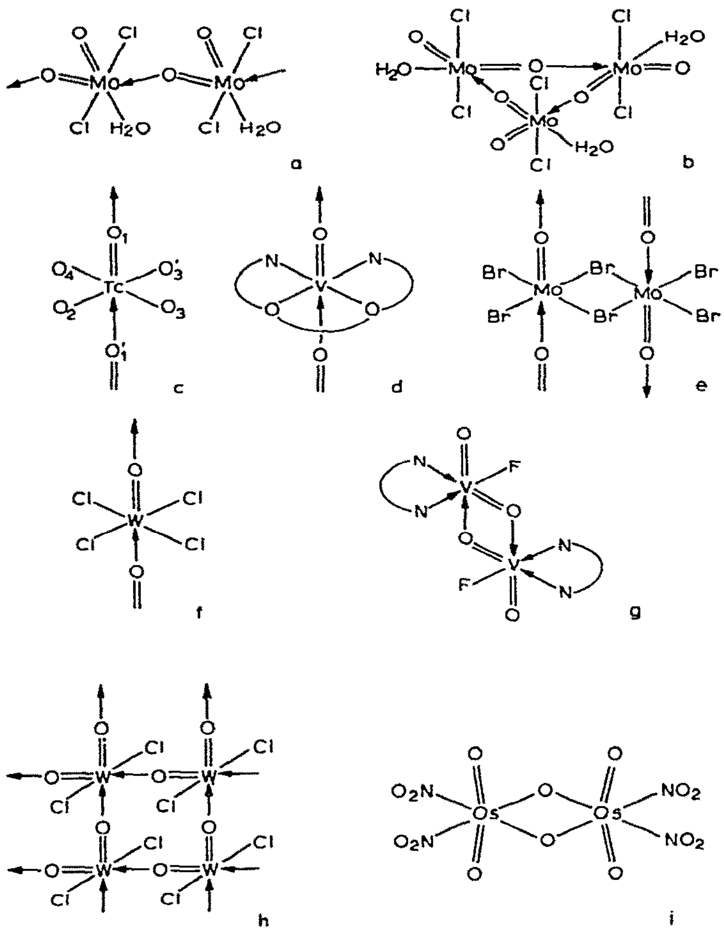


Fig. 8. The structures of polynuclear complexes with oxygen bridges: a, $MoO_2Cl_2.H_2O$; b, $(MoO_2Cl_2H_2O)_3.KCl$; c, β-$TeVO_4$; d, VO(salpn); e, $MoOBr_3$; f, $WOCl_4$; g, VO_2FBipy; h, WO_2Cl_2; i, $[Os_2O_6(NO_2)_4]^{4-}$.

being frequently close to that of a terminal oxygen atom. This, however, depends primarily on the degree of bridge asymmetry and as far as complex oxides are concerned on the general electron density distribution over all bonds.

On the other hand Table 5 shows that an oxygen atom in M⇆O⇄M or $\overleftrightarrow{\text{M—O—M}}$ bonds (two-electron three-center π-bonding with metal atoms of d^1 configuration) exhibits a weak but noticeable *trans*-influence. The xanthogenate and diethoxydithiophosphate complexes (79,80) are most illustrative: their sulfur atoms occupy three kinds of octahedral vertices: in *trans*-position to each other, to a bridging oxygen and to terminal oxygen atoms. On average, the Mo—S distances along the coordinate ⇆O⇄Mo—S are 0.06 Å longer and 0.20 Å shorter than those along S—Mo—S and O=Mo—S, respectively.

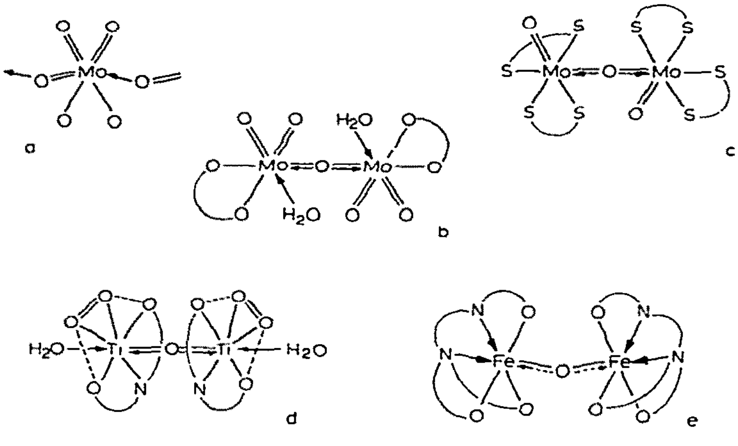


Fig. 9. The structures of complexes with single oxygen bridges and polydentate ligands: a, $[MoO_2(\mu\text{-}O)C_2O_4]^{2-}$; b, $[\{MoO_2(C_2O_4)H_2O\}_2O]^{2-}$; c, $\{MoO(S_2COEt)_2\}_2O$ and $\{MoO[S_2P(OEt)_2]_2\}_2O$; d, $[\{Ti(O_2)NC_5H_3(COO)_2(H_2O)\}_2O]^{2-}$; ε, $[\{Fe(HEDTA)\}_2O]^{2-}$.

In general, the *trans*-influence of symmetric bridges upon such *trans*-ligands as H_2O, NH_3 and Py considerably exceeds the similar influence upon Cl and C_2O_4. This problem will be discussed in section C (iii).

4. *Nitrosyl complexes*

The stereochemistry of transition metal nitrosyl complexes and particularly the structure of the M—NO group has been studied quite intensively. The crystal structures of nearly 70 nitrosocompounds of different metals have been determined. Octahedral coordination has been demonstrated for about 20 compounds and tetragonal-pyramidal structure for 10 complexes. The other structures contain trigonal bipyramidal and tetracoordinated complexes or π-complexes and cluster groups which are beyond the scope of the present review.

Recent structural investigations confirm the existence of two configurations of the M—NO fragment. Table 6 lists the data on octahedral nitrosyl complexes*. In the first (large) group of compounds the fragment M—NO is linear or almost linear; the M—N distance is relatively short which corresponds to multiple bonding. Here the MNO angle lies within 163—180°, the M—N distance ranging from 1.67 to 1.82 Å for the metals of the second transition period (Ru, Mo) and from 1.63 to 1.71 Å for metals of the first transition period (V, Cr, Mn, Fe)**. A different configuration of the M—NO frag-

---

* In $Mo(NO)(S_2CNR_2)_3$, R = Me, Et the molybdenum polyhedron is a pentagonal bipyramid. For additional data, see p. 86, paragraph 5.

** We do not account for the data on $K_4[Mo(NO)(CN)_5]$ having order-disorder character, nor for the structure of $Mo(NO)_2Cl_2(PPh_3)_2$ in which one of the nitrosogroups is fixed with poor accuracy owing to a disordered arrangement of this group and a chlorine atom along the ON—Mo—Cl coordinate.

ment has been found in three cobalt complexes (compounds 99—101) and in two binuclear platinum complexes: $[Pt_2(NO)_2Cl_8]^{2-}$ (compound 102) and $Pt_2(NO)_2Cl_6^{2-}$ (see p. 86). Here the M—NO group is essentially non-linear ($\angle$MNO = 112—135°) and the M—N distances are 1.82—1.87 Å in the Co compounds and 2.15 and 1.98 Å in two Pt complexes. The elongation of the M—N bond in passing from the first to the second group of complexes (taking account of the difference in metal atomic radii) is 0.2 Å for metals of the fourth period and about 0.2—0.4 Å upon replacement of Ru by Pt.

The difference in configuration and hence in the electronic structure of the metal—nitrosyl group is accompanied by a considerable difference in *trans*-elongation. Although in ruthenium compounds with linear M—NO fragments the substitution reactions involve mainly the position *trans* to the nitroso group [157] (large *trans*-effect), elongation of the *trans*-partner has not been observed at all (negligible *trans*-influence). *Trans*-elongation was revealed only in nitroso-tris-dithiocarbamates of Mo and Ru (compounds 97 and 91): in PBP-complexes of $MoNO(S_2CNR_2)_3$ Δ = 0.06 Å, in octahedral complexes of $RuNO(S_2CNR_2)_3$ Δ = 0.02 Å. Moreover, the value of Δ increases gradually from —0.02 to +0.04 Å in $[MNO(CN)_5]^{n-}$ complexes in the series: Fe, Mn, Cr. On the other hand, the $Ru—Cl_{trans}$ bond in $M_2[RuNOCl_5]$, where M=NH_4, K (7 and 8) is shorter with respect to $Ru—Cl_{eq}$ bonding: by 0.019 Å in ammonium and by 0.013 Å in potassium salts, the accuracy of distance determination being 0.001 Å*.

Unlike the linear M—NO group the angular group displays considerable *trans*-influence: *trans*-elongation amounting to 0.2—0.4 Å. It is particularly noticeable in binuclear Pt complexes. Figure 5h shows the structure of the $[Pt_2(NO)_2Cl_8]^{2-}$ complex. Here the $Pt—Cl_{bridge}$ distance *trans* to $Cl_{terminal}$ is 2.35 Å, whereas in *trans*-position to NO it is equal to 2.74 Å. In the $[Pt_2(NO)_2Cl_6]^{2-}$ complex the similar bond *trans* to $(NO)_{terminal}$ has the length of 2.62 Å.

Thus the nitroso group differs from the other ligands discussed. It exhibits maximum *trans*-influence in the case of relatively weak bonding with the metal. According to our model the specificity of the nodal character of the occupied MO's in the three-center X—M—L fragments serves as a fundamental basis for explaining such a difference in the *trans*-influence in nitrosyl complexes of the two types. Assuming the complex valence shell to be composed of three electrons from the nitroso group ($ON\rightleftarrows M$), one electron from each acid ligand and two electrons from each donor ligand, one will find that the total number of valence electrons is equal to or less than 18 in all the octahedral complexes with a linear configuration of the M—NO fragment, whereas it increases to 20 in all complexes with the angular M—NO structure. In the last case the extra pair of electrons is placed into a third (anti-bonding) three-

---

* An abnormally short [95] $V—CN_{trans}$ bond (1.853 Å) in $K_2[VNO(CN)_5]$ is explained by a disordered arrangement of nitroso- and cyano-groups along the axis of a bipyramid.

TABLE 6

Structural parameters and frequencies ν_{NO} in octahedral nitrosyl complexes

Nos	Compound	N a)	Distances, A		
			M–N_{NO}	M–L_{trans}	M–L_{equ}
(7)	$(NH_4)_2[RuNOCl_5]$	18	1.74	2.357 Cl	av. 2.376 Cl
(8)	$K_2[RuNOCl_5]$	18	1.747 1.799	2.359 Cl 2.369 Cl	av. 2.372 Cl av. 2.357 Cl
86	$OsNOCl_2(HgCl)(PPh_3)_2$	18	1.79	2.37 Cl	2.42 Cl av. 2.395 P 2.577 Hg
87	$K_2[RuNO(OH)(NO_2)_4]$	18	1.79	1.99 OH	av. 2.08 N_{NO_2}
88	$Na_2[RuNO(OH)(NO_2)_4]$	18	1.75	1.95 OH	av. 2.08 N_{NO_2}
89	$[RuNO(OH)(NO_2)_2(NH_3)_2]$	18	1.76	1.95 OH	av. 2.056 N_{NO_2} av. 2.126 NH_3
(23)	$(NH_4)_2[RuNO(H_2O)Cl_4]Cl.H_2O$	18	1.67	2.06 H_2O	av. 2.35 Cl
90	$[RuNO(NH_3)_5]Cl_3.H_2O$	18	1.80	2.19 NH_3	av. 2.08 NH_3
91	$RuNO(S_2CNEt_2)_3$	18	1.72	2.415 S	av. 2.395 S
92	$Na_2(FeNO(CN)_5].2H_2O$	18	1.63	1.90 C	av. 1.92 C
93	$K_3[MnNO(CN)_5].2H_2O$	18	1.66	2.01 C	av. 1.98 C
94	$[Coen_3][CrNO(CN)_5].2H_2O$	17	1.71	2.075 C	av. 2.033 C
95	$K_3[VNO(CN)_5]$ b)	16	1.66 b)	1.853 C b)	av. 2.17 C
96	$K_4[MoNO(CN)_5]$ b)	18	1.95	2.20 C	av. 2.13 C
97	$MoNO(S_2CNR_2)_3$ c)	18	1.73	2.568 S	av. 2.51 S
98	$Mo(NO)_2Cl_2(PPh_3)_2$ b)	18	1.82 1.91 b)	2.477 2.420 b) Cl	av. 2.596 P
99	$[CoNO(NH_3)_5]Cl_2$	20	1.87	2.220 NH_3	av. 1.98 NH_3
100	$[CoNOClen_2]ClO_4$	20	1.82	2.575 Cl	av. 1.96 N_{en}
101	$[CoNO(NCS)(DAS)_2](NCS)$	20	1.85	2.10 N_{NCS}	av. 2.36 As
102	$(C_9H_7NH)_2[Pt_2(NO)_2Cl_8]$	20	2.15	2.74 Cl_b	av. 2.30 Cl_t 2.36 Cl_b

a) N is the total number of valence electrons (see the text).
b) Partly disordered structure and the distances between statistically distributed atoms.
c) Mo c.n. is equal to 7, PBP polyhedron.
d) The second reference for the IR data.

center (σ or π) orbital* having nodes both in the M–L_{trans} and X–M regions resulting in a simultaneous weakening of both bonds.

Occupation of this antibonding orbital not only elongates the two bonds, but also stimulates dative electron transfer from the metal to the nitroso group. This last fact is responsible for the change of configuration in the M–NO fragment (reduction of the symmetry of the $MNOL_5$ complex from C_{4v} to C_s via the second order Jahn–Teller mechanism [158]).

---

* In the 20-electron nitrosyl complexes with purely donor *trans*-ligands NH_3 and en, the upper occupied orbital is probably $\sigma - \psi_3$. (See p. 8).

Nos	Δ	Δ'	N—O	∠ MNO°	ν_{NO}, cm^{-1}	Ref., fig.
(7)	—0.02	0	1.13	176.7	1887	[60,137] d)
(8)	—0.02 0.01	0 0.01	1.12 1.09	176.8 171	1905	[61a] [61b]
86	—0.05	0.01	1.03	178	1820	[138]
87		~0.02	1.12	171	1900	[139]
88		~0.02	1.13	180	1907	[140]
89		~—0.02	1.12	176.6	1869 1900	[141]
(23)		0.01	1.16	176	—	[142]
90	0.11	0.11	1.11	167	1922 1935	[143]
91	0.02		1.17	170	1830	[144]
92	—0.02		1.13	178	1939	[145]
93	0.03		1.21	174.3	1730	[146]
94	0.04		1.207	175.6	1645	[147]
95			1.29	171.4	1530	[148]
96	(0.07)		1.23	175	1455	[148,149] d)
97	0.06		1.15	173.2	1630	[150]
98		(0.08)	1.22 1.16 b)	163.1 160.4	1774 1652	[151,152] d)
99	0.24	~0.27	1.15	119	1646	[153]
100		~0.33	1.04	120	1611	[154]
101		~0.20	1.01	135		[155]
102	0.38		1.18	112	1750	[156], 5h

The data on tetragonal-pyramidal (TP) nitrosyl complexes also agree with such an interpretation. Complete loss of a donor *trans*-ligand with its electron pair may be regarded as an extreme case of *trans*-influence in the 20-electron octahedral complex. Indeed, in all the 18-electron TP-nitrosocomplexes investigated the NO group occupies an axial position and the M—NO fragment is found to be angular, the only exception being 113 (Table 7)*. When the number of electrons is smaller, this fragment becomes linear and the choice of a vertex by the nitroso group depends on the composition of the complex and other factors. In particular, the complexes $[Ru(NO)_2Cl(PPh_3)_2]^+$ and $[Os(NO)_2(OH)(PPh_3)_2]^+$ (111 and 112) each contain two nitroso groups. It

---

* For additional data, see p. 86, paragraph 5.

TABLE 7

Structural parameters and frequencies ν_{NO} of tetragonal pyramidal transition metal nitrosyl complexes

Nos	Compound	N a)	Distances, A
			M—NO (ax)
103	$\{FeNO[S_2C_2(CN)_2]_2\}^{2-}$	17	1.56
104	$FeNO(S_2CNEt_2)_2$	17	1.69
105	$FeNO(S_2CNMe_2)_2$	17	1.720
106	$CoNO(S_2CNMe_2)_2$	18	1.746
107	$[Ir(NO)Cl(CO)(PPh_3)_2]BF_4$	18	1.972
108	$[Ir(NO)I(CO)(PPh_3)_2]BF_4.C_6H_6$	18	1.89
109	$[Ir(NO)I(CH_3)(PPh_3)_2]$	18	1.91
110	$[Ir(NO)Cl_2(PPh_3)_2]$	18	1.94
111	$[Ru(NO)_2Cl(PPh_3)_2][PF_6]$	18	1.859 (1.738) b)
112	$[Os(NO)_2(OH)(PPh_3)_2][PF_6]$	18	1.98 (1.71) b)
113	$[Ru(NO)(Diphos)_2][BPh_4].Me_2CO$	18	1.735

a) N is the total number of valence electrons.

b) Parameters for linear NO groups in the base of pyramid are given in parentheses.

c) The second reference for the IR data.

is quite logical that here an "angular" group NO resides at the pyramid axis, while the "linear" one occupies a vertex of the base. The ligand in the position *trans* to the latter group (Cl and OH, respectively) is at an ordinary distance from the metal.

When comparing the iron and cobalt nitroso-bis-dimethyldithiocarbamates, the correlation between the geometry of the M—NO fragment and electronic occupation appears to be most convincing. The crystals are pseudo-isostructural: their molecular location and orientation are similar. A decrease of the M—NO angle from 170.4 to 136° when the electron number increases by unity appears to be the only difference*.

In conclusion, it seems useful to point out two other features of the crystal structures of nitrosyl compounds.

1. An interligand interaction. In all octahedral complexes with the linear M—NO fragment the $M—L_{cis}$ bonds are inclined towards the *trans*-partner of

---

* A question arises whether there exists a correlation between the MNO angle and M—N distance in the angular complexes. In most of these the MNO angle lies between 119—128°, and the M—N distance between 1.82—1.87 A (for Co) and between 1.89—1.98 A for Ir and Os. Only two compounds (106 and 111) do not fit this series. In $CoNO(S_2CNMe_2)_2$ and $[Ru(NO)_2Cl(PPh_3)_2](PF_6)$ the angles MNO are greater (136°) and, accordingly, the M—N distances are shorter (1.746 and 1.859 A, respectively). A state, to a certain extent intermediate between the two extremes, is likely to occur here.

Nos	Distances, A		∠MNO	ν_{NO}	Ref.
	M—L_{base}	N—O			
103	av. 2.27 S	1.06	168	1645	[159]
104	av. 2.28 S	1.16	174	1673	[160,161]$^{c)}$
105	av. 2.294 S	1.102	170	1670	[162]
106	av. 2.263 S	1.16	136	1626	[163]
107	1.86 C_{CO}, 2.343 Cl, av. 2.408 P	1.16	124	1680	[164]
108	1.70 C_{CO}, 2.666 I, av. 2.360 P	1.17	125	1720	[165]
109	2.05_2 CH_3, 2.726 I, av. 2.340 P	1.23	120	1525	[166]
110	av. 2.348 Cl, av. 2.376 P	1.03	123	1560	[167]
111	2.365 Cl, av. 2.428 P	1.17	136	1687	[168]
		(1.162)	(179.5)	(1845)	
112	2.00 OH, av. 2.435 P	1.12	127.5	1632	[169,170]$^{c)}$
		(1.25)	(~180)	(1842)	
113	av. 2.388 P	1.197	174		[171]

the nitroso group (N_{NO}—M—L_{equ} > 90°). In particular, the metal atom is shifted over 0.13 Å from the *cis*-ligand plane in $[RuNO(H_2O)Cl_4]^-$ (23), and over 0.20, 0.16 and 0.13 Å in the series of $[M(NO)(CN)_5]^{3-}$, M = Fe, Mn and Cr (92—94), respectively.

In octahedral complexes with the angular M—NO fragment displacement of the metal from the equatorial plane is considerably smaller: 0.09 Å in $[CoNOClen_2]^+$ (100), 0.05 Å in $[CoNO(NH_3)_5]^{2+}$ (99), 0.01 Å in $[Pt_2(NO)_2Cl_8]^{2-}$ (102). Thus a displacement takes place due only to the shortening of the M—NO bond, and does not depend on its *trans*-influence. On the one hand, it confirms that an interligand interaction is the main reason for the angular distortions in MX_5 complexes, on the other it shows that the "pressure" of equatorial ligands on a *trans*-ligand cannot be a primary reason for *trans*-elongation (p. 25).

In the 18-electron TP-complexes with an angular M—NO fragment the metal atom is shifted from the plane of the base towards a nitrosyl vertex. Since steric pressure of the NO-group on the other ligands in this case is minimal, this fact may serve as good evidence of essential rehybridization upon the replacement of a hexavertex polyhedron of C_s symmetry by a pentavertex one (p. 12).

This is even more obvious from the change of the angular characteristics of the nitrido-halogenide complexes on going from $[MNHal_5]^{n-}$ to $[MNHal_4]^{(n-1)-}$. Replacement of the sixth halogenide vertex by a lone pair retaining the hybrid state of the complex would enhance resistance to repulsion between N and Cl atoms, i.e. decrease the bond angles $NMCl_{cis}$. However, on going from $K_2[OsNCl_5]$ [55] to $(Ph_4As)[OsNCl_4]$ [172] an increase in these angles from 96.2 to 104.6° was observed. It is quite obvious that the lone pair electron density is not localized at the sixth vertex of the octahedron.

2. Intermolecular contacts. The electron density transfer from metal to a nitroso group upon replacement of the linear M—NO by the angular fragment was confirmed by an analysis of the intermolecular contacts in crystals. In all structures with the linear M—NO fragments the nitroso groups are in contact with the negatively charged atoms (Cl, O_{NO_2}, N_{CN}). Typical examples are the ruthenium nitroso compounds listed in Table 6 (see e.g. ref. 141). On the other hand, in crystals of compounds 99—102 the nitrosyl oxygen does not touch electronegative atoms. For example, in crystals of $(C_9H_7NH)_2[Pt_2(NO)_2Cl_8]$ (102) the nitroso group is surrounded by carbons of the quinolinium cations, in $[CoNO(NH_3)_5]Cl_2$ (99) its neighbours are the NH_3 groups. For a more detailed discussion of this problem and the correlation of the data of structural analysis, IR spectra and ESCA spectra see ref. 190.

5. *Carbonyl and molecular nitrogen complexes*

The majority of carbonyl compounds studied are π-complexes where the term "coordination number" is rather artificial and the *trans*-influence is obscured by the complicated pattern of multi-center interactions. On the other hand most of the carbonyl complexes which do not belong to this class are overloaded by carbonyl groups with a relatively small number of other ligands L, the latter being quite often atypical for ordinary transition metal complexes (Table 8). In addition, all these compounds contain metals in low oxidation states for which the "ordinary" ("standard") M—L distances (or the respective metal covalent radii) differ from the analogous distances and radii for metals in the highest oxidation state. The choice of such radii is rather questionable and the discrepancies among the published values are so considerable that they overlap the scope of the possible *trans*-elongation effect (standard metal radii in carbonyl and π-complexes have been discussed [191,192]).

One may, however, use another route. i.e. to trace the relative influence of the OC—M and L—M bonds on the identical *trans*-partners. This is more favourable because of the presence of a large number of carbonyl groups in the complexes. It can be seen from Table 8 that the M—CO distance along the OC—M—CO coordinate is always 0.02—0.10 Å longer than along the L—M—CO coordinate. For Mn, e.g. in the first case the Mn—CO distances are within the range 1.79—1.87 Å (mean value 1.840) while in the second case they are within the range 1.73—1.82 Å (mean value 1.786). Here the carbonyl group is a ligand subjected to the action of a *trans*-partner. Since its bonding with the metal is mainly π-acceptor (with a relatively weak σ-donor component), this case is somewhat unique: the *trans*-influence of a multiple bond is conveyed by π instead of a σ-mechanism. It is quite natural that the maximum

TABLE 8

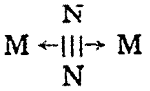
The metal—carbonyl group distances along OC—M—CO and L—M—CO coordinates

Nos	Compound	M—CO distances, Å		L	Δ	Ref.
		Along OC—M—CO	Along L—M—CO			
114	$(Me_4N)[B_3H_8Cr(CO)_4]$	1.885	1.83	H	0.05	[173]
115	$\{Me(MeO)C\}(PPh_3)Cr(CO)_4$	1.86	1.83	P a)	0.03	[174]
116	$Cr(Dien)(CO)_3$	—	av. 1.816	N		[175]
117	$(Et_5P_5)Mo(CO)_4$	2.01	1.93	P	0.08	[176]
118	$HMn(CO)_5$	1.840	1.821	H	0.02	[177]
119	$(CO)_4MnBr_2Mn(CO)_4$	1.865	1.760	Br	0.10	[178]
120	$(C_2F_2H)Mn(CO)_5$	1.79	1.73	C	0.06	[179]
121	$(CO)_4CoSnPh_2Mn(CO)_5$	1.84	1.79	Sn	0.05	[180]
122	$(\pi\text{-}C_5H_5)Fe(CO)_2Mn(CO)_5$	1.825	1.749	Fe	0.07	[181]
123	$(CO)_5MnFe(CO)_4Mn(CO)_5$	1.855	1.805	Fe	0.05	[182]
124	$(CO)_5ReHRe(CO)_4Mn(CO)_5$	1.83	1.80	Re	0.03	[183]
125	$(CO)_5MnMn(CO)_5$	1.83	1.79	Mn	0.04	[184a]
		1.86	1.82		0.04	[184b]
		1.873	1.803		0.07	[184c]
126	$(Et_3P)(CO)_4MnMn(CO)_4(PEt_3)$	1.81	—	Mn		[185]
127	$(CO)_4Mn(H)PPh_2Mn(CO)_4$	1.84	1.785	H P	0.05	[186]
128	$(NH_2CH_3)(CONHCH_3)Mn(CO)_4$	1.847	1.775	N	0.07	[187]
129	$CeC_6H_4C(O)Re(CO)_5$	2.00	1.96	C	0.04	[188]
130	$Me_3Sn(CO)_3Ru(SnMe_2)_2Ru(CO)_3SnMe_3$	1.90	1.86	Sn	0.04	[189]

a) The M—CO in *trans*-position to Me(MeO)C is not given.

effect is observed if the *trans*-influencing ligand is also a π-acceptor (i.e., a CO group), but this does not occur if a σ-component predominates in the bonding of this ligand. In particular, even the σ-bonded carbon atom, generally the most powerful *trans*-labilizer does not greatly influence the carbonyl group (compounds 115, 120, 129).

Structural data on transition metal molecular nitrogen complexes are rather poor. Table 9 lists only eight compounds. Five of them contain the terminal N_2 group, two compounds have a bridge with the linear $M \leftarrow N \equiv N \rightarrow M$ fragment, and one complex has the bridge with a "perpendicular" structure



$$M \leftarrow \overset{N}{\underset{N}{|||}} \rightarrow M$$

These data are rather obscure and contradictory with regard to the structural manifestation of the *trans*-influence. In ruthenium pentaammoniate (133) the groups N_2 and NH_3 are distributed statistically at the vertices of an octahedron, and it is difficult to discern a *trans*-elongation. In the similar osmium compound (135) the Os—NH_3 distances along the *trans*- and *cis*-coordinates are almost the same, but they are somewhat longer than those in the ordinary Os^{II} compounds. The same holds in the case of the binuclear ruthenium ammoniate (136). In the ruthenium azido-ethylenediamine complex (134) N_3 is in a *trans* position to N_2. The Ru—N_{N_3} and Ru—N_{en} bond lengths are nearly the same, but it is not clear how large the "normal" Ru—N_{N_3} distance should be. Finally, in the mixed binuclear complex of Re and Mo (137) no *trans*-elongation is observed. However, unlike the other (in particular, the second) binuclear complexes, this compound has particularly long N—N and short M—N bonds.

In $Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$ (131) the two N_2 groups are in *trans* positions to each other. The M—N_{N_2} distances are 0.15—0.20 Å longer than those in other compounds. In this case one may draw an analogy with carbonyl compounds: in both cases the M—X distances are elongated when the two X groups (X = CO or N_2) are in *trans* positions to each other. The Re—Cl bond in $Re(N_2)Cl(PMe_2Ph)_4$ (132) is also greater than the normal one. However, in the structural investigation [194] it was assumed that the distribution of Cl and N_2 is not quite regular in the two *trans*-positions of the octahedral complex; since upon inversion of the Cl—Re—M—N axis the chlorine atoms falls between two N atoms, this irregularity may account for the apparent decrease of the N—N, and increase of the Re—N, distances. Judging by the structural parameters (see Table 9) such an effect is really observed. But an opposite effect of the N atoms on the Cl coordinates revealed in the treatment of the experimental data is not excluded either. Thus the conclusion concerning the Re—Cl distance is not entirely reliable.

6. *Metal—metal bonds*

In principle metal—metal bonds of different multiplicity should exhibit a

TABLE 9

Metal—ligand distances in octahedral molecular nitrogen complexes

Nos	Compound	Distances, Å				Δ	Δ′	ref.
		M—N$_2$	N—N	M—L$_{trans}$	M—L$_{cis}$			
131	*trans*-$Mo(N_2)_2\{Ph_2PCH_2CH_2PPh_2\}_2$	2.10	1.10	2.10 N_2	av. 2.475 P		~0.12	[193]
132	$Re(N_2)Cl(PMe_2Ph)_4$	1.97	1.05	2.52 Cl	av. 2.422 P		0.13	[194]
133	$[Ru(N_2)(NH_3)_5]Cl_2$ a)	(2.10)	1.12	(2.10) NH_3	av. (2.10) NH_3	—	—	[195]
134	$[Ru(N_2)(N_3)(en)_2](PF_6)$	1.894	1.11	2.12 N_3	av. 2.125 N_{en}			[196]
135	$[Os(N_2)(NH_3)_5]Cl_2$	1.84	1.12	2.15 NH_3	av. 2.138 NH_3	0.01	0.07	[197]
136	$[Ru(NH_3)_5(N_2)Ru(NH_3)_5](BF_4)$	1.928	1.12	2.14 NH_3	av. 2.12 NH_3	0.02	0.06	[198]
137	$(PR_3)_4\overline{Cl}\overline{Re}(\overline{N}_2)\overline{Mo}Cl_4(OCH_3)$	{ 1.79 Re 1.89 Mo	1.21	2.41 Cl c) OCH_3	2.48 PR_3 c) Cl }		0.02	[199]
138	$[(PhLi)_6Ni_2N_2(Et_2O)_2]_2$ b)	av. 1.925	1.35	av. 2.645 Li	—			[200]

a) NH_3 and N_2 are statistically distributed at the octahedron vertices.

b) The central fragment of the complex has the configuration $M\text{—}\overset{N}{\underset{N}{|||}}\text{—}M$.

c) The bond length is not given.

TABLE 10

The *trans*-influence of the metal—metal multiple bond in binuclear complexes

Nos	Compound	d^n	q	Distances, A
				M—M
139	$K_4[Mo_2(SO_4)_4].2H_2O$	d^4	4	2.110
(16)	$Cs_4[Re_2Cl_8(H_2O)_2][Re_2Cl_8]$	d^4	4	2.111
(17)	$Re_2Cl_4(MeCOO)_2(H_2O)_2$	d^4	4	2.224
140	$K_3[Mo_2(SO_4)_4].3,5H_2O$	d^4-d^5	3.5	2.164
141	$Re_2Cl_5(Me_2C_2H_4S_2)_2$	d^4-d^5	3.5	2.293
142	$Rh_2(MeCOO)_4(H_2O)_2$	d^7	$\leqslant 3$	2.386
143	$Rh_2(HCOO)_4(H_2O)$	d^7	$\leqslant 3$	2.38
144	$Rh_2(C_4H_7N_2O_2)_4(PPh_3)_2H_2O.C_3H_7OH$	d^7	~1	2.934
145	$Co_2(PhCOO)_4(C_9H_7N)_2$	d^7	~1	2.832
(1)	$(NH_4)_2[Re_2(HCOO)_2Cl_6]$	d^4	4	2.260
146	$Re_2(PhCOO)_4Cl_2.2CHCl_3$	d^4	4	2.235
147	$Re_2(PrCOO)_3Cl_2ReO_4$	d^4	4	2.259
148	$Re_2(PrCOO)_4(ReO_4)_2$	d^4	4	2.251
(141)	$Re_2Cl_5(Me_2C_2H_4S_2)_2$	d^4-d^5	3.5	2.213
149	$Ru_2(PrCOO)_4Cl$	d^5-d^6	2.5	2.281
150	$(CN_3H_6)_2[Rh_2(MeCOO)_4Cl_2]$	d^7	$\leqslant 3$	2.47
151	$(NH_4)_4[Rh_2(MeCOO)_4Br_2]Br_2$	d^7	$\leqslant 3$	2.47
152	$Ba_3[Co_2(CN)_{10}].13H_2O$	d^5-d^6	~1	2.794 2.798

q = the multiplicity of the bond (see explanation in the text).

different labilizing effect on L_{trans} ligands. However, no such data were presented in Table 3, not only because of limitations in composition, but also because of the uncertainty of bond order. The last is not uniquely determined by the d^n configuration, but depends on the sequence of bonding and antibonding M—M orbitals of different types (σ, π, $\bar{\pi}$ and δ) (cf. [202]).

Additional data on binuclear clusters with different d^n metal orbitals are shown separately in Table 10. The upper section presents compounds with acid partners of the M—M bond. Besides illustrating the general M—L_{trans} bond elongation caused by M—M bonding, these data demonstrate (with account taken of the aforementioned limitation) a gradual decrease of *trans*-influence with weakening (elongation) of the metal—metal bond*.

---

* Replacement of the d^4—d^4 configuration by d^4—d^5 does not affect the value of Δ. As mentioned above the effect of a δ-bond on the *trans*-M—L bond is rather weak.

Nos	Distances, Å		Δ	Δ'	Ref., fig.
	M—L_{trans}	M—L_{equ}			
139	2.593←O_{SO_4}	2.13 O_{SO_4}	0.46	0.50	[203], 10a
(16)	2.44 H_2O	2.33 (2.17) Cl		0.36	[68], 10b
(17)	av. 2.507 H_2O	av. 2.30 Cl		0.43	[69], 10c
140	2.55 H_2O	2.064←O_{SO_4}	0.49	0.46	[204], 10a
141	3.22←Cl_b	2.337 Cl 2.439 S	0.88	0.83	[205], 10d
142	2.302 H_2O	2.04 O_c	0.26	0.28	[206,16,207], 10a
143	2.20 H_2O 2.45 O_c	2.03 O_c	0.17 0.42	0.18 0.43	[208], 10e
144	av. 2.438 P	av. 1.99 N		~0.05	[209], 10f
145	2.102 N	av. 2.02 O_c		~0.2	[210], 10a
(1)	2.71 Cl	av. 2.32 O_c	0.39	0.32	[54], 10c
146	2.489 Cl	av. 2.018 O_c 2.29 Cl		0.10	[211], 10a
147	2.280 O_{ReO_4}	2.22 Cl 2.01 O_c	0.27	0.20	[212], 10g
148	2.18 O_{ReO_4}	2.04 O_c	0.14	0.10	[213], 10a
(141)	2.493 Cl_b	2.337 Cl 2.439 S	0.15	0.10	[205], 10d
149	2.587 Cl_b	av. 2.00 O_c		(0.23)	[214], 10h
150	2.49 Cl	2.06 O_c		0.16	[215,16], 10a
151	2.53 Br	2.08 O_c		0.08	[215,16], 10a
152	1.946 C 1.961 C	av. 1.885 C av. 1.886 C	0.07 0.08	~0.1 ~0.1	[216a], 10b [216b]

Structural investigation shows as well that some form of *trans*-influence may take place in M_n clusters with $n > 2$. The weakest M—L bonds in such clusters are those in a *trans*-position from the center. In particular, this includes the trinuclear rhenium clusters $[Re_3Hal_{12}]^{3-}$ and their derivatives (Fig. 10i). Table 11 shows that the distances from Re to the terminal atoms in the plane of the rhenium triangle (Re—L_{trans}) considerably exceed those to the atoms above and under the triangular plane (Re—L_{cis}). Halogen ion substitution or elimination in $[Re_3Hal_{12}]^{3-}$ complex always takes place in L_{trans} positions [224].

The value of Δ in a triangular cluster is considerably smaller than those in binuclear complexes of rhenium. This is quite natural, since the formal metal—metal bond multiplicity decreases with the number of metal atoms. In particular, in octahedral clusters almost no structural *trans*-influence has been observed. For example [225], in $[Mo_6Br_8Br_4(H_2O)_2]$ the Mo_6 octa-

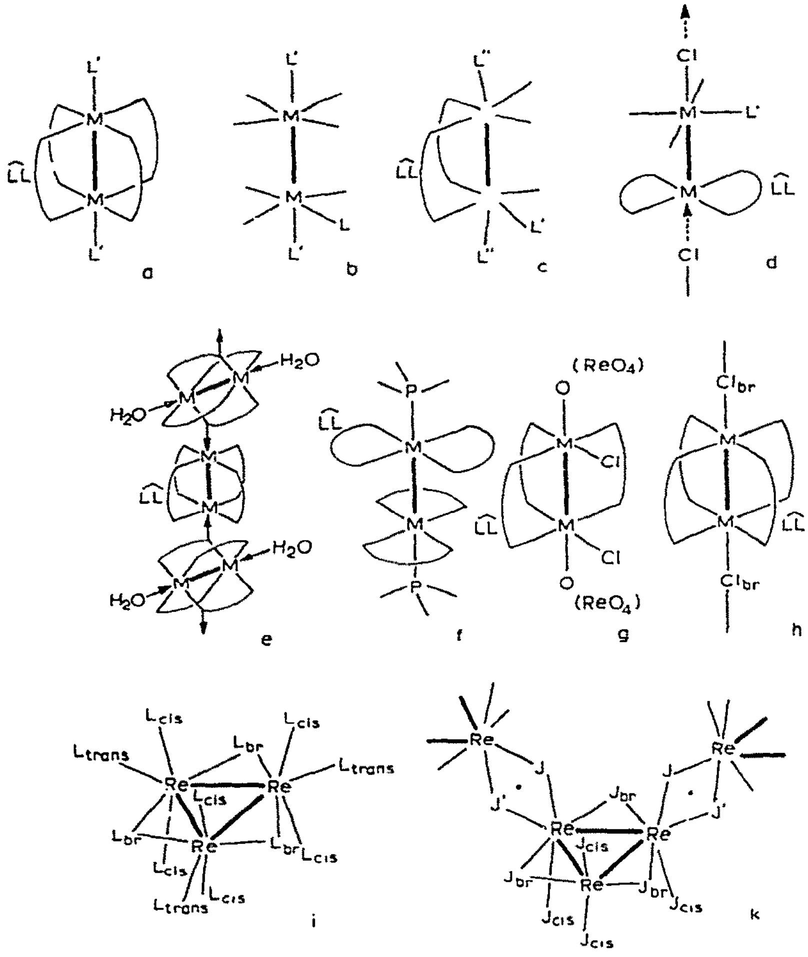


Fig. 10. The structures of complexes with metal—metal bonds: a, $M_2(\widehat{LL})_4L'_2$; b, $M_2L_8L'_2$; c, $M_2(\widehat{LL})_2L'_4L''_2$; d, $Re_2Cl_5(Me_2C_2H_4S_2)_2$; e, $Rh_2(HCOO)_4H_2O$; f, $Rh_2(C_4H_7N_2O_2)_4(PPh_3)_2$; g, $Re_2(PrCOO)_3Cl_2ReO_4$; h, $Ru_2(PrCOO)_4Cl$; i, $[Re_3L_{12}]^{3-}$; k, Re_3I_9.

hedron inscribed in the cube of Br bridge atoms has four Br atoms and two water molecules in *trans*-positions with respect to the centre of the cluster. The distances $Mo—Br_{trans}$ and $Mo—H_2O_{trans}$ are equal to 2.589 and 2.19 Å respectively, the values of Δ' being 0.05 and 0.10 Å. In W_6Br_{16} the similar $W—Br_{trans}$ distances are equal to 2.56 Å (Δ' = 0.03), in $MoCl_2$ the $Mo—Cl_{trans}$ distances [227] are reduced to 2.38 Å (Δ' = 0).

The carbonyl clusters may serve as an additional illustration of the dependence of Δ on the formal M—M bond multiplicity. The data on $(CO)_5M—M(CO)_5$, $(CO)_5M—M(CO)_4—M(CO)_5$ and some other clusters have already been given in Table 8. As commented previously in all cases the

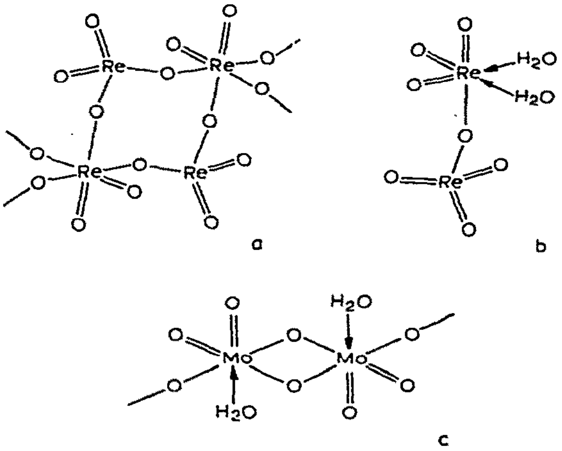


Fig. 11. The formation of M_2O_7 fragments: a, Re_2O_7; b, $Re_2O_7.2H_2O$; c, $[Mo_2O_7(H_2O)_2]^{2-}$.

M—CO distance in the *trans*-position to the M—M bond is shorter than the distance along the OC—M—CO coordinate. This means that the structural *trans*-influence of the ordinary metal—metal bond in the zero-valent metal complexes is weaker than that of the carbonyl group.

(iii) The role of L_{trans} ligand

In view of the model (section B), the weakening (elongation) of the M—L bond should depend both on the possibilities of competing with ligand X for

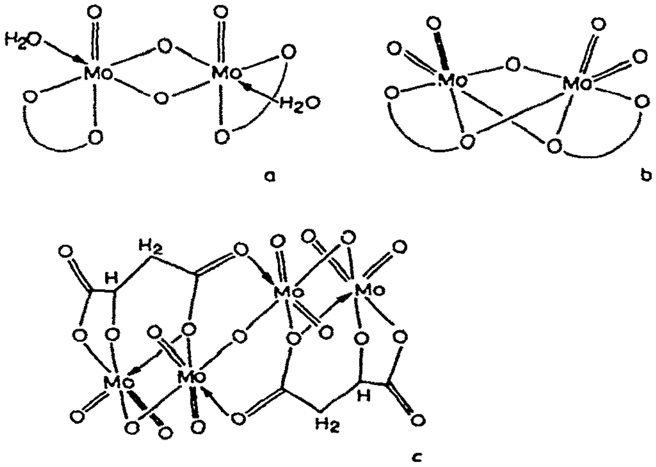


Fig. 12. The structures of complexes with double oxygen bridges and polydentate ligands: a, $[\{MoO(C_2O_4)(H_2O)\}_2O_2]^{2-}$; b, $[\{MoO_2(C_6H_4O_2)_2\}_2O]^{2-}$; c, $[Mo_4O_{11}(C_4H_3O_5)_2]^{4-}$.

TABLE 11

The *trans*-influence of the metal—metal bond in trinuclear rhenium complexes

Nos	Compound	Distances, A	
		M—M	$M-L_{trans}$
153	$Re_3Cl_9(PEt_2Ph)_3$	2.49	2.70 P
154	Re_3Cl_9	2.49	$2.66 \leftarrow Cl_b-$
155	Re_3I_9	2.440 2.507	$2.94 \leftarrow I_b-$
156	$(Ph_4As)_2[Re_3Cl_{11}(H_2O)]$	2.44 2.48	2.40 H_2O
157	$(C_9H_7NH)_2[ReBr_6][Re_3Br_9(H_2O)_3]$	av. 2.460	2.40 H_2O
158	$Cs_3[Re_3Cl_{12}]$	{ av. 2.477 av. 2.50	av. 2.52 Cl 2.60 Cl
159	$Cs_2[Re_3Br_{11}]$	{ 2.43 2.50 }	2.72 Br
(156)	$(Ph_4As)_2[Re_3Cl_{11}(H_2O)]$	{ 2.44 2.48 }	2.56 Cl

participation in σ-bonding MO's and on its ability for π-interaction with the central atom.

The first is readily traced by comparing the $M-L_{trans}$ distances in the compounds of identical composition with acid and donor ligands in the position *trans* to X. Table 12 shows data for about 40 compounds of different metals, the ligand L being F, Cl, Br anions or H_2O, NCR and NH_3 molecules. Compounds of similar composition (the same X and M, identical *cis*-ligands) are divided into groups*. It is quite clear that donor ligands are more *trans*-influenced than acidic ligands. The same difference is observed in the binuclear (M_2) and trinuclear (M_3) clusters (Tables 10 and 11). The molybdenum oxochlorides and oxobromides are an exception. In these compounds the Cl_{trans} and Br_{trans} bonds are weakened to the same extent as the bonds with $(H_2O)_{trans}$. One may also exclude ruthenium nitrosyl complexes which display practically no *trans*-influence even in the case of a donor *trans* ligand.

Additional data confirming considerable weakening of bonds of the metal with water and other monodentate donor ligands have been given already in Table 4 and other tables.

The result is less convincing in the case of polydentate ligands where the difference between the donor and acidic parts of a ligand is smoothed or vanishes absolutely while the steric factors could be quite significant. For an il-

---

* The majority of compounds have already been listed in Tables 3—7. To provide a clearer comparison the principal data for these compounds are re-presented here. More detailed data on compounds absent in the previous tables are given in Table 12a.

Nos	Distances, Å		Δ	Δ'	Ref., fig.
	M—L_{cis}	M—L_b			
153	av. 2.31 Cl	av. 2.38 Cl		~0.4	[217], 10i
154	2.29 Cl_t 2.40 —Cl_b	2.46 Cl	0.26	0.27	[218], 10k
155	av. 2.604 I_t 2.744 I_b	av. 2.739 I	0.20	~0.3	[219], 10k
156	av. 2.30 Cl	av. 2.35 Cl		0.32	[220], 10i
157	av. 2.445 Br	av. 2.533 Br		0.32	[211], 10i
158	av. 2.36 Cl	av. 2.39 Cl	0.26	0.13	[222a], 10i }
	av. 2.35 Cl	av. 2.43 Cl	0.25	0.21	[222b]
159	av. 2.43 Br	av. 2.55 Br		0.18	[223]
(156)	av. 2.30 Cl	av. 2.35 Cl		0.17	[220], 10i

lustration, Table 13 shows the distances from M to O or N atoms (of polydentate ligands) occupying positions *trans* to terminal (or bridging) oxygen atoms in the complexes, the formal type of bonding (acidic or donor) is also noted.

Table 13 is divided into two parts: the first part includes complexes with planar (unsaturated) bidentate ligands; the second part contains non-planar (saturated) polydentate ligands. Each part, firstly, lists the purely acidic polydentate ligands or those with formally acid atoms in *trans*-position to the multiple bond, then mixed "acid-donor" ligands and, finally, the purely donor ligands or those with donor atoms in *trans*-position to the multiple bond. As a whole, once again the distances from metal to donor-bonded atoms are somewhat longer than those to acid, or formally acid, ligands.

In this respect, Mo (and Nb) complexes with unsaturated ligands are most illustrative. The acid ligands are represented mainly by oxalate, while the donor ligands are bipyridine and phenanthroline. The Mo—O distances lie within 2.05—2.24 Å, the Mo—N and Nb—N distances ranging from 2.26 to 2.45 Å. The difference in the mean values (2.167 and 2.337 Å) exceeds by about an order of magnitude the usual difference in Mo—O and Mo—N distances in complexes with planar bidentate ligands. Secondly, attention may be drawn to the great difference (0.2 Å) between the Mo—O and Mo—N distances in trioxomolybdenum-EDTA complexes (57).

It goes without saying that the inequivalence of M—ligand bonds in metal chelate rings may be caused for different reasons and also arise in the absence of multiple metal—ligand bonds. A *trans*-influence however, may increase such an inequivalence, thereby indicating the direction of shift of electron

TABLE 12

Elongation of bonds with acid and donor ligands

Nos in tables	L_{trans}—acid ligand Compound	M—L_{trans}	Δ	Δ'
160	$(Ph_4As)[NbO(NCS)_5]$	2.27 NCS	0.21	
(28)	$K_2[NbOF_5]$	2.06 F	0.22	~0.2
(29)	$K_2[MoOF_5].H_2O$	2.03 F	0.17	~0.2
161	$K_2[MoOCl_5]$	2.631 Cl	0.23	0.23
162	$(NH_4)_2[MoOBr_5]$	2.83 Br	0.27	0.30
(10)	$ReOCl_3(PEt_2Ph)_2$	2.47 Cl	0.05	0.08
(3)	$K_2[ReOCl_5]$	2.47 Cl	0.08	0.08
(9)	$ReNCl_2(PEt_2Ph)_3$	2.56 Cl	0.11	0.17
(2)	K_2OsNCl_5	2.50 Cl	0.14	0.11
(146)	$Re_2(PhCOO)_4Cl_2.2CHCl_3$	2.489 Cl		0.10
(141)	$Re_2Cl_5(S_2C_4H_{10})_2$	2.493 Cl	0.16	0.10
(150)	$(CN_3H_6)[Rh_2(MeCOO)_4Cl_2]$	2.49 Cl		0.15
(151)	$(NH_4)_4[Rh_2(MeCOO)_4Br_2]Br_2$	2.53 Br		0.05
163	Re_2O_7	av. 2.12 O_b		~0.05
164	$Re_2O_7(H_2O)_2$	2.06 O_b		~0
(8)	$Re(NMe)Cl_3(PEtPh_2)_2$	2.411 Cl	−0.01	0.02
(13)	$Re(NC_6H_4COCH_3)Cl_3(PEt_2Ph)_2$	2.41 Cl	−0.02	0.02
(14)	$Re(NC_6H_4OCH_3)Cl_3(PEt_2Ph)_2$	2.43 Cl	0.01	0.04
(15)	$K_2[RuNOCl_5]$	2.369 Cl	0.01	0.02
(5)	$K_4[Ru_2Cl_{10}O]$	2.36 Cl	0	0
(4)	$Cs_4[Os_2Cl_{10}O]$	2.433 Cl	0.06	0.07
(6)	$K_4[Re_2Cl_{10}O].H_2O$	2.38 Cl	0	−0.01

[a] Pentagonal bipyramidal coordination with the X—M—L_{trans} fragment along bipyramid axis.

density in the metal chelate. In particular, this refers to planar chelates which have a symmetric composition and unequal M—L distances. In Table 13, dissimilar metal ligand distances in oxomolybdenum xanthogenate (79) and di-

Nos in tables	L_{trans}—donor ligand Compound	M—L_{trans}	Δ	Δ'
(41)	$K[MoOCl_4(H_2O)]$	2.27 H_2O		0.18
(42)	$(Ph_4As)[MoOBr_4(H_2O)]$	2.39 H_2O		0.30
(20)	$ReOCl_4(H_2O)$	2.27 H_2O		0.19
(21)	$(Et_4N)[ReOBr_4(H_2O)]$	2.32 H_2O		0.24
165	$(Ph_4N)[ReOBr_4NCMe]$	2.31 N_{NCMe}		~0.25
166	$\{VO(acac)_2\}_2(dioxan)$	2.51 O_{diox}	0.52	~0.50
167	$VO(NO_3)_3(NCMe)$ [a]	2.24 N_{NCMe}	0.21	~0.30
(61)	$K_2[\{MoO(O_2)_2(H_2O)\}_2O]$ [a]	av. 2.45 H_2O		0.36
(62)	$PyH[\{MoO(O_2)_2(H_2O)\}_2O]$ [a]	2.43 H_2O		0.34
(64)	$(PyH)_2[\{MoO(O_2)_2\}_2(\mu\text{-}OOH)_2]$ [a]	2.39 OOH	0.34	~0.3
168	$K_2[ReN(NC)_4].H_2O$	2.44←N—		~0.33
(18)	$K[OsNCl_4(H_2O)]$	2.50 H_2O		0.45
(19)	$K[OsNBr_4(H_2O)]$	2.42 H_2O		0.37
(17)	$Re_2Cl_4(MeCOO)_2(H_2O)_2$	2.502 H_2O		0.42
(141)	$Re_2Cl_5(S_2C_4H_{10})_2$	3.22←Cl—	0.88	0.83
(142)	$Rh_2(MeCOO)_4(H_2O)_2$	2.302 H_2O	0.26	0.28
(143)	$Rh_2(HCOO)_4H_2O$	2.20 H_2O	0.17	0.18
		2.45←O<	0.42	0.43
169	$VOSO_4.5H_2O$	2.223 H_2O	0.18	~0.30
(164)	$Re_2O_7(H_2O)_2$	2.21 H_2O		0.13
170	$(UO_2)[Mo_2O_7(H_2O)_2]H_2O$	av. 2.305 O_b	0.35	~0.25
		av. 2.295 H_2O		0.20
170'	$[MoO(\mu\text{-}O)_2(H_2O)].H_2O$	2.293 H_2O		0.20
171	$W(NC_2Cl_5)Cl_4(NCCCl_3)$	2.37 N		~0.3
(23)	$(NH_4)_2[RuNOCl_4H_2O]Cl.H_2O$	2.06 H_2O		0.01
(22)	$K_3[Ru_2Cl_8(H_2O)_2N]$	2.18 H_2O		0.13
(82)	$[Cr_2(NH_3)_{10}O]Cl_4.H_2O$	2.14 NH_3	0.04	0.12

ethoxydithiophosphate (80) complexes are designated by — and →. Similarly (although tentatively) the oxygen atoms are so designated in the complex of molybdenum trioxide with a malic acid anion (186).

Structural data on complexes with a monodentate *trans*-ligand L capable of π-interaction with the metal atom are rather limited. No such data are

TABLE 12a

The M—X, M—L_{trans} and M—L_{equ} distances in compounds not listed previously in the tables

Nos	Compound	d^n	Distances, A			Δ	Δ'	ref., fig.
			X—M	M—L_{trans}	M—L_{cis}			
160	$(Ph_4As)[NbO(NCS)_5]$	d^0	1.70	2.27 NCS	av. 2.092 N	0.21		[228]
161	$K_2[MoOCl_5]$	d^1	1.67	2.631 Cl	av. 2.40 Cl	0.23	0.23	[56]
162	$(NH_4)_2[MoOBr_5]$	d^1	1.86	2.83 Br	av. 2.56 Br	0.27	0.30	[229]
163	Re_2O_7	d^0	av. 1.69 O_t av. 1.740 O_b	av. 2.125 O_b av. 2.07 O_b			~0.05 ~0	[230], 11a
164	$Re_2O_7(H_2O)_2$	d^0	1.74 1.76	2.21 H_2O 2.06 O_b			0.13 ~0	[231], 11b
165	$(Ph_4N)[ReOBr_4NCMe]$	d^2	1.73	2.31 N_{NCMe}	av. 2.48 Br		~0.25	[232]
166	$\{VO(acac)_2\}_2(dioxan)$	d^1	1.62	2.51 O_{diox}	av. 1.990 O_{acac}	0.52	~0.50	[233]
167	$VO(NO_3)_3(NCMe)$ a)	d^0	1.55	2.24 N_{NCMe}	av. 2.03 N_{NO_3}	0.21	~0.3	[234]
168	$K_2[ReN(NC)_4].H_2O$	d^2	1.53	2.44←N≡	2.13 N_{NC}		~0.33	[235]
169	$VOSO_4.5H_2O$	d^1	1.591	2.223 H_2O	av. 2.010 O_{SO_4} av. 2.041 H_2O	0.18	~0.3	[236]
170	$(UO_2)[Mo_2O_7(H_2O)_2]H_2O$	d^0	av. 1.615 av. 1.830	av. 2.305 O_b av. 2.295 H_2O	av. 1.955 O_b	0.35	~0.25 0.20	[237], 11c
170'	$[MoO(\mu\text{-}O)_2H_2O]H_2O$	d^0	1.690	2.293 H_2O	av. 1.942 O_b		0.20	[316]
171	$W(NC_2Cl_5)Cl_2(NCCCl_3)$	d^0	1.70	2.37 N	av. 2.295 Cl		~0.3	[238]

a) Pentagonal bipyramidal coordination.

available on compounds with X = N or O and L = RN, NO. Only three binuclear complexes with the linear $\mathrm{O} \Rrightarrow \mathrm{Re}\overset{\longleftarrow\ \longrightarrow}{-\mathrm{O}-}\mathrm{Re} \Lleftarrow \mathrm{O}$ fragments are known (compounds 189—191, Table 14). In all three compounds the $Re—O_{bridge}$ distances exceed those in $K_4[Re_2OCl_{10}].H_2O$ by 0.05—0.055 Å. This difference is smaller than the elongation of a *trans*-partner in any of the rhenium oxo compounds where X is $O_{terminal}$ and L_{trans} is the usual acid or donor ligand (Table 12).

Table 14 also lists data for several mononuclear transdioxo complexes. The $M—L_{trans}$ distances in these compounds, in three previous ones and in numerous MXL_4H_2O complexes serve as additional evidence of the gradual increase in *trans*-influence upon L_{trans} replacement in the series $O_{terminal} < \overset{\leftarrow\ \rightarrow}{=O=} < \leftarrow OH_2$ or $\leftarrow O =$. The last case includes all complexes with very asymmetric oxygen bridges, the longer bond of the fragment $M \leftarrow O \rightrightarrows M$ being in the position *trans* to the multiple X=M bond. Some examples of polynuclear complexes and chains with $\leftarrow O \rightrightarrows M \leftarrow O \rightrightarrows M$ fragments were listed in Table 5. Several structures in Table 5 also contain the fragments $O_t \Rrightarrow M \leftarrow O_b \rightrightarrows M$. In all cases the bond to the bridge O atom *trans* to terminal $O \Rrightarrow M$ is considerably lengthened. This confirms indirectly the predominantly donor character of the $M \leftarrow O_b \rightrightarrows M$ bond. Electron density transfer from such an oxygen atom to the metal is smaller than in the case of an ordinary M—O bond.

It is quite natural to assign the bonds with bridge halogen atoms *trans* to X (in the fragment X—M←Hal—M) to the same group of "donor" bonds. The data on oxofluorides and oxochlorides are shown in the upper part of Table 4 and in Table 3, respectively.

Comparison of polymeric oxohalogenides with mononuclear oxohalogenides in these tables reveals that *trans*-elongation of the $M—Hal_{bridge}$ bond is definitely greater than for the $M—Hal_{terminal}$ bond. Such a difference in *trans*-elongation is retained even if the $M—Hal_{bridge}$ distance is compared not with $M—Hal_{terminal}$ but with $M—Hal_{bridge}$ in the *cis*-position to ligand X.

As a whole, comparison of $M—L_{trans}$ distances in complexes with the same multiple-bonded ligands X shows that *trans*-elongation increases in the series:

$$L_{acido} < L_{donor} < L_{bridge}$$

The specific nature of the carbonyl group as the L_{trans} ligand has already been discussed on pp. 50 and 54.

(iv) The role of electronic configuration and of the nature of the metal atom

Comparing the $M—L_{trans}$ distances in molybdenum and rhenium oxopentachlorides and bearing in mind the numerous examples of a strong *trans*-influence in the hexavalent molybdenum oxocomplexes Glovak [56] has come to the conclusion that weakening of a bond *trans* to oxygen is enhanced in the series $d^2 < d^1 < d^0$. The experimental data, however, do not provide sufficient evidence for such a conclusion. For comparison one has to include compounds of the same metal (but of different valency) with the same ligand

TABLE 13

The *trans*-influence of the multiple bond in complexes with polydentate ligands in *trans*-position to oxygen

Nos	Compound	d^n	MO_n
172	$(NH_4)_3[VO_2(C_2O_4)_2]$	d^0	VO_2
173	$(NH_4)_2[VO(C_2O_4)_2H_2O].2H_2O$	d^1	VO
(49)	$K_2[\{MoO_2(C_2O_4)H_2O\}_2O]$	d^0	MoO_2 (MoO_3)
(76)	$NH_4Na[MoO_2(\mu\text{-}O)C_2O_4].2H_2O$	d^0	MoO_2 (MoO_3)
174	$Ba[\{MoO(C_2O_4)H_2O\}_2O_2].3H_2O$	d^1	MoO
(68)	$K_2[MoO(O_2)_2(C_2O_4)]$ [a]	d^0	MoO
175	$K_2[MoO_2(C_6H_4O_2)_2].2H_2O$	d^0	MoO_2
176	$(NH_4)_2[\{MoO_2(C_6H_4O_2)_2\}_2O]$	d^0	MoO_2 (MoO_3)
177	$MoO_2(acac)_2$	d^0	MoO_2
178	$MoO_2(S_2CNEt_2)_2$	d^0	MoO_2
(79)	$\{MoO(S_2COEt)_2\}_2O$	d^1	MoO (MoO_2)
(80)	$\{MoO[S_2P(OEt)_2]_2\}_2O$	d^1	MoO (MoO_2)
179	$MoO_2(C_9H_6NO)_2$	d^0	MoO_2
180	MoO_2Br_2Bipy	d^0	MoO_2
181	$NbO(OEt)Cl_2Bipy$	d^0	NbO (NbO_2)
(74)	$\{VO_2FBipy\}_2$	d^0	VO (VO_2)
(66)	$CrO(O_2)_2(Phen)$ [a]	d^0	CrO

Nos	Distances, A				Δ	Ref., fig.
	X–M	M–L_{trans}	L_{trans}	M–L_{equ}		
172	O_t 1.626	2.186	–O_L	av. 2.005 O_L	0.18	[239a]
	O_t 1.667	2.258	–O_L		0.25	
	O_t 1.635	2.185	–O_L	av. 1.980 O_L	0.20	[239b]
	O_t 1.648	2.235	–O_L		0.26	
173	O_t 1.61	2.18	–O_L	av. 1.960 O_L 2.04 H_2O	0.22	[240]
(49)	O_t 1.700	2.187	–O_L	—	0.22 b)	[102]
	O_b 1.876	2.087	–O_L		—	
	(O_t 1.680)	(2.330)	H_2O		(0.36) b)	
(76)	O_t 1.815	2.235	–O_L	—		[127], 9a
	O_t 1.85	2.242	–O_L			
	(O_b 1.88)	(2.230)	O_b			
174	O_t 1.70	2.11	–O_L	2.14 O_L 2.22 H_2O av. 1.905 O_b	−0.03	[241], 12a
(68)	O_t 1.68	2.26	–O_L	2.08 O_L av. 1.945 O_2	0.18	[119], 7a
175	O_t 1.77	2.15	–O_L	2.05 O_L	0.10	[242]
	O_t 1.77	2.15	–O_L	2.05 O_L	0.10	
176	O_t 1.66	2.15	–O_L	—	0.23 b)	[243], 12b
	O_t 1.70	2.35			0.43 b)	
	O_b 1.90	1.94	–O_L		—	
177	O_t 1.62	2.16	O_L	av. 1.99 O_L	0.17	[244a]
	O_t 1.71	2.24	O_L		0.25	[244b]
178	O_t 1.63	2.63	S_L	av. 2.44 S_L	0.19	[245]
	O_t 1.63	2.63	S_L		0.19	
(79)	O_t av. 1.647	av. 2.697	←S_L	av. 2.486 S_L	0.21	[130], 9c
	O_b av. 1.862	av. 2.535	–S_L		0.05	
(80)	O_t 1.65	2.801	←S_L	av. 2.470 S_L	0.33	[131], 9c
	O_b 1.86	2.547	–S_L		0.08	
179	O_t 1.71	2.32	←N_L	av. 1.98 O_L		[246]
	O_t 1.71	2.32	←N_L			
180	O_t 1.64	2.26	←N_L	2.461 Br		[247]
	O_t 1.83	2.45	←N_L	2.781 Br		
181	O_t 1.71	2.35	←N_L	av. 2.445 Cl		[228]
	OEt 1.87	2.32	←N_L			
(74)	(O_t 1.60)	(2.35)	O_b	1.81 F		[125], 8g
	O_b 1.68	2.19	←N_L	2.14 N_L	0.05	
(66)	O_t 1.56	2.26	←N_L	2.11 N_L av. 1.835 O_2	0.15	[118], 7a

TABLE 13 (continued)

Nos	Compound	d^n	MO_n
182	$Na_2[\{MoO(L{-}SCH_2CH(NH_2)COO)\}_2O_2]$	d^1	MoO
183	$Na_2[\{MoO(L{-}SCH_2CH(NH_2)COO)\}_2S_2]$	d^1	MoO
184	$\{MoO[NHCHNHCHC(CH_2CHNH_2COO)]\}_2O_2$	d^1	MoO
185	$\{MoO[NHCHNHCHC(CH_2CHNH_2COO)]\}_2S_2$	d^1	MoO
186	$(NH_4)_4[Mo_4O_{11}(C_4H_3O_5)_2]$	d^0	MoO_2 (MoO_3)
(56)	$H[MoO_2N(CH_2CHO)_3]$	d^0	MoO_2
(57)	$Na_4[(MoO_3)_2EDTA].8H_2O$	d^0	MoO_3
(55)	$[(MoO)_2(\mu\text{-}S)_2EDTA].2H_2O$	d^1	MoO
(58)	$MoO_3NH(CH_2CH_2NH_2)_2$	d^0	MoO_3
187	$NH_4[VO_2(H_2EDTA)].3H_2O$	d^0	VO_2
188	$Na_3[VO_2(EDTA)].4H_2O$	d^0	VO_2

a) Pentagonal bipyramidal coordination.
b) Δ in comparison with av. M—O in *cis* position to M—O_t.

X, equivalent L_{trans} ligands and equivalent or at least similar L_{eq} ligands, i.e. the complexes $[MXL'_4L]^{n-}$ with different charge *n*. No structural data satisfying all these requirements are available. Table 15 summarizes a few examples where one requirement, the same metal, is neglected. It can be seen from these examples that the *trans*-influence series $d^2 < d^1 < d^0$ applies only for L_{trans} = F, Cl and Br, but does not manifest itself when water or a bridging fluorine occupies the *trans*-position. Probably, in the case of donor ligands *trans*-elongation is sensitive to many other factors which are more significant than electronic configuration.

However, even in complexes $[MOHal_5]^{n-}$ the experimental data can hardly be interpreted unequivocally since in the series of complexes investigated

Nos	Distances, A				Δ	Ref., fig.
	X—M	M—L$_{trans}$	L$_{trans}$	M—L$_{qu}$		
182	O_t 1.71	2.30	—O_L	av. 1.93 O_b 2.23 N_L 2.49 S_L	0.37	[248]
183	O_t av. 1.62	av. 2.365	—O_L	av. 2.332 S_b 2.265 N_L 2.495 S_L		[249]
184	O_t 1.71	2.21	—O_L			[250]
185	O_t av. 1.71	av. 2.23	=O_L	av. 2.318 S_b av. 2.235 N_L		[251]
186	O_t 1.73	2.32	←O_L	—	0.37 b)	[252], 12c
	O_t 1.80	2.21	—O_L		0.26	
	O_b 1.85	2.00	—O_L		0.05	
	O_t 1.68	2.38	←O_L		0.43 b)	
	O_t 1.70	2.31	—O_L		0.36	
	(O_b 1.91)	(2.04)	O_b		0.09	
(56)	O_t 1.76	2.34	—O_L	av. 1.940 O_L	0.38	[109]
	O_t 1.815	2.43	←N_L			
(57)	O_t 1.75	2.18	—O_L	—		[110], 6d
	O_t 1.75	2.22	—O_L			
	O_t 1.73	2.40	←N_L			
(55)	O_t 1.683	2.448	←N_L	av. 2.111 O_L av. 2.293 S		[108], 6c
(58)	O_t 1.735	2.32	←N_L	—		[111]
	O_t 1.735	2.32	←N_L			
	O_t 1.740	2.33	←N_L			
187	O_t 1.623	2.351	←N_L	av. 2.002 O_L		[253]
	O_t 1.657	2.362	←N_L			
188	O_t 1.639	2.366	←N_L	av. 2.000 O_L		[254]
	O_t 1.657	2.359	←N_L			

apart from the electronic configuration, the nature of the metal also changes. Thus it is not clear what is causing the *trans* bond to shorten: additional electrons in the valence shell, or specificity of level interaction upon replacement of Nb and Mo nuclei by Os (in oxofluorides) or Mo by Re (in oxochlorides and oxobromides). The last explanation seems to be more suitable for two reasons.

1. A change from d^0 to d^1 and d^2 should mainly result in a relative decrease of the *trans*-influence, namely elongation of the M—L$_{cis}$ bond rather than shortening of the M—L$_{trans}$ bond due to repulsion between p_π-electrons of donor *cis*-ligands and d_{xy} metal electrons. The structural data do not confirm the existence of such an elongation.

TABLE 14

Complexes with metal—oxygen multiple bonds in *trans*-position to each other

Nos	Compound	d^n	Distances, Å			Δ'	Ref., fig.
			O—M	M—L_{trans}	M—L_{cis}		
189	$[Pt(NH_3)_4]_2[Re_2O_3(CN)_4]$	d^2	1.698	1.915 O_b	2.120 CN	0.055	[255]
190	$Re_2O_3(S_2CNEt_2)_4$	d^2	1.735	1.910 O_b	av. 2.437 S	0.05	[256]
191	$Re_2O_3en_2Cl_4$	d^2	1.67	1.912 O_b	av. 2.18 N_{en} av. 2.41 Cl	0.05	[257]
192	$K_3NaMoO_2(CN)_4$	d^2	1.83	—	2.20 CN	—	[258]
193	$K_3[ReO_2(CN)_4]$	d^2	1.773 1.781	— —	2.123 2.135 CN	—	[259a] [259b]
194	$[ReO_2en_2]Cl$	d^2	av. 1.73	—	av. 2.182 N_{en}	—	[260a]
195	$[ReO_2Py_4]Cl.H_2O$	d^2	av. 1.76	—	av. 2.135 N_{Py}	—	[261]
196	$K_2[OsO_2Cl_4]$	d^2	1.75	—	av. 2.379 Cl	—	[262a]
197	$K_2[OsO_2(OH)_4]$	d^2	1.77	—	2.03 OH	—	[263]
198	$K_4[\{OsO_2(NO_2)_2\}_2O_2]$	d^2	1.79	—	{ 2.08 O_b av. 2.205 NO_2 }	—	[264], 8i

TABLE 15

A comparison of the *trans*-elongation in complexes of transition metals with d^0, d^1 and d^2 configurations of similar composition

Nos	Compound	d^n	Distances, Å M—L_{trans}	Δ	Δ'	ref.
(28)	$K_2[NbOF_5]$	d^0	2.06 F	0.22	0.22	[82]
(29)	$K_2[MoOF_5]H_2O$	d^1	2.03 F	0.17	0.21	[83]
199	$OsOF_5$ [a]	d^2	1.72 F (O)	−0.06	−0.06	[265]
(162)	$(NH_4)_2[MoOBr_5]$	d^1	2.83 Br	0.28	0.30	[229]
(161)	$K_2[MoOCl_5]$	d^1	2.631 Cl	0.23	0.23	[56]
(3)	$K_2[ReOCl_5]$	d^2	2.47 Cl	0.08	0.08	[56]
(20)	$ReOCl_4H_2O$	d^1	2.27 H_2O		0.19	[72]
(41)	$K[MoOCl_4H_2O]$	d^1	2.27 H_2O		0.18	[56]
(42)	$(Ph_4As)[MoOBr_4H_2O]$	d^1	2.39 H_2O		0.30	[95]
(21)	$(Et_4N)[ReOBr_4H_2O]$	d^2	2.32 H_2O		0.24	[73]
(34)	$(VOF_3)_\infty$	d^0	2.34 F_b	0.40	~0.40	[88]
(37)	$(MoOF_4)_\infty$	d^0	$\left\{ \begin{matrix} 2.31 \\ 2.27 \end{matrix} F_b \right\}$	0.34	0.35	[91]
(40)	$(WOF_4)_4$ [b]	d^0	2.10 F_b		0.16	[94]
(35)	$(ReOF_4)_\infty$	d^1	av. 2.295 F_b	0.30	0.35	[89]
(36)	$(TcOF_4)_3$	d^1	2.26 F_b	0.37	~0.32	[90]

[a] With partial disorder in the distribution of O and F atoms at the octahedron vertices. The Os—O and Os—F_{equ} distances are 1.72 and 1.78 Å respectively.

[b] See Table 4, note [c].

2. In crystal structures of metal oxides the metals of groups V and VI display a different stereochemical behaviour from metals of groups VII and VIII. In particular, the former exhibit a tendency to localize the π-interaction more often and more distinctly than does the second type of metal. The latter argument appears to be less convincing if we take into account the difference in stability of the highest oxides of the related compounds (see section E).

D. THE ARRANGEMENT OF THE MULTIPLE BONDS IN DI- AND TRIOXO TRANSITION METAL COMPLEXES

The role of the electronic configuration of the metal is much more apparent in choosing a mutual arrangement for two or three M=O bonds in a complex. This problem was first discussed for molybdenum oxocomplexes in refs. 12 and 266 (see also ref. 51). On the basis of data available up to 1965 the authors [12] formulated three general rules for the structure of oxocomplexes of hexa- and pentavalent molybdenum

1, *cis*-arrangement of oxygen atoms forming the multiple bonds,

2, *trans*-bond elongation and
3, correlation between the formal M—O bond multiplicity and bond length (see also ref. 267).

Analysis [13,268] of structural data on oxides and oxohalides of Mo, W, Nb and some other metals made it possible to extend these rules to a wider class of metals and compounds. The dependence of the mutual arrangement of multiple bonds in transition metal complexes upon the metal electronic configuration has been considered [269].

In an octahedral complex possessing O_h symmetry M—ligand π-bonding is generally realized through the t_{2g} (d_{xy}, d_{xz}, d_{yz}) metal AO's. All three orbitals could be used in principle in the d^0 configuration. If only two oxygens are available, then only their *cis*-location could utilize all three orbitals. With three oxygen atoms their *cis—cis* (facial) location is usually more preferable than the *cis—trans* (rib) arrangement, since only in the first case are all three atoms equivalent i.e. the equivalence of the three π-orbitals is retained in ideal C_{3v} symmetry).

This statement may be considered to be general. It is confirmed by a large number of di- and trioxo-complexes of hexavalent molybdenum and tungsten (see Tables 4, 5 and 13) and by many data on molybdates and tungstates with "complexes" joined together to produce an infinite framework*. Unfortunately structural data on dioxocompounds of other transition metals with d^0 configuration are rather scanty. For rhenium we can mention only the oxides Re_2O_7 (163) and $Re_2O_7.2H_2O$ (164, Table 12). The crystal structures of both oxides contain tetrahedra and octahedra linked via common vertices. In the former structure they form infinite layers, the second structure contains binuclear molecules. The octahedra have the same type of structure. In Re_2O_7 there are two terminal oxygen atoms and a shortened bond with a bridge oxygen, while $Re_2O_7.2H_2O$ has three terminal oxygens in an octahedron. In both cases they occupy the adjacent vertices of an octahedron ("facial isomers") (see Fig. 11).

No structural data are available on dioxocompounds of heptavalent technetium. Similar compounds of Ru^{VIII} and Os^{VIII} (with octahedral metal coordination) seem to be unknown.

Dioxocompounds of pentavalent vanadium are known. The *cis*-arrangement of oxygen atoms [270] in $K_3[VO_2F_4]$ and [271] $(NH_4)_3[VO(C_2O_4)_2].2H_2O$ was revealed through IR spectra. Somewhat later, this was confirmed for the second compound by direct structural investigation [239]. A similar configuration of the VO_2 group is observed in $K_2VO_2F_3$ (compound 38), $NH_4[VO_2(H_2EDTA)].3H_2O$ (187), $Na_3[VO_2EDTA].4H_2O$ (188) and $[VO_2FBipy]_2$ (74) (see Tables 4, 5 and 13).

Angular VO_2 fragments were found in $K_2Zn[V_{10}O_{28}].16H_2O$ [272],

---

* Details are given in the next section.

$Ca_3[V_{10}O_{28}].16H_2O$ [273] and other oxygen compounds of pentavalent vanadium.

Niobium structures containing dioxocomplexes have not been investigated, but there are data on the chain and framework structures of several niobium (V) oxohalogenides, e.g. Nb_3O_7F [317], Nb_3O_7Cl [318], $MoNb_{15}O_{40}F$ [319] and other oxygen compounds of niobium (V). One may consider separately the NbO_2 groups (with terminal O atoms) in these structures. In all cases such groups have the same *cis*-construction.

In the oxoethoxocomplex NbO(OEt)Cl(Bipy) the Nb—OEt distance (1.87 Å) as well as the $Nb—O_{terminal}$ bond (1.71 Å) are somewhat shortened, which may be regarded as a consequence of some $d_\pi—p_\pi$ interaction in the Nb—OEt bond. Once again the oxygen atoms $O_{terminal}$ and O_{OEt} occupy adjacent vertices of an octahedron*.

In transition metal dioxocomplexes with a d^2 electron configuration only two of the three t_{2g} orbitals can take part in π-bonding. In principle, a π-interaction may occur for both the *trans*- and the *cis*-arrangement of oxygen atoms. However, in MO_2X_4 complexes with equivalent or quasi-equivalent X ligands interaction of the π-electrons of the O and X ligands with the metal pair makes a *trans*-configuration preferable. In this case the energy of electron repulsion of the M=O bonds with each other and with the metal lone pair is minimal [45,275]**. This is true of complexes of tetravalent Mo and W, pentavalent Re and Tc, hexavalent Ru and Os and trivalent V, Nb and Ta.

Structural data in Table 14 are rather scanty as yet. In all cases the complexes actually have a *trans*-structure.

$NaK_3[MoO_2(CN)_4].6H_2O$ (192) is the only structurally studied molybdenum (IV) dioxocompound. But it is quite evident that the fragment MoO_2 is also linear in $K_4[MoO_2(CN)_4].6H_2O$, the crystallographic and spectral data of both compounds being similar [276]. The *trans*-structure of ReO_2A_4 complexes, has been confirmed, by the structural investigation of six compounds (Table 14), and also on the basis of spectroscopic characteristics for a large group of Re^V dioxotetramine compounds [277—280]. The same holds true for hexavalent osmium dioxocomplexes confirmed by structural study of three compounds (Table 14).

An a priori statement on the stereochemistry of transition metal dioxocompounds with a d^1 electronic configuration is less unequivocal. If an unpaired electron is retained during complex formation both configurations are, in principle, possible. If a diamagnetic binuclear complex with single or double oxygen bridges is formed and there is a direct or superexchange interaction between the metal atoms then again all three t_{2g} metal orbitals participate in π-bonding. In this case the terminal oxygen atoms (atom) should again occupy *cis*-positions with respect to each other and to the bridging oxy-

---

* For the same reason the ethoxygroup OEt replaces *cis*- (instead of *trans*-) fluorine in Mo^{VI} and W^{VI} monooxofluorides [274].

** Ligand L inequivalence, steric hindrance or limitations concerning metal binding with polydentate ligands may stimulate a *cis* configuration for the oxygen atoms.

gen atom (atoms). On the basis of structural data one may conclude that such a structure is preferable for Mo^V oxocompounds than a mononuclear structure with an unpaired electron (compounds 79, 80, 174, 182—185, Table 13). Similar structures may be expected in the case of dioxocompounds of other metals with a d^1 configuration. Unfortunately no structural data are as yet available. Judging from the IR spectrum the group $(ReO_2)^{2+}$ is also non-linear in $(NH_4)[ReO_2Cl_4]SO_2Cl_2$: the Re—O stretching mode is split into two bands [281], 960 and 997 cm^{-1}. An analogous splitting has been observed in the spectrum of a similar Tc^{VI} compound [282].

The available data are in good agreement on the whole, with the general points stated above; thus one may predict the structure of a dioxo group in compounds which have not yet been investigated. In particular, the linear O—M—O configuration should be observed not only in $(OsO_2)^{2+}$, $(ReO_2)^{1+}$ and $(MoO_2)^0$, but also in $(VO_2)^-$, while the angular structure should occur with V^V, Mo^{VI}, W^{VI}, Re^{VII} and also with Os^{VIII} and Ru^{VIII} compounds.

E. MAIN FEATURES OF THE STRUCTURE OF METAL—OXYGEN OCTAHEDRA IN MOLYBDENUM AND TUNGSTEN OXYGEN COMPOUNDS

(i) Localization of the π-interaction in transition metal oxygen compounds

The multiple bond *trans*-influence model proposed in this work is, strictly speaking, only applicable to mononuclear complexes. In general, polymeric structures require an essentially different theoretical approach based on the band structure of the energy spectrum. However, in previous sections we have already discussed, not only mononuclear, but also di-, tri-, tetra- and polynuclear structures analysing the mutual atomic influence within the fragments composed of the metal and its closest environment. Such wide use of the model is based on the well-known relationship between the stereochemistry observed in mononuclear complexes and that observed in coordination structures in the broad sense, in particular, the three-dimensional structures of simple and complex oxides, sulphides, halogenides and so on. Such an analogy manifests itself not only in the specifically preferred coordination polyhedra for different metals, but also in the structure of certain classes of chemical compounds. For example, the comparatively rare trigonal prismatic metal coordination in simple Nb, Ta, Mo and W sulfides has its analogue in tris-dithiolate and related complexes with sulfur-containing five-membered chelate rings. The cluster structures typical for the same metals in simple halogenides are observed in their complex halogenides as well. The same analogy is seen between the mixed oxocomplexes and simple oxygen or complex oxides of V, Nb, Ta, Mo and W in their highest oxidation states. For oxygen octahedra linked into a polymeric framework the *trans*-influence may be described most readily as localization of the π-interaction in one, two or three bonds of an octahedron resulting in turn in the inequivalency of σ-bonds. That is the σ-bonds become stronger where the M—O distances are shorter due to π-interaction, and such strengthening, in its turn, may loosen other M—O σ-bonds via the mechanism considered.

In this respect metals of groups V and VI differ sharply from those of VII and VIII. As already mentioned, this stereochemical difference becomes particularly obvious, if we compare the structural characteristics of ReO_3 and WO_3 crystals. The rhenium trioxide structure is cubic, composed of —O—Re—O—Re—O chains crossed in three perpendicular directions with rhenium atoms in the nodes. The chains are strictly linear, all Re—O distances being equivalent (1.876 Å). On the other hand the structural patterns of all modifications of tungsten trioxide are similar but distorted; the chains are non-linear, and the W—O distances to the opposite vertices of the octahedron are unequal. For example, they are 1.72 and 2.16; 1.79 and 2.13; 1.89 and 1.91 Å (in one of the independent octahedra) and 1.75—2.15, 1.85—2.01, 1.85—1.92 Å (in another octahedron) in the monoclinic modification [283, 284]. Such a difference between WO_3 and ReO_3 may be a reflection of the general tendency towards increasing the localization of the π-interaction in the metal oxygen polyhedra in passing from group VIII to group VI in the periodic chart, and upon change of electron configuration d^n in the series $n = 2, 1, 0$.

It is not obvious which of these two factors is dominant. The difficulty in solving this problem is connected with the fact that the highest oxidation states of group VII and VIII metals are not very specific and their oxygen compounds have not been studied adequately. However, attention should be drawn to the following facts.

1. Asymmetric oxygen bridges often appear in Mo^{VI} oxocomplexes, while Mo^{V} and Mo^{IV} compounds are usually built up of binuclear complexes with symmetric oxygen bridges.
2. Passing from MoO_3 to $Mo(O_{0.8},F_{0.2})$ due formally to a decrease in metal valency from 6 to 5.4 causes all six Mo—X bonds in a Mo octahedron to become equivalent [315].
3. Re_2O_7 has a network of octahedra and tetrahedra in which the former have the 3 + 3 distortion typical of the d^0 metals (compare ReO_3 where all the bonds are equivalent).

These data may demonstrate as far as the problem of localization or delocalization of the π-interaction is concerned that the electron configuration of the metal is no less important than the transition from groups V and VI to VII and VIII.

(ii) Structural studies

The molybdates have been studied most thoroughly among the oxygen compounds of the transition metals. Since tungsten is, as a rule, isostructural with molybdenum the general pattern is even more clear. Fewer data are available on the structures of niobium and vanadium oxygen compounds.

Numerous Mo and W oxides of complex composition including the mixed

Mo and W oxides as well as the mixed oxides of one of these metals with niobium have been investigated. Molybdenum and tungsten oxygen compounds containing alkali metals, ammonium and its analogs, monovalent Cu, Ag and Tl, alkaline-earth metals, bivalent transition metals (Mn, Fe, Co, Ni, Zn, Cd), trivalent transition metals, aluminium and the lanthanides have also been studied in detail. Recently, the structures of anions of many salts of the iso- and heteropolyacids have been established. An interesting group of molybdenum and tungsten phosphates has also been studied thoroughly. Altogether nearly 120 structural types have been found. Considering isostructural species this embraces about 300 different compounds.

Among these structures one can distinguish a family of layer and column structures based on ReO_3, a family of polygonal network structures, the packet structures related to the MoO_3 pattern, the family of block structures with octahedra linked by edges, structures with anion chains of octahedra and tetrahedra etc. Nevertheless, in spite of the variety of these crystal structures, they have some common features. Leaving aside the molybdates and tungstates with mononuclear tetrahedral anions $(MO_4)^{2-}$, all include some type of combination of molybdenum—oxygen octahedra having common vertices or edges (rarely faces) either with each other or with other polyhedra or with polyhedra of other metals. It should also be noted that quite often the unit cell contains several symmetrically independent metal—oxygen octahedra (e.g. in $Mo_{18}O_{52}$ there are 17 of them*). This means that the special geometric features of the oxygen polyhedra of Mo and W (as well as Nb and Ta) which will be discussed below are based on an extremely large amount of statistical data.

A more detailed list of Mo and W oxygen compounds, with a description of their crystal structures and their structural classification has been published [53]. Here we deal only with the stereochemical aspect of the structures of these compounds.

(iii) The geometry of metal—oxygen octahedra in molybdenum and tungsten compounds

The analysis of the stereochemistry of Mo and W oxygen compounds requires knowledge of the structural function of oxygen atoms at the different vertices of octahedra. The oxygen atoms may link together different numbers of polyhedra, thus having different coordination numbers with regard to the metal atoms. They may be terminal (coordination number = 1) or bridging. In the latter case the oxygen atoms may join together from two to six metal atoms simultaneously.

The oxide structures of the ReO_3 family are mainly composed of octahedra whose vertices are the linear bridges (c.n. = 2). Octahedra with oxygen c.n.

---

* References for this and other oxygen compounds are given in Tables 16, 17 and the schemes of Fig. 16.

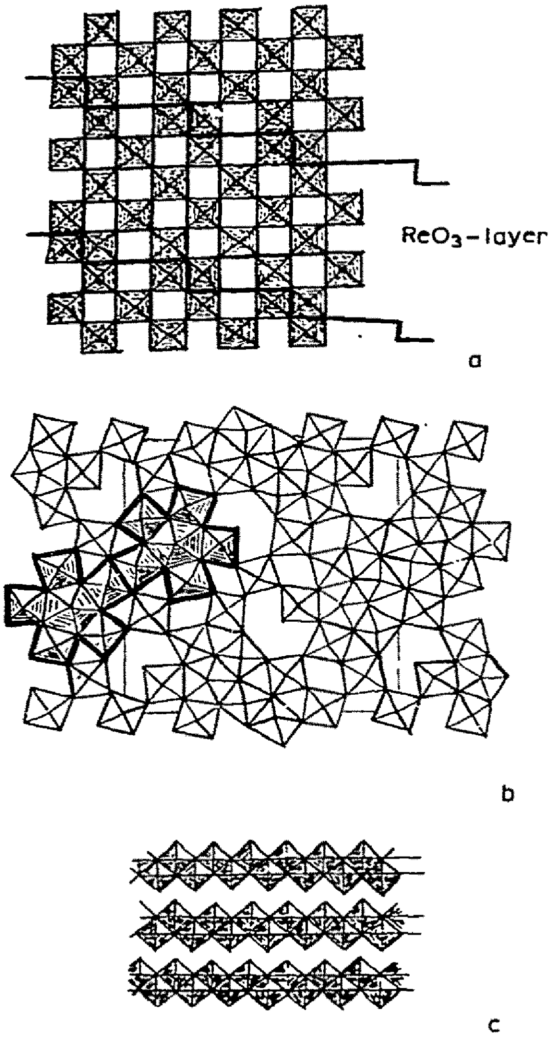


Fig. 13. Fragments of crystal structures of some molybdenum oxides: a, Mo_8O_{23}; b, $Mo_{17}O_{47}$; c, MoO_3.

equal to 2 and 3 occur only at layer (column) boundaries. As an example, Fig. 13a shows a fragment of the Mo_8O_{23} structure. The same is more or less true for polygonal network structures. Here, we also come across oxygen atoms with c.n. = 2 forming non-linear bridges. In addition, in some of these structures (e.g. $Mo_{17}O_{47}$, Fig. 13b) there may also occur terminal oxygen atoms (one per octahedron).

Structures of the MoO_3 family are mainly composed of such octahedra. Figure 13c shows the structure of MoO_3 itself, as an example. Here, the typical octahedron involves one terminal oxygen atom, two oxygens with c.n. = 2 (linear bridges) and three oxygen atoms with c.n. = 3.

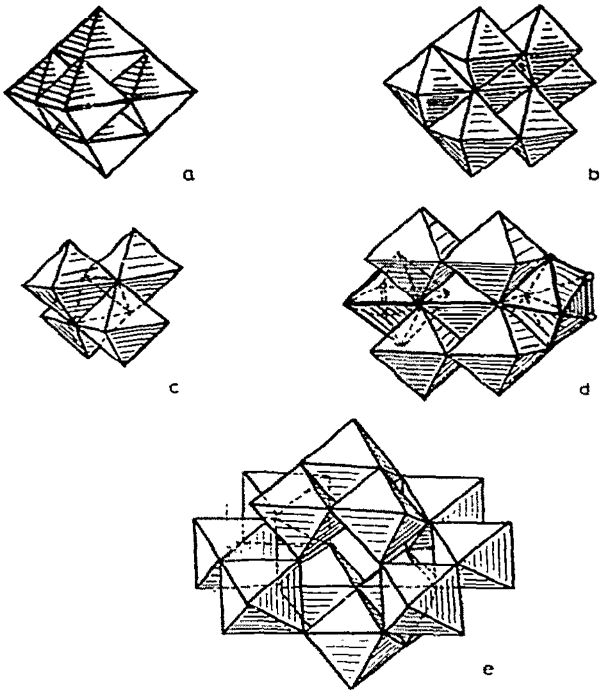


Fig. 14. The structures of blocks in crystals: a, $(Bu_4N)_2[W_6O_{19}]$; b, $(NH_4)_6[Mo_7O_{24}].4H_2O$; c, $Li_{11}Fe(WO_4)_3[W_4O_{16}]$; d, $K_6[Mo_7O_{22}(O_2)_2].8H_2O$; e, $(NH_4)_{10}[H_2W_{12}O_{42}].4H_2O$.

Most different combinations of octahedra occur in block structures. Here, the oxygen vertices may possess all possible coordination numbers from 1 to 6 (the latter number is observed in $(Bu_4N)_2[W_6O_{19}]$). In this family typical octahedra have one, two and even three terminal oxygen atoms. As examples, Fig. 14 shows the block of octahedra in $(Bu_4N)_2[W_6O_{19}]$, $(NH_4)_6[Mo_7O_{24}]$. $4H_2O$, $(Li_{11},Fe)(WO_4)_3[W_4O_{16}]$, $K_6[Mo_7O_{22}(O_2)_2].8H_2O$ and $(NH_4)_{10}[H_2W_{12}O_{42}].4H_2O$ (compounds 77 and 78 in Table 5). The family of chain structures is also composed of similar octahedra. In this case, however, oxygen atoms of other octahedra vertices usually have c.n. = 2 (but not higher as in the block type structures). The alkali metal double oxides $Na_2Mo_2O_7$ [285,286] (Fig. 15a) and $K_2Mo_2O_7$ [287] (Fig. 15b) serve as examples.

In spite of these diverse oxygen functions and thus variety of "stereochemical" types of MO_6 octahedra they all have some features typical of Mo and W. Namely:

1. The molybdenum— and tungsten—oxygen octahedra are always distorted: the M—O bond lengths are quite different, the bond directions not being perpendicular to each other. This concerns not only octahedra with

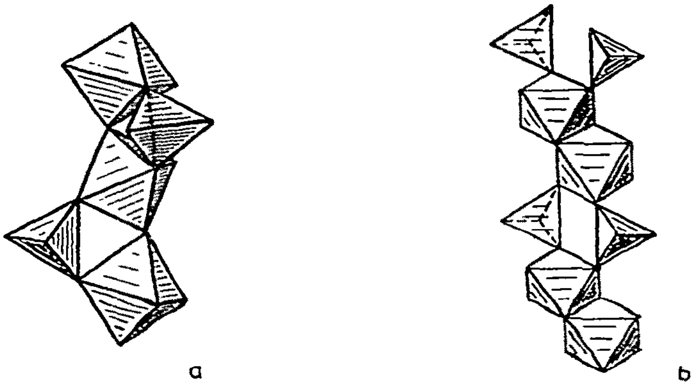


Fig. 15. Examples of chain structures in oxygen compounds of molybdenum: a, $Na_2Mo_2O_7$; b, $K_2Mo_2O_7$.

oxygen vertices having different structural functions, but also those with equivalent vertices: with the oxygen atoms playing the role of linear (or pseudolinear) bridges (ReO_3 family).

Among the several hundred independent MO_6 octahedra investigated one could find no regular octahedra and moreover no octahedra with relatively small difference in bond lengths (less than 0.1—0.2 Å).

Distortion of metal oxygen octahedra proves to be a specific feature of molybdenum and tungsten in their highest oxidation states*. This feature is no less typical for Mo and W than distortion of octahedra and tetrahedra in any compound of divalent copper (although the type of distortion is certainly different). Such constant inequality in the Mo—O and W—O distances is the most direct evidence for the tendency of metals towards localization of the π-interaction in certain bonds of the octahedron**.

2. To a first approximation, distortions in metal—oxygen octahedra in hexa- and pentavalent Mo and W compounds can be described as a shift of the metal from the center of an octahedron to some vertex, edge or face. In other words, the shortened M—O bonds are always in a *cis*-position to each other, their *trans*-sites always being occupied by the longest (thus weakest) bond. No example can be found among the numerous hexavalent Mo and W

---

* It also includes the M_nO_m oxides with indefinite metal oxidation state (between 5 and 6).

** Some exceptions have been observed in the case of tungsten, however. They include ternary oxides MM'_2WO_6, in particular MBa_2WO_6, where M = Ca, Co and Ni (ReO_3 family) [288, 289]. In this case the WO_6 are regular octahedra. Half of the tungsten atoms in $Nd_4W_3O_{15}$ [290] have almost regular octahedral coordination (1.92, 1.94 and 1.96 Å). These exceptions might be explained by statistical orientation of the distorted octahedra or by collective vibrational displacements of metal atoms with respect to oxygen atoms in the distorted octahedra. Alternatively, in MBa_2WO_6 the high symmetry may be due to the fact that Ca, Co and Ni atoms demanding regular octahedral coordination overcome the tungsten resistance to delocalization of the π-interaction.

compounds with a *trans*-allocation of the two shortened M—O bonds.

This is true not only for octahedra with terminal oxygen atoms at some vertices, but also for those with all oxygen vertices linked with neighbouring polyhedra.

Thus we see that the oxygen octahedral polyhedra of these metals and their complexes (in particular, oxo halides and organooxo compounds) have identical geometrical features. This concerns not only the general arrangement of "short" and "long" bonds, but also numerical data for the bond lengths. As an illustration, Table 16 gives the $Mo—O_{terminal}$ and $Mo—O_{trans}$ distances in octahedra observed in the four most precisely investigated structures: MoO_3, $Mo_{18}O_{52}$ and $Mo_4O_{10}(OH)_2$ (MoO_3 family) and $Mo_{17}O_{47}$ (the family of polygonal network structures). Each octahedron here contains one terminal oxygen atom. Table 17 lists all Mo—O distances in the octahedra with structurally equivalent vertices (all oxygen atoms have c.n. = 2 with a linear arrangement of bonds). These data refer to the structures of two modifications of Mo_4O_{11}, Mo_8O_{23} (ReO_3 family) and $Mo_{17}O_{47}$ (the family of polygonal network structures). As a rule, in these octahedra two or even three *cis*-bonds are shortened*.

These data demonstrate that in octahedra with terminal oxygen the lengths of the shortened bonds range between 1.64—1.72 Å (only in one of 20 octahedra is it 1.83 Å), the weakened bonds in the *trans*-positions are 2.19—2.40 Å (shorter only in three cases) and those in the *cis*-positions are 1.87—2.06 Å. In octahedra without terminal oxygen the same bond lengths are: 1.75—1.84, 1.98—2.37 and 1.91—2.07 Å respectively (however, since the two *cis*-bonds are not entirely equivalent, these last limits are not precisely defined).

These results are so convincing that they need no further comment.

It may be worth noting that similar distortions of the metal—oxygen octahedra were observed in crystals of ferroelectrics with the perovskite structure. In particular, above the Curie point barium titanate has a cubic structure with regular octahedral titanium coordination. Below this point each of the three consecutive ferroelectric phases is specific in the direction of displacement of titanium atoms from the centers of octahedra: to a vertex, to an edge and to a face. This permits us to make a supposition that the same theoretical interpretation has to exist for both isolated complexes with multiple bonds and three-dimensionally coordinated ferroelectric crystals.

3. Localization of the π-interaction is most evident in octahedral chains having common vertices. This can be distinctly seen in comparing data on the distorted octahedra in two modifications of Mo_4O_{11} to those observed in Mo_8O_{23} and $Mo_{17}O_{47}$. None of the octahedra in Mo_4O_{11} contain two trans-

---

* In accordance with the numbering order the following bonds are in the *trans*-position to each other: 1 and 4, 2 and 5, 3 and 6.

TABLE 16

The Mo—O and O...O distances in octahedra with one terminal oxygen vertex

Compound		Atoms Mo—O_t	Mo—O_{trans}	O_t...O_{trans}	O_{equ}...O_{equ}
$Mo_{18}O_{52}$	I	1.70	2.39	4.09	3.88 4.02
	II	1.69	2.30	3.99	3.93 3.92
	III	1.69	2.26	3.95	3.96 3.89
	IV	1.63	2.39	4.02	3.88 3.93
	V	1.65	2.40	4.05	3.85 3.95
	VI	1.71	2.33	4.04	3.91 3.94
	VII	1.68	2.24	3.92	3.99 4.03
	VIII	1.66	2.39	4.05	3.88 3.99
	IX	1.69	2.35	4.03	3.83 3.97
	X	1.66	2.27	3.93	3.93 3.95
	XI	1.67	2.32	3.99	4.04 3.96
	XII	1.64	2.45	4.09	4.02 3.87
	XIII	1.66	2.09	3.75	3.76 4.02
	XIV	1.72	2.25	3.87	3.84 3.86
	XV	1.83	2.19	4.02	3.92 4.06
	XVI	1.54	2.47	4.01	3.89 4.02
	XVII	1.72	2.40	4.01	3.89 4.02
MoO_3		1.671	2.332	4.003	3.985 3.896
$Mo_{17}O_{47}$		1.677	2.165	3.842	3.992 3.977
$Mo_4O_{10}(OH)_2$		1.687	2.332	4.129	3.900 3.740
Mean value		1.678	2.310	3.990	3.913

lationally equivalent oxygen atoms. In all octahedra in Mo_8O_{23} such oxygen atoms are present (in Figs. 13a and b the appropriate translation axis is normal to the projection plane). Molybdenum atoms are mainly displaced along

TABLE 17

The Mo—O and O...O distances in MoO_6 octahedra conjugated at all vertices

Atoms	Mo_4O_{11}, rhombic modification			Mo_4O_{11}, monoclinic modification			Mo_8O_{23}		$Mo_{17}O_{47}$		
	I	II	III	I	II	III	I	II	I	II	III
Mo—O_1	1.858	1.781	1.750	1.866	1.751	1.748	1.683	1.695	1.757	1.794	1.857
Mo—O_2	1.893	1.807	1.759	1.871	1.775	1.750	1.872	1.825	1.806	1.882	1.896
Mo—O_3	1.913	1.832	1.772	1.924	1.810	1.770	1.907	1.839	1.938	1.954	1.925
Mo—O_4 (O_1')	1.993	2.090	2.107	2.023	2.092	2.150	2.369	2.362	2.199	2.157	2.096
Mo—O_5	1.989	2.079	2.164	1.983	2.057	2.145	1.923	1.972	1.988	1.882	1.957
Mo—O_6	2.007	2.112	2.069	2.005	2.056	2.110	1.967	2.039	2.056	1.954	1.931
$(Mo—O)_{av.}$	1.942	1.950	1.936	1.945	1.933	1.944	1.953	1.955	1.957	1.937	1.943

the octahedral axis connecting the translationally equivalent atoms. This holds true not only in the case of $Mo_{17}O_{47}$ but for all other polygonal network structures and refers not only to octahedra but also to the chains along the axes of pentagonal bipyramidal polyhedra (e.g. in $Mo_{14}O_{47}$, cf. Fig. 13b)*. Thus the density redistribution along the simple (linear) chain —Mo—O—Mo—O is likely to occur more easily and intensively than in the case where several crystallographically independent metal and oxygen atoms act simultaneously in the bonding. Here we return again to the analogy with the stereochemistry of mononuclear oxocomplexes: *trans*-elongation in monooxocomplexes is somewhat stronger than in di- and trioxocomplexes.

4. One peculiar detail in the distortion of molybdenum octahedra with terminal oxygen proves to be the inequality of its dimensions along the three axes. As can be seen from Table 16, the distance between the oxygen atoms in O_{term}—Mo—O_{trans} is usually somewhat longer than in the O_{eq}—Mo—O_{eq} fragment. For the examples listed in the table the mean values are 3.99 and 3.91 Å, respectively. This difference is in agreement with the general concept of multiple bond *trans*-influence: decreasing the energy of the M—O_{trans} bond stimulates the additional shift of O_{trans} to the point corresponding to an equilibrium between M—O_{trans} and O_{eq}—O_{trans} interactions. Here again the "*cis*-bonds" are always inclined somewhat to a *trans*-partner, thus levelling the mean $O_{terminal}\cdots O_{eq}$ and $O_{trans}\cdots O_{eq}$ distances, as was earlier observed with mononuclear complexes.

5. In the family of block structures the distribution of oxygen atoms with different coordination numbers is governed by quite distinct rules. These latter can be seen readily from the patterns of blocks in various isopolymolybdenum compounds and in some other related structures shown in Fig. 16. These patterns expose the arrangement of "different" vertices of octahedra in the blocks. For the sake of simplicity the terminal oxygen atoms are designated by t, while bridged atoms are labelled by digits from 2 to 6 according to the number of metal atoms combined by oxygen. The linear and nonlinear oxygen bridges with c.n. = 2 are given as 2_g and 2_u. The shortened bonds of high multiplicity are shown by solid lines.

If the point group symmetry of the block is considered to be ideal, then for the eleven species given in Fig. 16 we would find 28 independent octahedra. The total number of octahedra actually reaches 72**. Most of the octahedra contain terminal, along with bridging, oxygen atoms: one terminal oxygen atom in 29 cases, two terminal oxygen atoms in 37 cases, and three terminal oxygen atoms in four cases (in $[W_4O_{16}]^{n-}$ anion). Among the 72 octahedra only two contain only bridging oxygen atoms.

Analysis of Fig. 16 demonstrates the following common rules valid in all cases:

---

* Compare with the specific distortions of Mo and W pentagonal bipyramidal oxoperoxocomplexes.

** In the infinite blocks in $Ag_6Mo_{10}O_{33}$ and $K_2Mo_4O_{13}$ only symmetrically independent species are taken into account.

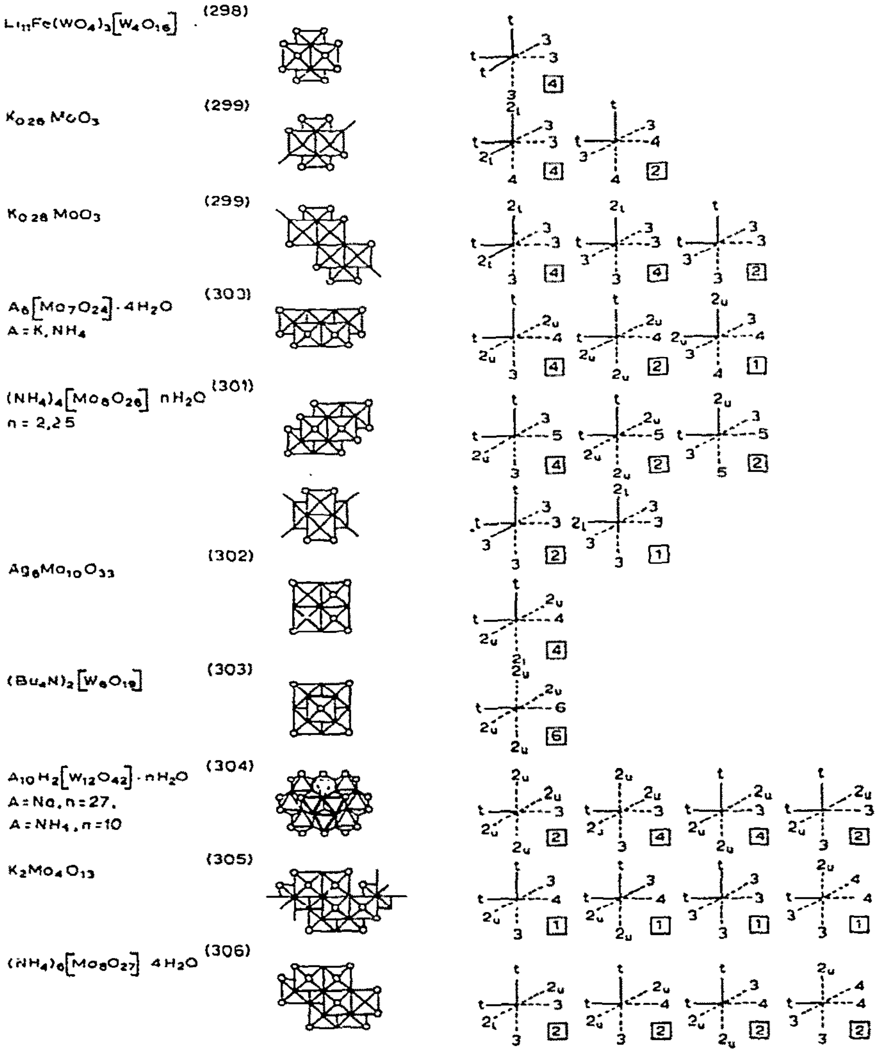


Fig. 16. The structures of blocks and the analysis of linkage of octahedral vertices in some isopolyanions and related complexes.

1. The shortened M—O bonds in *cis*-positions to each other refer to oxygen atoms of the lowest bridge multiplicity: either to terminal t, or bridged 2_ℓ or (in the absence of the latter) to bridged 2_u. The 2_ℓ bridges are asymmetric.

2. The oxygen atoms of maximum bridge multiplicity are always found in a *trans*-position to t atoms. In particular, such positions are occupied by oxygens connecting 4, 5 or 6 metal atoms. There is one exception. In one of the $K_{0.26}MoO_3$ octahedra the atom with c.n. 3 is in a *trans*-position to t, although

there is an oxygen atom connecting four metal atoms. However, this atom is also in a *trans*-position to a pseudo-terminal one 2_Q.

These rules could, of course, be regarded as a trivial sequence of the block structures of crystals. It is natural that t atoms are located on the "outer" sides of blocks, while the oxygen atoms with maximum bridge multiplicity are situated "inside" the blocks. It should be noted, however, that the block structure itself (in particular, the existence of polyatomic isopoly- and heteropolyanions) is basically a feature of group V and VI transition metals. This can be easily understood. Localization of the π-interaction and its resultant *trans*-influence stabilize most such structures in which the "hardest" donors are situated in a *trans*-position to $\mathrm{M}\underset{\leftarrow}{=}\mathrm{O}$ bonds. These are naturally the oxygen atoms participating in bonds with several metal atoms simultaneously. This results in the formation of closed blocks.

Thus the very fact of the existence of stable polyatomic anions of iso- and heteropolyacids is based on two general regularities: the tendency of groups V and VI metals (or metals with d^0—d^1 configuration) towards localization of π-interaction and the *trans*-influence of the multiple bond.

The rules of distribution of the various oxygen atoms in block structures are in apparent agreement with the general differentiation of Mo—O and W—O distances in the family of ReO_3 structures where most of the octahedra are linked only via the vertices (all vertices) and thus all oxygen atoms are of the same type. On the other hand, the block oxygen compounds are stereochemically more close to the mononuclear complexes with multiple M—ligand bonds. Their analysis is the next step after transition from the mononuclear oxocomplexes to the binuclear ones $[(MOL_4)_2O]^{n-}$ or $[(MO_2L_3)_2O]^{n-}$ and other similar compounds. Thus we again point out the community of rules which govern the stereochemistry of metals of the sixth (and apparently fifth and neighbouring groups) in compounds with ligands capable of π-interaction with the metal independently whether the crystals contain isolated complexes or a continuous net of bonds.

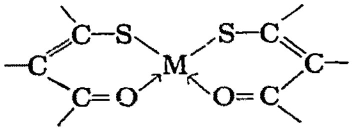
F. ADDITIONAL COMMENTS

(i) Trans-influence and position of the metal in the periodic chart

In sections B(iii) and C(iv) difficulties were mentioned that arise if we try to compare the *trans*-influence in complexes of metals arranged in the same period in the periodic chart. Such a comparison is impossible to make with all other factors equal; the metal oxidation state, or total charge of the complex or its composition would change. At first sight it seems more favourable to compare metals of the same group: their compounds could be equivalent in all the parameters but for the identity of the metal. It is well known, however, that the change in electronic (and geometric) characteristics of atoms in passing from the first to the lower transition series is rather great. It may decisively affect not only the stability and magnetic state of the complex but also its composition. Thus the data which could provide, in principle, a comparison of physical and in particular structural parameters are very limited. The bulk of information on crystal structures actually investigated is even more limited.

Indeed, among 200 complexes listed in the tables of this review, nearly 60 compounds contain Mo, less than 10 contain W, and there are only a few Cr compounds. For group VII there are about 40 Re, one Tc and about 10 Mn (generally carbonyl) compounds. For group V there are about 20 V, 6 Nb and no Ta complexes. Moreover, the Cr and Mo, Mn and Re or V and Nb complexes, all have rather different composition. The absence of analogy in composition and structure is also characteristic of complexes which contain no multiple-bonded ligands. Most typical are the differing magnetic states and/or coordination numbers of the metal in compounds with the same ligands (e.g. in Ni, Pd and Pt compounds). There are very few structural data for completely analogous complexes with different metals of the same group. Such data mainly involve ML_n complexes with identical ligands L (e.g. Ni, Pd and Pt tetracyanides) and some other compounds which are of no special interest for the problem of *trans*-influence.

Among the Ni, Pd and Pt compounds the most interesting might be the chelate complexes $M(\widehat{AX})_2$ where $\widehat{AX}$ is a chelating ligand linked to the metal via different atoms. Among such compounds low-spin nickel complexes are found quite frequently. However, in chelates the problem of the mutual influence of ligands is complicated by the problem of distribution of the π-interaction over the chelate rings. Virtually, no *trans*-influence was observed in the bis-salicylaldiminates studied in detail. The molecules of *cis*-bis-monoisobutyryl acetonate of nickel [307] and *cis*-bis-monothiodibenzoylmethanate of palladium [308] seem to be the only pair permitting comparison. The alternation of distances in these compounds corresponds to a canonical formula:



In the nickel compound the M—S and M—O bond lengths are 2.15 and 1.87 Å, respectively, for palladium they are equal to 2.23 and 2.10 Å, respectively. Elongation of the former bond on going from Ni to Pd is only 0.08 Å with respect to the 0.23 Å in the second bond. It is not clear, however, whether such a difference is due to the change of *trans*-influencing ability on going from Ni to Pd or is a result of different conditions in the chelate rings independently of the nature of the *trans*-partner in the central unit. The last assumption seems more reasonable if one takes into account that in a third related compound, the mesoallyl-monothiodibenzoylmethanate of palladium [309] the Pd—S and Pd—O distances are practically the same as in the above compound (2.29 and 2.067 Å), although the *trans*-partner here is quite different.

In principle, the trivalent cobalt, rhodium and iridium series is most favourable for comparison: Co^{III} unlike its neighbours in the period forms many low-spin compounds. There are many stucturally studied compounds with octahedral complexes: more than 150 Co^{III}, nearly 30 Rh^{III} and about 20 Ir^{III} compounds (according to the data available). However, among them complexes of the same type are very rare, and those containing strong *trans*-influencing ligands are almost absent.

One of the commonly adopted concepts predicts an increase in *trans*-influence on proceeding down the periodic chart. The above remarks show that such a concept has insufficient experimental evidence at least as far as the structural evidence for this effect is concerned. Probably the same is true with other physical parameters specifying the mutual ligand influence in isolated (non-interacting) complexes. It seems that confidence in this concept is based on the intuitive transfer of results, obtained while studying the kinetic *trans*-effect, to the properties of an isolated molecule and on the fact that both the *trans*-effect and *trans*-influence have up to now been studied mainly with platinum complexes.

(ii) Effective atomic charges and bond lengths

It is well known that atomic charge is an artificially defined quantity rather than a directly observed physical property (see, e.g. ref. 310). Nevertheless, being rather careful, one may interpret electron density distribution in molecules in terms of effective atomic charges. In particular, binding energies of the core atomic electrons, determined by ESCA (X-ray photoelectron spectroscopy) [311], prove to be a very convenient indicator of the change of effective atomic charge.

The relevant experimental data have recently been reviewed [34]. For transition metal complexes the most important conclusion is the fact that the electron density redistribution over the ligands usually results in no important change of electron density of the central atom. Moreover, at a given coordination number an increase in the formal oxidation state does not necessarily result in a higher effective charge of the central atom. For example the Re $4f_{5/2}$ binding energy is not changed [312] in going from $ReCl_4(PPh_3)_2$ to $ReOCl_3(PPh_3)_2$ or to $ReOBr_3(PPh_3)_2$ (recall that in the last two compounds the *trans*-influence of the "ylic" oxygen is very important).

The relationship between *trans*-lengthening and the ionic character of the bond is more complicated. In principle, weakening of the M—ligand covalent bond corresponds to a higher ionic character and hence to negative charge accumulation on the acidoligand. In this case one should expect a lower ionization energy for an appropriate ligand level, say Cl 2*p*. In general, this conclusion has been confirmed experimentally [34], however, most data on the *trans*-influence are indirect. Firstly, differences in effective charges (shifts of the Cl 2*p* level) of *trans*- and *cis*-chlorine atoms are usually too small to be experimentally distinguished. Secondly, strong *trans*-influencing ligands (such as $\mathrm{O}\overset{\rightarrow}{=}$ or $\mathrm{N}\equiv$) may sometimes cause a smaller decrease in the Cl 2*p* binding energy than ordinary weak *trans*-influencing σ-donors (such as PR_3 or thiourea) (see, e.g. ref. 312). Besides, even relative estimations of the bond ionic character are complicated due to the noticeable dependence of the χ-level shifts (for both the ligand and the central atom) on spin—orbit components of the split level[*] $\chi_{1\pm 1/2}$.

As has already been mentioned in section B (ii), when donor-acceptor or dative bonds are formed it is meaningless to speak of their ionic character. If an atom (say, oxygen) simultaneously forms both covalent and dative bonds then its resulting effective atomic charge should be higher than that of an atom forming only a covalent bond. Thus, e.g. the $\mathrm{O}\overset{\rightarrow}{\equiv}\mathrm{M}$ triple bond formation in the terminal oxogroup should result in a higher O 1*s* binding energy than in the case of double bonds in the linear $\mathrm{O{=}M{=}O}$ dioxogroup. Similarly, in the $\mathrm{O{=}M}\overset{\leftarrow}{=}\mathrm{O}\overset{\rightarrow}{=}\mathrm{M{=}O}$ fragment the O 1*s* binding energy of the bridge oxygen atom should exceed that of the terminal oxygen atoms. Experimental data confirm this conclusion [312]. However, in the first case the bond between the metal and the more positive oxygen is stronger, while in the second case the bond is weaker. For the same reason, the 2*p* binding energy of the bridging chlorine should be greater than that of the terminal atom. The relevant ESCA data on rhenium [313] and platinum [314] chlorides are rather convincing illustrations of this conclusion. In the examples cited above the bridging O and Cl atoms are less negative than the terminal ones. Though the relevant bridge bonds are less polar, they are, however, known to be considerably weaker (longer) than the terminal bonds. Thus, it is impossible to establish a simple a priori correlation between effective atomic charges and M—ligand bond length[**].

G. SUPPLEMENT [***]

1. In non-transition element complexes, as the latest ab initio SCF—MO—LCAO calculations have shown, the contribution of virtual *nd*-orbitals of the central atom in bonding is insignificant. Moreover, while taking into account *nd*-orbitals the decrease in the total SCF energy of the complex is due mainly

---

[*] In general, energy shifts in X-ray photoelectron spectra are not a sensitive stereochemical indicator. For example, one cannot establish non-equivalency of the Re atoms in the anion $Re_3Cl_{11}^{2-}$ or non-equivalency of "apical" and "equatorial" terminal Cl atoms in the anions $Re_3Cl_{11}^{2-}$ and $Re_3Cl_{12}^{3-}$ (though in $Re_3Cl_{12}^{3-}$ the difference of the relevant $Re—Cl_t$ bond length [313] is 0.15 Å.

[**] In the bridged compounds of non-transition elements (whose acceptor abilites thanks to the use of outer orbitals are very small) as well as probably in most compounds with bridging fluorine (which is the poorest donor), bridging atoms are more negative than terminal ones [34]. In such cases the correlation of effective atomic charge with bond length may be unequivocal.

[***] This supplement contains some independent parts which cover a number of important papers published after this review had been written.

to changes of interelectronic integrals, while the energies of almost all one-electron MO's may even increase. For such complexes the scheme of "hypervalent" bonds with only *np*, and (partly) *ns*, orbitals of the central atom would be the best (see discussion in refs. 320—323). Lately systematic calculations of different coordination compounds have been performed in the framework of the SCF—SW—Xα method. This method [324—326], in comparison with the usual SCF—MO—LCAO technique, is very encouraging for quantitative treatment of large molecules. For example, the SCF—SW—Xα population analysis shows that in SF_6 and SO_4^{2-} molecules one can neglect participation of sulphur 3*d* orbitals in bonding [324]. At the same time in MnO_4^- all valence orbitals of the transition metal atom (including its virtual 4*p* orbitals) are involved in Mn—O bonds [324].

2. The application of X-ray photoelectron spectroscopy to inorganic chemistry has recently been reviewed [327]. This review article contains a number of new and interesting examples that confirm our previous statements concerning the nature of chemical bonding in both transition and non-transition element complexes. In particular, discussing the role of *nd* orbitals of non-transition elements, the author concludes: "All in all, the data offer little support for the use of *d* orbitals in the bonding of silicon compounds. The same conclusion can be drawn from analogous data for germanium compounds" (ref. 327, p. 70).

3. The problem of the definition of effective atomic charges in molecules has been further developed. On the one hand, an approach unifying both main schemes of population analysis — by Mulliken and by Löwdin — has been put forward [328]. On the other hand, a new approach has been developed using the technique of projection and electron density operators [329,330]. Though the latter approach has a number of intrinsic advantages (namely, the procedure is rather general, results are invariant to any orthogonal transformations, etc.) the results obtained are not always easy to interpret in accepted terms. For example, all atomic charges (even in homonuclear two-atomic molecules from Li_2 through F_2) prove to be negative [329].

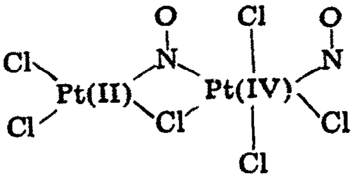
4. A molecular orbital study of the *trans*-effect in Pt^{II} $XYCl_2$ complexes in the framework of the CNDO approximation has recently been published [331]. It was found that the *trans*-effect and *trans*-influence series coincide only for σ-bonding ligands. Further, the *trans*-weakening of the Pt—Cl bond can be correlated with its Wiberg's index only if the series of neutral and of acid ligands are considered separately. It is rather curious that in Zeise's salt, $Pt(C_2H_4)Cl_3^-$, the $Pt—Cl_{cis}$ bonds proved to be more ionic and weaker than the $Pt—Cl_{trans}$ bond (the existing experimental data do not confirm such a conclusion). The main contribution in the strength of Pt—Cl bonds is attributed to 5*d* rather than to 6*p* orbitals of the platinum atom in conformity with the results of ref. 40.

5. New structural investigations of nitrosyl complexes provide additional data for characterization of the *trans*-influence in complexes with linear and angular M—NO fragments.

Refinement [332] of the structure $[Ru(NO)(NH_3)_5]Cl_3.H_2O$ previously solved with low accuracy (see Table 6, compound 90) shows that in the $[Ru(NO)(NH_3)_5]^{3+}$ complex as well as in other complexes with linear Ru—NO fragments, *trans*-elongation is absent: the $Ru—(NH_3)_{trans}$ bond length is 2.017 Å, the $Ru—(NH_3)_{cis}$ distances range from 2.042 Å to 2.133 Å, the average shortening is 0.075 Å. The Ru—NO bond length is 1.770 Å, the Ru—N—O angle is equal to 172.8°.

A similar result was obtained in the course of the structural investigation [332] of $[Ru(NO)(NH_3)_4(OH)]Cl_2$. Here the distances were found to be: Ru—NO = 1.735 Å, $Ru—(OH)_{trans}$ = 1.961 Å, $Ru—(NH_3)_{cis}$ = 2.099—2.106 Å; the Ru—N—O angle is 173.8°.

Besides the three cobalt complexes and the binuclear platinum compound $[Pt_2(NO)_2Cl_8]^{2-}$ mentioned in Table 6, the second platinum compound [333] $(Et_4N)_2[Pt_2(NO)_2Cl_6]$ may serve as another example of a complex with an angular structure of the M—NO fragment. This platinum compound contains binuclear complexes which are built of Pt^{II} and Pt^{IV} (instead of two Pt^{IV} atoms as in the case of $[Pt_2(NO)_2Cl_8]^{2-}$):



Divalent platinum has the usual square coordination, tetravalent platinum has an octahedral one. The coordination polyhedron of this latter comprises terminal NO, bridging NO and four Cl atoms. The $Pt^{IV}—(NO)_{terminal}$ fragment has the angular structure: the angle at the N atom is equal to 122°, the Pt^{IV}—N distance is 1.98 Å. The bridge Cl atom is in a *trans*-position to this nitrosogroup; the $Pt^{IV}—Cl_{bridge}$ distance is 2.62 Å. The $Pt^{IV}—Cl_{terminal}$ distances *cis* to terminal (NO) are 2.33 to 2.38 Å. The $Pt^{IV}—(NO)_{bridge}$ distance is 1.93 Å in length, and the $Pt^{IV}—N—O_{bridge}$ angle is 118°.

Table 7 contains examples of the complete loss of the sixth vertex of an octahedron *trans* to the angular M—NO group. The following complexes may serve as additional examples: Co(NO)(EA), Co(NO)(AB) where EA = *N*,*N*'-ethylenebis(acetylacetoneiminate), EB = *N*,*N*'-ethylenebis(benzoylacetoneiminate) [334,335], Co(NO)(TPP) [336] and Fe(NO)(TPP) [337] where TPP is α, β, γ, δ-triphenylporphin.

In the four cases the tetradentate ligand forms the base of a tetragonal pyramid, the nitrosogroup being arranged at its vertex. The metal atom is shifted from the center of the base towards the vertex by 0.1—0.2 Å. The Co—NO bond lengths are 1.821 to 1.833 Å; the Co—N—O angles vary between 122.4 and 135.2°.

TABLE 18

The *trans*-weakening series of the M—L bond in the X—M—L fragment (dependence on X and L)

X	$(\mathrm{CO}, \mathrm{N_2})\rightleftarrows < \mathrm{ON}\rightleftarrows < \mathrm{RN}\rightrightarrows < \mathrm{O}\rightrightarrows < \mathrm{N}\equiv$ $\leftleftarrows\mathrm{O}\rightrightarrows < \leftleftarrows\mathrm{N}= < \leftarrow\mathrm{O}=$ $\mathrm{M}- < \mathrm{M}\equiv < \mathrm{M}\equiv$
L	$-$ L (acid) < $\leftarrow$ L (σ-donor) Terminal L < Bridging L

H. CONCLUSION

The model developed to discuss the mutual influence of ligands is general enough for an understanding of the most important features of the structure of transition metal coordination compounds with multiple metal—ligand bonds. Yet, this model is sufficiently explicit to describe the peculiarities of various classes of these compounds. On this basis we may compose a *trans*-weakening series which depends on different components of the complexes. Table 18 summarizes the principle results of our work.

In conclusion we should note the following. The energetic and geometric structure of coordination compounds depends on the mutual influence of all ligands (and the central atom) which is determined by the combination of many factors. They are often difficult to separate and their effects are small. In such cases healthy caution and thorough analysis of the vast statistical material is necessary. Therefore it is of great importance to find a field where one can discover a dominating factor, the influence of which could be analyzed unequivocally. In compounds with multiple metal—ligand bonds such a factor does exist and this is the three-center interaction in the $\mathrm{X—M—L}_{trans}$ fragment. The model developed on this basis permits us to interpret without contradiction all available experimental data (several hundred compounds studied by the X-ray method). Thus, one may assume that this model is sufficiently adequate for the description of the electronic structure and stereochemistry of the compounds in question.

ACKNOWLEDGEMENTS

The authors are very grateful to Mrs. V.N. Shchurkina for her assistance in checking the references and especially to Dr. N.A. Porai-Koshits for compiling the tables of experimental data.

NOTE ADDED IN PROOF

trans-Influence is usually regarded as the influence of the ligand X on equilibrium properties of the $\mathrm{M—L}_{trans}$ bond [2,3]. Since in MXL_n complexes substitution of the ligand X influences all M—L bonds, this definition needs to be changed. We deal with the *trans*-influence in an MXL_n complex (where the positions of formally identical ligands L are non-equivalent) if the influence of the ligand X on the equilibrium properties of the $M—L_{trans}$ bond is stronger than that on the properties of the $M—L_{cis}$ bond. Similarly, in the case of a *cis*-influence the properties of the $M—L_{cis}$ bond are more sensitive to influence of the X ligand. Let us stress the fact that in the framework of such a definition the *trans*(*cis*)-influence can result in either weakening or strengthening of the $M—L_{trans}(M—L_{cis})$ bond, given that the corresponding changes in the $M—L_{cis}$-$(M—L_{trans})$ bond are less significant.

If the strength of M—X bonds in MXL_n complexes increases in the series

$$\cdots X_1 < X_2 < \cdots < X_i < L < X_{i+1} < X_{i+2} \cdots , \qquad (30)$$

then in the case of a *trans*-influence we must see the weakening (lengthening) of the $M—L_{trans}$ bond beginning with X_{i+1} and the strengthening (shortening) of this bond up to X_i. In other words, while moving along series (30) the values of $\Delta_j = R(M—L_{trans}) - R(M—L_{cis(\mathrm{stand})})$ (for X_j) will increase monotonically in series (31) with change of the sign of Δ_j at the point L ($X_i < L < X_{i+1}$)

$$\cdots \Delta_1 < \Delta_2 < \cdots \Delta_i < \Delta_L \quad = 0 < \Delta_{i+1} < \Delta_{i+2} \cdots \qquad (31)$$

$$\xleftarrow[\textit{trans}\text{-shortening increases}]{\qquad\qquad\qquad\qquad} \Big| \xrightarrow[\textit{trans}\text{-lengthening increases}]{\qquad\qquad\qquad\qquad}$$

Multiple covalent $M \doteq X$ bonds, discussed in the present review article, include a strong σ-component and therefore cause (as a rule) *trans*-lengthening. However, weak M—X σ-bonds may cause the *trans*-shortening which is obviously expected for donor—acceptor M←X bonds. Actually, for loosely bound donors such as H_2O or NH_3 one observes *trans*-shortening which, for example, in $[RuCl_5(H_2O)]^{2-}$ [338] and $[Fe(CN)_5(NH_3)]^{2-}$ [339], reaches 0.04 and 0.05 Å, respectively. In quasi-triple $M \leftrightarrows NO$ and $M \rightleftarrows CO$ bonds the σ-components are of donor—acceptor character (these σ-bonds are weak due to very low energies of the relevant donor orbitals) and *trans*-shortening in some nitrosyls and carbonyls therefore takes place (see Tables 6 and 8 and the relevant pages of the text).

In general, the degree of the influence of the X ligand in MXL_n complexes may depend significantly on the nature of both the metal atom M and other ligands L. For some ligands X (such as H—, H_3C—, N≡, M≡) considerable weakening (lengthening) of the $M—L_{trans}$ bond is always observed. The typical picture is that for the same ligand X in different MXL_n complexes the $M—L_{trans}$ bond may be weakened, unchanged, or even strengthened. In spite of the seeming chaos in the display of the mutual influence of ligands in transition metal complexes this display always corresponds to a *trans*-influence (in the sense of our definition) because regardless of changes (in both directions) of the $M—L_{trans}$ bond length the corresponding $M—L_{cis}$ bond lengths remain less sensitive.

For transition metal complexes MXL_n all theoretical models (in agreement with experiment) predict *trans*-influence, but for non-transition element complexes AXL_n the picture is rather obscure and here different models give different conclusions [13,340,341]. If for non-transition element complexes we accept the model of hypervalent orbital-deficient bonds [320,323] one can expect that *trans*-influence will dominate though in some cases *cis*-influence may occur [341]. In the context of this review, one should point out first the difference between the influence of the multiply bonded ligand X in non-transition AXL_n compared to transition MXL_n element complexes. Let us remember that, for example, in C_{4v}-complexes MXL_5 the formation of M—X π-bonds takes place due to metal $(n-1)d$ orbitals (d_{xz}, d_{yz}) practically without involving metal equatorial np orbitals (p_x, p_y) which participate in the formation of $M-L_{cis}$ σ-bonds. At the same time in similar AXL_5 complexes (say, in IOF_5 or $TeOF_5^-$) the formation of the π-component of the multiple A—X bond requires the participation of the relevant equatorial p orbital of the central atom and this results in weakening of $A-L_{cis}$ bonds. Therefore in such AXL_n complexes, contrary to MXL_n the *trans*-lengthening must be insignificant; moreover, some *trans*-shortening may even take place. Unfortunately, there are no experimental data concerning bond lengths of the compounds in question. However this conclusion agrees with some indirect data, for example, from NMR ^{19}F spectra of complexes $ReOF_5$ and IOF_5 where chemical shifts of axial and equatorial F atoms prove to be inverted [342].

With orbital-deficient C_{4v}-complexes AL_5, the $A-L_{ax}$ bond must be stronger (shorter) than the $A-L_{eq}$ bonds regardless of the presence of a "lone pair" or "vacant orbital" on the central atom [341]. The only difference is displayed in valence $L_{ax}AL_{eq}$ angles, as shown in Fig. 3a and 3b, respectively. The 12 electron complexes XeF_5^+, IF_5 or TeF_5^- [343] and 10 electron complexes $Sb(C_6H_5)_5$ [344] and $InCl_5^{2-}$ [345] are typical examples of the "lone pair" and "vacant orbital" cases, respectively. Experimental (X-ray) data agree completely with this theoretical prediction. This means that it would be wrong to attribute the non-equivalency of A—L bonds in AL_5 complexes to the influence of "lone pair" or "vacant orbital". It proves again (see p. 13) that directed influence is determined by the strength of M—X (A—X) bond rather than by the donor ability of the X ligand (because "lone pair" and "vacant orbital" may be regarded as the opposite extreme cases of the donor ability of the X ligand).

REFERENCES

1 I.I. Chernyaev, Izv. Instituta platiny Akad. Nauk SSSR, 4 (1926) 261; Izv. Sektora platiny Instituta Obshchei i Neorganich. Khim., Akad. Nauk SSSR, 5 (1927) 118.

2 A. Pidcock, R.E. Richards and L.M. Venanzi, J. Chem. Soc. A, (1966) 1707; L.M. Venanzi, Chem. Brit., 4 (1968) 162.

3 T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.

4 K.B. Yatsimirskii, Zh. Neorg. Khim., 15 (1970) 925; Pure and Appl. Chem., (XV ICCC Plenary Lecture, Moscow, 1973), 38 (1974) 341.

5 F.R. Hartley, Chem. Soc. Rev., 2 (1973) 163.

6 C.H. Langford and H.B. Gray, Ligand Substitution Processes, Benjamin, New York, 1965.

7 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd ed., Wiley, New York, 1967.

8 C.H. Langford, Can. J. Chem., 49 (1971) 1497.

9 U. Belluco, Coord. Chem. Rev., 1 (1966) 111.

10 R. McWeeny, R. Mason and A.D.C. Towl, Discuss. Faraday Soc., 47 (1969) 20.

11 R. Mason and A.D.C. Towl, J. Chem. Soc. A, (1970) 1601.

12 M.A. Porai-Koshits and E.A. Gilinskaya, Uspekhi kristallokhimii kompleksnykh soedinenii. I., Seriya, Itogi nauki. Kristallokhimiya, VINITI Pub. House, Moscow, 1966, pp. 5—153.

13 M.A. Porai-Koshits and L.O. Atovmyan, Uspekhi kristallokhimii kompleksnykh soedinenii. III., Kristallokhimiya koordinatsionnykh soedinenii molibdena i vol'frama, VINITI Pub. House, Moscow, 1968, pp. 5—113.

14 M.A. Porai-Koshits, A.S. Antsyshkina, G.A. Kukina, V.I. Sokol and T.S. Khodashova, Uspekhi kristallokhimii kompleksnykh soedinenii. IV., Kristallicheskie struktury koordinatsionnykh soedinenii khroma, margantsa, zheleza i kobalta, VINITI Pub. House, Moscow, 1967, pp. 5—197.

15 M.A. Porai-Koshits, V.N. Vorotnikova, V.S. Sergienko and V.I. Sokol, Uspekhi kristallokhimii kompleksnykh soedinenii. VI., Kristallicheskie struktury koordinatsionnykh soedinenii molibdena, vol'frama, reniya i tekhnetsiya, VINITI Pub. House, Moscow, 1971, pp. 5—147.

16 M.A. Porai-Koshits, T.S. Khodashova and A.S. Antsishkina, Uspekhi kristallokhimii kompleksnykh soedinenii, VII., Kristallicheskie struktury koordinatsionnykh soedinenii ruteniya, osmiya i iridiya, VINITI Pub. House, Moscow, 1971, pp. 5—141.

17 M.A. Porai-Koshits and G.A. Kukina, Uspekhi kristallokhimii kompleksnykh soedinenii. IX. Kristallicheskie struktury koordinatsionnykh soedinenii palladiya i platiny, VINITI Pub. House, Moscow, 1973, pp. 5—96.

18 V.I. Nefedov and Yu.A. Buslaev, Zh. Neorg. Khim., 18 (1973) 3163.

19 E.M. Shustorovich, Zh. Strukt. Khim., 10 (1969) 947.

20 S.F.A. Kettle, Coord. Chem. Rev., 2 (1967) 9.

21 I.B. Golovanov, A.K. Piskunov and N.M. Sergeev, Elementarnoe vvedenie v kvantovuyu biokhimiyu, Nauka Publ. House, Moscow, 1969, p. 153.

22 E.M. Shustorovich, Zh. Strukt. Khim., 15 (1974) 123.

23 E.M. Shustorovich, M.A. Porai-Koshits, T.S. Khodashova and Yu.A. Buslaev, Zh. Strukt. Khim., 14 (1973) 706.

24 C.H. Langford, private communication.

25 D.A. Brown, W.J. Chambers and N.J. Fitzpatrick, Inorg. Chim. Acta Rev., 6 (1972) 7.

26 C.K. Jørgensen, Modern Aspects of Ligand Field Theory, North-Holland Publishing, Amsterdam, 1971.

27 C.K. Jørgensen, Chimia, 27 (1973) 203.

28 R.J. Gillespie, J. Chem. Educ., 47 (1970) 18.

29 J. Jarvie, W. Wilson, J. Doolittle and C. Edmiston, J. Chem. Phys., 59 (1973) 3021.

30 P.L. Orioli, M. Di Vaira, M. Ciampolini and L. Sacconi, Proc. of 9th ICCC, St. Moritz-Bad, Sept. 1966, 3 Mon 5.

31 L. Sacconi, Pure and Appl. Chem., 17 (1968) 95.

32 A.R. Rossi and R. Hoffman, Inorg. Chem., 14 (1975) 365.

33 E.M. Shustorovich, Yu.A. Buslaev and Yu.V. Kokunov, Zh. Strukt. Khim., 13 (1972) 111.

34 (a) V.I. Nefedov and M.A. Porai-Koshits, Nat. Res. Bull., 7 (1972) 1543;
(b) V.I. Nefedov, Stroenie molekul i khimicheskaya svyaz'. Primenenie retgenoelektronnoi spektroskopii v khimii, VINITI Pub. House, Moscow, 1973.

35 Ya.K. Syrkin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1948) 69.
36 M.E. Dyatkina and N.M. Klimenko, Zh. Strukt. Khim., 14 (1973) 173.
37 H.B. Gray, Electrons and Chemical Bonding, Benjamin, New York and Amsterdam, 1965, Table 32.
38 C.E. Moore, Atomic Energy Levels, Nat. Bur. Stand. USA, Washington, 1 (1949); 2 (1952).
39 O.P. Charkin, Zh. Strukt. Khim., 14 (1973) 389 and references cited therein.
40 S.S. Zumdahl and R.S. Drago, J. Amer. Chem. Soc., 90 (1968) 6669.
41 (a) V.I. Baranovskii, O.V. Sizova and A.I. Stetsenko, Teor. Eksp. Khim., 9 (1973) 435;
(b) V.I. Baranovskii and O.V. Sizova, Teor. Eksp. Khim., 9 (1973) 807;
(c) O.V. Sizova, Thesis, Leningrad State University, 1974.
42 (a) G.E. Maciel, J.W. McIwer, Jr., N.S. Ostlund and J.A. Pople, J. Amer. Chem. Soc., 92 (1970) 1, 11;
(b) A.C. Blizzard and D.P. Santry, Chem. Commun., (1970) 87.
43 R.G. Pearson, Inorg. Chem., 12 (1973) 712.
44 R.S. Drago, Inorg. Chem., 12 (1973) 2211; R.T. Myers, Inorg. Chem., 13 (1974) 2040.
45 E.M. Shustorovich, Zh. Strukt. Khim., 4 (1963) 245.
46 F.A. Cotton, Accounts Chem. Res., 2 (1969) 241.
47 C.K. Jorgensen, S.M. Horner, W.E. Hatfield and S.Y. Tyree, Int. J. Quantum Chem., 1 (1967) 191.
48 J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York, 1970.
49 A.I. Popov, in Halogen Chemistry, Acad. Press, London and New York, 1966, p. 229.
50 J.M. Williams and E.F. Schneemeyer, J. Amer. Chem. Soc., 95 (1973) 5780.
51 E.M. Shustorovich, Elektronnoe stroenie polimernykh molekul s kratnymi svyazyami v osnovnoi tsepi, Nauka Pub. House, Moscow, 1967.
52 T.C. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
53 M.A. Porai-Koshits and L.O. Atovmyan, Kristallokhimiya i Stereokhimiya koordinatsionnykh soedinenii molibdena, Nauka Pub. House, Moscow, 1974.
54 P.A. Koz'min, M.D. Surazhskaya and T.B. Larina, Zh. Strukt. Khim., 15 (1974) 64; see also Proc. 15th ICCC, Moscow, 1973, p. 43.
55 (a) L.O. Atovmyan and V.V. Tkachev, Zh. Strukt. Khim., 9 (1968) 708;
(b) D. Bright and J.A. Ibers, Inorg. Chem., 8 (1969) 709.
56 T.G. Glovak, Diss, Universitet Wraclaw, 1967.
57 K.F. Teble and H.G. Schnering, Z. Anorg. Allg. Chem., 396 (1973) 66.
58 A. Mathieson, D.P. Mellor and N.C. Stephenson, Acta Crystallogr., 5 (1952) 185.
59 J.C. Marrow, Acta Crystallogr., 15 (1962) 851.
60 J.T. Veal and D.J. Hodson, Inorg. Chem., 11 (1972) 1420.
61 (a) J.T. Veal and D.J. Hodson, Acta Crystallogr. Sect. B, 28 (1972) 3525;
(b) T.S. Khodashova and G.B. Bokii, Zh. Strukt. Khim., 5 (1964) 90.
62 P.W.R. Corfield, R.J. Doedens and J.A. Ibers, Inorg. Chem., 6 (1967) 197.
63 H.W.W. Ehrlich and P.G. Owston, J. Chem. Soc., (1963) 4368.
64 (a) L. Monojlovič-Muir, Chem. Commun., (1971) 147;
(b) L. Monojlovič-Muir, J. Chem. Soc. A, (1971) 2796.
65 J. Chatt, L. Monojlovič-Muir and K.W. Muir, Chem. Commun., (1971) 655.
66 D. Bright and J.A. Ibers, Inorg. Chem., 8 (1969) 703.
67 D. Bright and J.A. Ibers, Inorg. Chem., 7 (1968) 1099.
68 P.A. Koz'min, G.N. Novitskaya and V.G. Kuznetsov, Zh. Strukt. Khim., 14 (1973) 680.
69 P.A. Koz'min, M.D. Surazhskaya and V.G. Kuznetsov, Zh. Strukt. Khim., 11 (1970) 311.
70 L.O. Atovmyan and V.V. Tkachev, Zh. Strukt. Khim., 11 (1970) 933.

71 L.O. Atovmyan, Doctoral Thesis, Institute of Gen. and Inorg. Chem. Acad. Sci. USSR, Moscow, 1971. Thesis Referate, Moscow, 1971.
72 P.W. Frais and C.J.L. Lock, Can. J. Chem., 50 (1972) 1811.
73 F.A. Cotton and S.J. Lippard, Inorg. Chem., 4 (1965) 1621.
74 M. Ciechanovich and A.C. Skapski, Chem. Commun., (1969) 574.
75 T.S. Khodashova, M.A. Porai-Koshits, V.S. Sergienko, N.A. Parpiev and G.B. Bokii, Zh. Strukt. Khim., 13 (1972) 1105.
76 A.J. Edwards, J. Chem. Soc. Dalton, (1972) 584.
77 (a) G. Ferguson, M. Murcer and D.W.A. Sharp, J. Chem. Soc. A, (1969) 2415; (b) M.G.B. Drew and I.B. Tomkins, J. Chem. Soc. A, (1970) 22.
78 M.G.B. Drew and R. Mandyczewsky, J. Chem. Soc. A, (1970) 2815.
79 M.G.B. Drew, G.W.A. Fowles, D.A. Rice and M. Rolfe, Chem. Commun., (1971) 231.
80 V.C. Adam, U.A. Gregori and B.T. Rilborg, Chem. Commun., (1970) 1400.
81 V.S. Sergienko, T.S. Khodashova and M.A. Porai-Koshits, Zh. Strukt. Khim., 13 (1972) 461.
82 G.Z. Pinsker, Kristallografiya, 21 (1966) 736.
83 D. Grandjean and R. Weiss, Bull. Soc. Chim. Fr., 8 (1967) 3054.
84 D. Grandjean and R. Weiss, Bull. Soc. Chim. Fr., 8 (1967) 3044.
85 I. Larking and R. Stromberg, Acta Chem. Scand., 24 (1970) 2043.
86 G.Z. Pinsker and V.G. Kuznetsov, Zh. Strukt. Khim., 13 (1968) 74.
87 D. Grandjean and R. Weiss, Bull. Soc. Chim. Fr., 8 (1967) 3049.
88 A.J. Edwards and P. Taylor, Chem. Commun., (1970) 1474.
89 A.J. Edwards and G.R. Jones, J. Chem. Soc. A, (1968) 2511.
90 A.J. Edwards, G.R. Jones and R.J. Sills, Chem. Commun., (1968) 1177.
91 A.J. Edwards and B.R. Stevenson, J. Chem. Soc. A, (1968) 2503.
92 R.R. Ryan, S.H. Mastin and M.J. Reisfeld, Acta Crystallogr. Sect. B, 27 (1971) 1270.
93 L.O. Atovmyan, O.N. Krasochka and M.Ya. Rachlin, Chem. Commun., (1971) 610.
94 A.J. Edwards and G.R. Jones, J. Chem. Soc. A, (1968) 2074.
95 I.G. Scane, Acta Crystallogr., 23 (1967) 85.
96 L.O. Atovmyan and Z.G. Aliev, Zh. Strukt. Khim., 12 (1971) 732.
97 L.O. Atovmyan and O.N. Krasochka, Zh. Strukt. Khim., 12 (1971) 91.
98 L.O. Atovmyan and O.N. Krasochka, Zh. Strukt. Khim., 16 (1975) (in press).
99 R. Florian and E.R. Corey, Inorg. Chem., 7 (1968) 723.
100 L.O. Atovmyan, O.A. D'yachenko and E.B. Lobkovskii, Zh. Strukt. Khim., 11 (1970) 469.
101 B. Kojić-Prodić, R. Liminga and S. Scavničar, Acta Crystallogr. Sect. B, 29 (1973) 864.
102 G. Harris and F.J. Harris, J. Chem. Phys., 31 (1959) 1450.
103 V.A. Kuznetsov, D.L. Rogachev, M.A. Porai-Koshits and L.M. Dikareva, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 2167.
104 A.A. Kashaev and G.B. Sokolova, Kristallografiya, 18 (1973) 620.
105 J.A. Beaver and M.G.B. Drew, J. Chem. Soc. Dalton, (1973) 1376.
106 W. Jeitschko and A.W. Sleight, Acta Crystallogr. Sect. B, 29 (1973) 869.
107 R. Strandberg, Acta Chem. Scand., 27 (1973) 1004.
108 B. Spivack and Z. Dori, J. Chem. Soc. Dalton, (1973) 1173.
109 L.O. Atovmyan and O.N. Krasochka, Chem. Commun., (1970) 1670.
110 J.J. Park, M.D. Glick and J.L. Hoard, J. Amer. Chem. Soc., 91 (1969) 301.
111 A.W. Hanson, Acta Crystallogr., 6 (1953) 32.
112 R.E. Drew and F.W.B. Einstein, Inorg. Chem., 12 (1973) 829.
113 J.M. LeCarpentier, R. Schupp and R. Weiss, Acta Crystallogr. Sect. B, 28 (1972) 1278.
114 R. Stomberg, Acta Chem. Scand., 22 (1968) 1076.
115 J.M. LeCarpentier, A. Mitschler and R. Weiss, Acta Crystallogr. Sect. B, 24 (1972) 1288.

116 F.W.B. Einstein and B.R. Penford, Acta Crystallogr., 17 (1964) 1112.
117 I.B. Svensson and R. Stomberg, Acta Chem. Scand., 25 (1971) 898.
118 R. Stomberg, Ark. Kemi, 24 (1965) 111.
119 R. Stomberg, Acta Chem. Scand., 24 (1970) 2024.
120 G. Meúnier, J. Darriet and J. Galy, J. Solid State Chem., 6 (1973) 67.
121 K.A. Wilhelmi and K. Waltersson, Acta Chem. Scand., 24 (1970) 3409.
122 M. Mathew, A.J. Carty and G.J. Palenik, J. Amer. Chem. Soc., 92 (1970) 3197.
123 M.G.B. Drew and I.B. Tomkins, Acta Crystallogr. Sect. B, 26 (1970) 1161.
124 H. Hess and H. Harting, Z. Anorg. Allg. Chem., 344 (1966) 157.
125 A.J. Edwards, D.R. Slim, J. Sala-Pala and J.E. Guerchais, C.R. Acad. Sci. Ser. C, 276 (1973) 1377.
126 O. Jarchov, F. Schröder and H. Schulz, Z. Anorg. Allg. Chem., 363 (1968) 58.
127 L.O. Atovmyan and G.B. Bokii, Zh. Strukt. Khim., 4 (1963) 576.
128 I. Larking and R. Stomberg, Acta Chem. Scand., 26 (1972) 3708.
129 H. d'Amour and R. Allman, Z. Kristallogr. Kristallgeometrie, Kristallphys. Kristallchem., 136 (1972) 23.
130 A.B. Blake, F.A. Cotton and S. Wood, J. Amer. Chem. Soc., 86 (1964) 3024.
131 J.R. Knox and C.K. Prout, Acta Crystallogr. Sect. B, 25 (1969) 2281.
132 D. Schwarzenbach, Inorg. Chem., 9 (1970) 2391.
133 A. Urushiyama, Bull. Chem. Soc. Jap., 45 (1972) 2406.
134 O.S. Mills and A.D. Redhouse, Chem. Commun., (1966) 814.
135 E. Fleischer and S. Hawkinson, J. Amer. Chem. Soc., 89 (1967) 720.
136 S.J. Lippard, H. Schugar and C. Walling, Inorg. Chem., 6 (1967) 1825.
137 J.R. Durig, W.A. McAllister, J.N. Willis, Jr. and E.E. Mercer, Spectrochim. Acta, 22 (1966) 1091.
138 G.A. Benetley, K.R. Laing, W.R. Roper and J.W. Waters, Chem. Commun., (1970) 998.
139 L.A. Butman; T.S. Khodashova, L.Kh. Minacheva and V.I. Tayukin, Zh. Strukt. Khim., 5 (1964) 250.
140 S.H. Simonsen and M.H. Mueller, J. Inorg. Nucl. Chem., 27 (1965) 309.
141 T.S. Khodashova, V.S. Sergienko and M.A. Porai-Koshits, Zh. Strukt. Khim., 12 (1971) 478.
142 T.S. Khodashova, Zh. Strukt. Khim., 6 (1965) 717.
143 A. Domenicano, A. Vaciago and L. Zambonelli, Chem. Commun., (1966) 476.
144 P.T. Manoharan and W.C. Hamilton, Inorg. Chem., 2 (1963) 1043.
145 A. Tullberg and N.-G. Vannerberg, Acta Chem. Scand., 21 (1967) 1462.
146 J.H. Enemark, M.S. Quinby, L.L. Reed, M.J. Steuck and K.K. Walters, Inorg. Chem., 9 (1970) 2397.
147 S. Jagner and N.-G. Vannerberg, Acta Chem. Scand., 24 (1970) 1988.
148 D.H. Svedung and N.-G. Vannerberg, Acta Chem. Scand., 22 (1968) 1551.
149 R.F. Riley and L. Ho, J. Inorg. Nucl. Chem., 24 (1962) 1121.
150 T.F. Brennan and J. Bernal, Chem. Commun., (1970) 138.
151 M.O. Visscher and K.G. Caulton, J. Amer. Chem. Soc., 94 (1972) 5923.
152 M.W. Anker, R. Colton and J.B. Tomkins, Aust. J. Chem., 21 (1962) 1121.
153 C.S. Pratt, B.A. Coyle and J.A. Ibers, J. Chem. Soc. A, (1971) 2146.
154 D.A. Snyder and D.L. Weaver, Inorg. Chem., 9 (1970) 2760.
155 G.H. Enermark and R.D. Feltham, 9th Intern. Congress on Crystallogr., Kyoto, Japan, 1972.
156 T.S. Khodashova, V.S. Sergienko, M.A. Porai-Koshits, A.I. Stetsenko and L.A. Butman, Zh. Strukt. Khim., 15 (1974) 471.
157 (a) N.M. Sinitsin and O.E. Zvyagintsev, Dokl. Akad. Nauk SSSR, 145 (1962) 109; (b) J.M. Fletcher, I.L. Jenkins, F.M. Lever, F.S. Martin, A.R. Powel and R. Todd, J. Inorg. Nucl. Chem., 1 (1955) 378.
158 (a) D.M.P. Mingos, Nature (Phys. Sci.), 229 (1971) 197;

(b) C.G. Pierpont and R. Eisenberg, J. Amer. Chem. Soc., 93 (1971) 4905.
159 A.J.M. Rae, Chem. Commun., (1967) 1245.
160 M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago and L. Zambonelli, Chem. Commun., (1967) 583.
161 B.F.G. Johnson and J.A. McCleverty, Progr. Inorg. Chem., 7 (1966) 277.
162 J.K. Davies, J.A.J. Jarvis, B.T. Kilbourn, R.H.B. Mais and P.G. Owston, J. Chem. Soc. A, (1970) 1275.
163 J.H. Snemark and R.D. Feltham, 9th Intern. Congress of Crystallogr., Kyoto, Japan, 1972, p. S86, abstr. VI-36.
164 D.J. Hudson and J.A. Ibers, Inorg. Chem., 7 (1968) 2345.
165 D.J. Hudson and J.A. Ibers, Inorg. Chem., 8 (1969) 1282.
166 D.M. Mingos, W.T. Robinson and J.A. Ibers, Inorg. Chem., 10 (1971) 1043.
167 D.M. Mingos and J.A. Ibers, Inorg. Chem., 10 (1971) 1035.
168 C.G. Pierpont and R. Eisenberg, Inorg. Chem., 11 (1972) 1088.
169 J.M. Waters and K.R. Whittle, Chem. Commun., (1971) 518.
170 K. Grundly, K.P. Laing and W.R. Roper, Chem. Commun., (1970) 1500.
171 C.G. Pierpont and R. Eisenberg, Inorg. Chem., 12 (1973) 199.
172 S.R. Fletcher, W.P. Griffith, D. Pawson, F.L. Phillips and A.C. Skapski, Inorg. Nucl. Chem. Lett., 9 (1973) 1117.
173 F. Klanberg and L.J. Gugenberger, Chem. Commun., (1967) 1293.
174 O.S. Mills and A.D. Redhouse, Chem. Commun., (1966) 814.
175 F.A. Cotton and D.C. Richardson, Inorg. Chem., 5 (1966) 1851.
176 G. Hüttner and O.S. Mills, Chem. Commun., (1968) 344.
177 S.I. La Placa, W.C. Hamilton and J.A. Ibers, Inorg. Chem., 3 (1964) 1491.
178 L.F. Dahl and W. Chin-Hsuan, Acta Crystallogr., 16 (1963) 611.
179 F.W.B. Einstein, H. Luth and J. Trotter, J. Chem. Soc. A, (1967) 89.
180 B.P. Biryukov, K.N. Anisimov, Yu.T. Struchkov, N.E. Kolobova, O.P. Osipova and M.Ya. Zakharova, Zh. Strukt. Khim., 8 (1967) 554.
181 P.L. Hansen and R.A. Jacobson, J. Organometal. Chem., 6 (1966) 389.
182 P.A. Agron, R.D. Allison and H.A. Levy, Acta Crystallogr., 23 (1967) 1079.
183 H.D. Kaesz, R. Ban and R. Churchill, J. Amer. Chem. Soc., 89 (1967) 2775.
184 (a) L.F. Dahl and R.E. Rundle, Acta Crystallogr., 16 (1963) 419;
(b) N.I. Gapotchenko, N.V. Alekseev, K.N. Anisimov, N.E. Kolobova and I.A. Ronova, Zh. Strukt. Khim., 9 (1968) 892;
(c) A. Allmeningen, G.G. Jacobson and H.M. Seip, Acta Chem. Scand., 23 (1969) 685.
185 M.J. Bennett and R. Mason, J. Chem. Soc. A, (1968) 75.
186 R.J. Doedens, W.T. Robinson and J.A. Ibers, J. Amer. Chem. Soc., 89 (1967) 4323.
187 D.M. Chirman and R.A. Jacobson, Inorg. Chim. Acta, 1 (1967) 393.
188 I.S. Astakhova, A.A. Johannsson, V.A. Senion, Yu.T. Struchkov, K.N. Anisimov and N.E. Kolobova, Chem. Commun., (1969) 488.
189 S.F. Watkins, J. Chem. Soc. A, (1969) 1552.
190 M.A. Porai-Koshits, V.S. Sergienko and T.S. Khodashova, Zh. Neorg. Khim., 18 (1973) 3290.
191 V.G. Andrianov, B.P. Biryukov and Yu.T. Struchkov, Zh. Strukt. Khim., 10 (1969) 1129.
192 B.P. Biryukov and Yu.T. Struchkov, Usp. Khim., 39 (1970) 1672.
193 T. Uchida, Y. Uchida, M. Hidai and T. Kodama, Bull. Chem. Soc. Jap., 44 (1971) 2833.
194 B.D. Davis and J.A. Ibers, Inorg. Chem., 10 (1971) 578.
195 F. Bottomley and S.C. Nyburg, Acta Crystallogr. Sect. B, 24 (1968) 1289.
196 B.R. Davis and J.A. Ibers, Inorg. Chem., 9 (1970) 2768.
197 J.E. Fergusson, J.L. Love and W.T. Robinson, Inorg. Chem., 11 (1972) 1662.
198 I.M. Treitel, M.T. Flood, R.E. March and H.B. Gray, J. Amer. Chem. Soc., 91 (1969) 6513.

199 M. Mercer, Chem. Commun., (1973) 808.
200 (a) K. Jonas, Angew. Chem. Int. Ed. Engl., 12 (1973) 997;
(b) C. Krüger and Yi-Hung Tsay, Angew. Chem. Int. Ed. Engl., 12 (1973) 998.
201 V.I. Nefedov, W.S. Lenenko, V. Shur, M.E. Vol'pin and M.A. Porai-Koshits, Inorg. Chim. Acta, 7 (1973) 499.
202 E.M. Shustorovich and D.V. Korol'kov, Zh. Strukt. Khim., 13 (1972) 682.
203 C.L. Angell and F.A. Cotton, Chem. Commun., (1973) 399.
204 F.A. Cotton, B.A. Frenz and T.R. Webb, J. Amer. Chem. Soc., 95 (1973) 4431.
205 M.J. Bennett, F.A. Cotton and R.A. Walton, Proc. Roy. Soc. Ser. A, 303 (1968) 175.
206 M.A. Porai-Koshits and A.S. Antsyshkina, Dokl. Akad. Nauk SSSR, 146 (1962) 1102.
207 F.A. Cotton, B.G. de Boer, M.D. La Prade, J.R. Piral and D.A. Ucko, J. Amer. Chem. Soc., 92 (1970) 2926.
208 A.S. Antsyshkina, Acta Crystallogr. Sect. A, 21 (1966) 140.
209 K.G. Caulton and F.A. Cotton, J. Amer. Chem. Soc., 21 (1969) 6518.
210 J. Drew, M.B. Hursthouse, P. Thornton and A.J. Welch, Chem. Commun., (1973) 52.
211 M.J. Bennett, W.K. Bratton, F.A. Cotton and W.R. Robinson, Inorg. Chem., 7 (1968) 1570.
212 C. Calvo, N.C. Jaedevan and C.J.L. Lock, Can. J. Chem., 47 (1969) 4213.
213 C. Calvo, N.C. Jaedevan, C.J.L. Lock and R. Restivo, Can. J. Chem., 48 (1970) 219.
214 M.J. Bennett, K.G. Caulton and F.A. Cotton, Inorg. Chem., 8 (1969) 1.
215 L.M. Dikareva, Acta Crystallogr. Sect. A, 21 (1966) 140.
216 (a) G.L. Simon, A.W. Adamson and L.F. Dahl, J. Amer. Chem. Soc., 94 (1972) 7654;
(b) L.D. Brown, K.N. Raymond and S.Z. Goldberg, J. Amer. Chem. Soc., 94 (1972) 7664.
217 F.A. Cotton and J.T. Mague, Inorg. Chem., 3 (1964) 1094.
218 F.A. Cotton and J.T. Mague, Inorg. Chem., 3 (1964) 1402.
219 M.J. Bennett, F.A. Cotton and B.M. Foxman, Inorg. Chem., 7 (1968) 1563.
220 B.R. Penford and W.T. Robinson, Inorg. Chem., 5 (1966) 1758.
221 F.A. Cotton and S. Lippard, Inorg. Chem., 4 (1965) 59.
222 (a) J.A. Bertrand, F.A. Cotton and W.A. Dollase, Inorg. Chem., 2 (1963) 1166;
(b) W.T. Robinson, J.E. Fergusson and B.R. Penfold, Proc. Chem. Soc., (1963) 116.
223 M. Elder and B.R. Penfold, Inorg. Chem., 5 (1966) 1763.
224 (a) J.E. Fergusson, B.R. Penfold and W.T. Robinson, Nature, 201 (1964) 181;
(b) F.A. Cotton and J.T. Mague, Inorg. Chem., 3 (1964) 1094;
(c) B.H. Robinson and J.E. Fergusson, J. Chem. Soc., (1964) 5683.
225 L.J. Gugenberger and A.W. Sleight, Inorg. Chem., 8 (1969) 2041.
226 R. Siepman and H.G. Schnering, Z. Anorg. Allg. Chem., 357 (1968) 289.
227 H. Schäfer and H.G. Schnering, Angew. Chem., 76 (1964) 833.
228 B. Kamenar and C.K. Prout, J. Chem. Soc. A, (1970) 2379.
229 L.O. Atovmyan, O.A. D'yachenko and E.B. Lobkovskii, Zh. Strukt. Khim., 11 (1970) 469.
230 B. Krebs, A. Müller and H. Beyer, Chem. Commun., (1968) 263.
231 H. Beyer, L. Clemers and B. Krebs, Angew. Chem., 80 (1968) 286.
232 F.A. Cotton and S.J. Lippard, Inorg. Chem., 5 (1966) 416.
233 A. Brossi, Chem. Commun., (1970) 1296.
234 F.W.B. Einstein, E. Enwall, D.M. Morris and D. Sutton, Inorg. Chem., 10 (1971) 678.
235 W.O. Davies, N.P. Johnson and P. Johnson, Chem. Commun., (1969) 736.
236 C.J. Ballhausen, B.F. Djurinskij and K.J. Watson, J. Amer. Chem. Soc., 90 (1968) 3305.

237. V.N. Serezhkin, V.F. Chuvaev, L.M. Kovba and V.K. Trunov, Dokl. Akad. Nauk SSSR, 210 (1973) 873.

238. M.G.B. Drew, K.C. Moss and N. Rolfe, Inorg. Nucl. Chem. Lett., 7 (1971) 1219.

239. (a) L.O. Atovmyan and V.A. Sokolova, Zh. Strukt. Khim., 12 (1971) 934;
(b) W.R. Scheidt, Chun-che Tsai and J.L. Hoard, J. Amer. Chem. Soc., 93 (1971) 3867.

240. G.E. Form and E.S. Raper, Chem. Commun., (1972) 945.

241. F.A. Cotton and S.M. Morehouse, Inorg. Chem., 4 (1965) 1377.

242. L.O. Atovmyan, Yu.A. Sokolova and V.V. Tkachev, Dokl. Akad. Nauk SSSR, 195 (1970) 1355.

243. L.O. Atovmyan, V.V. Tkachev and G.G. Shipova, Dokl. Akad. Nauk SSSR, 205 (1972) 609.

244. (a) B. Kamenar, M. Penavič and C.K. Prout, Cryst. Struct. Commun., 2 (1973) 41;
(b) B.M. Craven, K.C. Ramaj and W.B. Wise, Inorg. Chem., 10 (1971) 2626.

245. A. Kopwilem and P. Kierkegaard, Acta Chem. Scand., 23 (1968) 2184.

246. L.O. Atovmyan and Yu. Sokolova, Chem. Commun., (1969) 649.

247. R.H. Fenn, J. Chem. Soc. A, (1969) 1764.

248. J.R. Knox and C.K. Prout, Acta Crystallogr. Sect. B, 25 (1969) 1857.

249. D.H. Brown and J.A.D. Jeffreys, J. Chem. Soc. Dalton, (1973) 732.

250. L.T.J. Delbeare and C.K. Prout, Chem. Commun., (1971) 162.

251. B. Spivack, A.P. Gaughan and Z. Dori, J. Amer. Chem. Soc., 93 (1971) 5265.

252. M.A. Porai-Koshits, L.A. Aslanov, G.V. Ivanova and T.N. Polynova, Zh. Strukt. Khim., 9 (1968) 475.

253. W.R. Scheidt, D.M. Collins and J.L. Hoard, J. Amer. Chem. Soc., 93 (1971) 3873.

254. W.R. Scheidt, R. Countryman and J.L. Hoard, J. Amer. Chem. Soc., 93 (1971) 3878.

255. R. Shandler, E.O. Schlemper and R.R. Murmann, Inorg. Chem., 10 (1971) 2785.

256. C.R. Fletcher, J.E. Rowbotton, A.C. Skapski and G. Wilkinson, Chem. Commun., (1970) 1572.

257. T.G. Glowiak, T. Lis and B. Jezowska-Tszebiatowska, Proc. 3rd Conf. Coord. Chem., Smolenice, Bratislava, 1971, p. 73.

258. V.W. Day and J.L. Hoard, J. Amer. Chem, Soc., 90 (1968) 3374.

259. (a) R.H. Fenn, A.J. Graham and N.P. Johnson, J. Chem. Soc. A, (1971) 2880;
(b) R.K. Murmann and E.O. Schlemper, Inorg. Chem., 10 (1971) 2352;
(c) K. Lukaszewicz and T. Glowiak, Bull. Acad. Pol. Sci. Ser. Sci. Chim., 9 (1961) 613.

260. (a) G.K. Babeshkina, T.S. Khodashova and M.A. Porai-Koshits, Proc. XIIIth ICCC, (1970) 225, p. 95;
(b) T. Glowiak, M. Kubiak and T. Lis, Proc. XIIIth ICCC (1970) 416, p. 372.

261. C. Calvo, N. Krishnamachari and C.J.L. Lock, J. Cryst. Mol. Struct., 1 (1971) 161.

262. (a) F.H. Kruse, Acta Crystallogr., 14 (1961) 1035;
(b) J.L. Hoard and J.D. Grenko, Z. Kristallogr. A, 87 (1934) 100.

263. (a) M.A. Porai-Koshits, L.O. Atovmyan and V.G. Andrianov, Zh. Strukt. Khim., 2 (1961) 743;
(b) L.O. Atovmyan, V.G. Andrianov and M.A. Porai-Koshits, Zh. Strukt. Khim., 3 (1962) 685.

264. L.O. Atovmyan and O.A. D'yachenko, Zh. Strukt. Khim., 8 (1967) 169.

265. N. Bartlett and J. Trotter, J. Chem. Soc. A, (1968) 543.

266. E.M. Shustorovich, cited in Yu.A. Buslaev and V.A. Shcherbakov, Zh. Strukt. Khim., 7 (1966) 345.

267. F.A. Cotton and R.M. Wing, Inorg. Chem., 4 (1965) 867.

268. M.A. Porai-Koshits and L.O. Atovmyan, 3-e Vsesoyuznoe Soveshchyanie po primeneniya fizicheskikh metodov k issledovaniyu koordinatsionnykh soedinenii, 1968, Theses of papers, p. 8.

269. L.O. Atovmyan and M.A. Porai-Koshits, Zh. Strukt. Khim., 10 (1969) 853.

270 W.P. Griffith and T.D. Wickins, J. Chem. Soc. A, (1968) 400.
271 S.N. Sathyanarayana and C.C. Patel, Bull. Chem. Soc. Jap., 37 (1964) 1736.
272 H.T. Evans, Jr., Inorg. Chem., 5 (1966) 967.
273 H.T. Evans, Jr., A.G. Swallow and W.H. Barnes, J. Amer. Chem. Soc., 86 (1964) 4204.
274 Yu.A. Buslaev, Yu.V. Kokunov, V.A. Bochkaryova and E.M. Shustorovich, J. Inorg. Nucl. Chem., 34 (1972) 2861.
275 K.A. Lott and M.C.R. Symons, J. Chem. Soc. A, (1963) 973.
276 S.J. Lippard and B.J. Russ, Inorg. Chem., 6 (1967) 1943.
277 B. Jezowska-Trzebiatowska and J. Donawska, Z. Phys. Chem. (Leipzig), 212 (1959) 29.
278 N.P. Johnson, C.J.L. Lock and G. Wilkinson, Chem. Ind. (London), (1963) 333.
279 N.P. Johnson, C.J.L. Lock and G. Wilkinson, J. Chem. Soc., (1964) 1054.
280 J.H. Beard, J. Casey and R.K. Murmann, Inorg. Chem., 4 (1965) 797.
281 K.W. Bagnall, D. Brown and R. Colton, J. Chem. Soc., (1964) 3017.
282 R. Colton and I.B. Tomkins, Aust. J. Chem., 21 (1968) 1981.
283 S. Tanisaki, J. Phys. Soc. Japan, 15 (1960) 566.
284 B.O. Loopstra and P. Boldrini, Acta Crystallogr., 21 (1966) 158.
285 M. Seleborg, Acta Chem. Scand., 20 (1966) 2195.
286 M. Seleborg, Acta Chem. Scand., 21 (1967) 499.
287 S.A. Margarill and R.F. Klevtsova, Kristallografiya, 16 (1971) 742.
288 E.G. Steward and H.P. Rooksby, Acta Crystallogr., 4 (1951) 503.
289 D.E. Cox, G. Shirane and B.C. Fraser, J. Appl. Phys., 38 (1967) 1459.
290 T.M. Polyanskaya, S.V. Borisov and N.V. Belov, Kristallografiya, 15 (1970) 1135.
291 L. Kilberg, Ark. Kemi, 21 (1963) 357.
292 L. Kilborg, Ark. Kemi, 21 (1964) 443.
293 L. Kilborg, Acta Chem. Scand., 17 (1963) 1485.
294 K.A. Wilhelmi, Acta Chem. Scand., 23 (1969) 419.
295 L. Kilborg, Ark. Kemi, 21 (1963) 365.
296 S. Asbrink and L. Kilborg, Acta Chem. Scand., 18 (1964) 1571.
297 (a) A. Magneli, Acta Chem. Scand., 2 (1948) 501;
(b) L. Kilborg, Ark. Kemi, 21 (1964) 461.
298 S.V. Borisov, R.F. Klevtsova and N.V. Belov, Kristallografiya, 13 (1968) 980.
299 (a) N.C. Stephenson and A.D. Wardsley, Acta Crystallogr., 19 (1965) 241;
(b) J. Graham and A.D. Wardsley, Acta Crystallogr., 20 (1966) 93;
(c) T.A. Bitcher, J.L. Gillson and H.S. Young, Inorg. Chem., 5 (1966) 1559.
300 H.E. Evans, J. Amer. Chem. Soc., 90 (1968) 3275.
301 (a) L.O. Atovmyan and O.N. Krasochka, Zh. Strukt. Khim., 13 (1972) 343;
(b) J. Lindqvist, Ark. Kemi, 2 (1950) 349.
302 (a) B.M. Gatehouse and P. Leverett, Chem. Commun., (1969) 1093;
(b) B.M. Gatehouse and P. Leverett, J. Solid State Chem., 1 (1970) 484.
303 G. Henning and A. Hüllen, Z. Kristallogr. Kristallgeometrie Kristallphys. Kristallchem., 130 (1969) 162.
304 (a) G. Weiss, Z. Anorg. Allg. Chem., 368 (1969) 279;
(b) R. Allman, Acta Crystallogr. Sect. B, 27 (1971) 1393.
305 B.M. Gatehouse and P. Leverett, Chem. Commun., (1970) 740.
306 I. Böschen, B. Buss, B. Krebs and O. Glemser, Angew. Chem., 85 (1973) 409.
307 J. Von Sieler, Ph. Thomas, E. Urlemann and E. Höhne, Z. Anorg. Allg. Chem., 380 (1971) 160.
308 L.M. Shkol'nikova, Yu.M. Yutas', E.A. Shugam and A.N. Knyazeva, Zh. Strukt. Khim., 14 (1973) 92.
309 S.J. Lippard and S.M. Morehouse, J. Amer. Chem. Soc., 91 (1969) 2504.
310 E.M. Shustorovich, Khimicheskaya svyaz', Nauka Pub. House, Moscow, 1973, ch. 5.
311 K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G.

Johanson, T. Bergmark, I. Lindgren and B. Lindberg, ESCA, Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy, Almquist and Wiksells, Uppsala, 1967.

312 D.G. Tisley and R.A. Walton, J. Mol. Struct., 17 (1973) 401.

313 D.G. Tisley and R.A. Walton, J. Inorg. Nucl. Chem., 35 (1973) 1905.

314 W.E. Moddeman, J.R. Blackburn, G. Kumar, K.A. Morgan, R.G. Albridge and M.M. Jones, Inorg. Chem., 11 (1972) 1715.

315 J.W. Pierce and M. Vlasse, Acta Crystallogr. Sect. B, 27 (1971) 158.

316 B. Krebs, Chem. Commun., (1970) 50.

317 G. Andersson, Acta Chem. Scand., 18 (1964) 2339.

318 C. Brosset, Naturwissenschaften, 51 (1964) 552.

319 J. Galy and G. Andersson, Acta Crystallogr. Sect. B, 24 (1968) 1027.

320 J.I. Musher, J. Amer. Chem. Soc., 94 (1972) 1370.

321 V. Koutecky and J.I. Musher, Theor. Chim. Acta, 33 (1974) 227.

322 H. Nakatsuji and J.I. Musher, Chem. Phys. Lett., 24 (1974) 77.

323 J.I. Musher, Tetrahedron, 30 (1974) 1747.

324 K.H. Johnson, Adv. Quantum Chem., 7 (1973) 143.

325 K.H. Johnson, Int. J. Quantum Chem., S7 (1973) 347.

326 J.C. Slater, Int. J. Quantum Chem., S7 (1973) 533.

327 W.L. Jolly, Coord. Chem. Rev., 13 (1974) 47.

328 K. Jug, Theor. Chim. Acta, 31 (1973) 63.

329 K.R. Roby, Mol. Phys., 27 (1974) 81.

330 K.R. Roby, Theor. Chim. Acta, 33 (1974) 105.

331 D.R. Armstrong, R. Fortune and P.G. Perkins, Inorg. Chim. Acta, 9 (1974) 9.

332 F. Bottomley, J. Chem. Soc. Dalton Trans., (1974) 1600.

333 J.M. Epstein, A.H. White, S.B. Wild and A.C. Willis, J. Chem. Soc. Dalton Trans., (1974) 436.

334 R. Wiest and R. Weiss, J. Organometal. Chem., 30 (1971) C33.

335 R. Wiest and R. Weiss, Rev. Chim. Miner., 9 (1972) 655.

336 W.R. Scheidt and J.L. Hoard, J. Amer. Chem. Soc., 95 (1973) 8281.

337 W.R. Scheidt and J.L. Hoard, unpublished.

338 T.E. Hopkins, A. Zalkin, D.H. Templeton and M.G. Adamson, Inorg. Chem., 8 (1966) 1431.

339 A. Tullberg and N.-G. Vannerberg, Acta Chem. Scand., 26 (1972) 3382.

340 N.A. Popov, Koord. Khim. (USSR), 1 (1975) 731.

341 E.M. Shustorovich and Yu.A. Buslaev, Koord. Khim. (USSR), 1 (1975) 740, 1820.

342 N. Bartlett, S. Beaton, L.W. Reeves and E.J. Wells, Can. J. Chem., 42 (1964) 2531.

343 R.R. Ryan and D.T. Cromer, Inorg. Chem., 11 (1972) 2322.

344 A.L. Beauchamp, M.J. Bennet and F.A. Cotton, J. Amer. Chem. Soc., 90 (1968) 6675.

345 D.S. Brown, F.W.B. Einstein and D.G. Tuck, Inorg. Chem., 8 (1969) 14.