Translated from *Uspekhi Khimii*, **59** 86–105 (1990) U.D.C. 548.736

Specific features of the chemical structure of the oxo-complexes of d^0 and d^2 metals with monodentate and polydentate ligands

M A Porai-Koshits, V S Sergienko
Kurnakov Institute of General and Inorganic Chemistry, USSR Academy of Sciences, Moscow

ABSTRACT. The structure of the oxo-complexes of transition d^0 and d^2 Group V–VII metals is discussed. Two types of distortion isomerism are considered: the *trans*-influence isomerism (the lengthening of the M=O multiple bond on passing from one isomer to another is accompanied by a shortening of the M–L_{trans} bond) and the multiple bond isomerism (the lengthening of the M=O bond is not accompanied by a shortening of the M–L_{trans} bond). The choice of the *trans*-partner out of the set of competing functional groups for the d^0 metal is determined by the self-consistency principle, while for the d^2 metal the rule becomes more complex and the choice of the *trans*-partner of the oxo-ligand depends on the individual features of the *trans*-ligand (on the combination of its σ- and π-donor properties). It is shown in relation to the d^0-MoO_2 and d^2-ReO complexes with isotypical chelate O, N-donor ligands that the latter are coordinated to the metal in different ways.

The bibliography includes 58 references.

Contents

I. Introduction 52
II. The lability of the length of the M=O multiple bond in complexes of d_1 and d_2 metals 53
III. The choice of the *trans*-partner in complexes of d^0 and d^2 metals 54
IV. The *trans*-influence isomerism in mixed halogeno-phosphine complexes of d^2 metals 56
V. Analysis of the disposition of the chelate organic ligands in oxo-complexes of d^0 and d^2 metals 58

I. Introduction

The stereochemistry of transition metal complexes with ligands linked by multiple bonds and in particular the stereochemistry of d^0 and d^2 metals has now been investigated comprehensively by Soviet and foreign workers. It is distinguished by the following principal features.

1. The mutual disposition of the ligands X linked by multiple bonds in octahedral dioxo-complexes of Group V–VII is determined by the electronic configuration of the metal: *cis*- and *trans*-dispositions occur for the d^0 and d^2 metals respectively.[1–3] This rule has a completely evident model quantum-chemical interpretation. The *cis*-disposition of two or (three) ligands linked by multiple bonds in complexes of d^0 metal ensures the maximum involvement of all three t_{2g} orbitals of the octahedral metal polyhedron (or, in other words, the d_{xy}, x_{xz}, and d_{yz} orbitals) in the π-acceptance of electrons by the multiple bond-linked ligands X. The *trans*-disposition of two multiple bond-linked ligands in complexes of the d^2 metal is determined by the fact that this ensures the minimum electron-electron repulsion between the orbital occupied by the lone electron pair of the metal and the π- and σ-electrons of the bond formed by the ligands X (Fig. 1)†.

2. The *trans*-influence of the X≡M...L multiple bond, manifested by the lengthening (weakening) of the bond with the *trans*-partner, depends on the nature and multiplicity of the bond involving the ligand X, the nature of the *trans*-partner L, and the electronic configuration of the metal M:[4] (a) the *trans*-influence diminishes in the following series of ligands X:

$$M\equiv > N\equiv, =O > RN= > =O > ON\rightleftarrows, OC\rightleftarrows;$$

(b) the bond with a neutral donor ligand L (the *trans*-partner of the multiple bond-linked ligand X) is weakened to a greater extent than the bond with the acido-ligand L^{n-}; (c) depending on the electronic configuration of the metal, the *trans*-influence diminishes in the sequence $d^0 \geqslant d^1 > xd^2$.[5]

3. The choice of the *trans*-partner from the set of competing functional groups is determined by the self-consistency principle.

It has been shown[6] that the *trans*-influence of the multiple bond-linked ligand is transmitted via the σ-mechanism: the π-interaction, leading to the shortening of the X–M distance, increases σ-overlap and hence the σ-exchange integral between X and M, diminishing it in the region of M and L_{trans}. The most "convenient" *trans*-partners are therefore as a rule *N*- and *O*-donors (in particular ammonia and water molecules), the degree of localisation of the lone pairs of which can vary within wide limits in such a way that the equilibrium X–M–L_{trans} configuration is obtained for the given multiple bond-linked ligand X.

Thus the labilising effect exerted by the multiple bond-linked ligand on the bond between the metal and the *trans*-partner makes preferable the participation of the least polarisable σ-donor in this bond. As will be shown below, the application of this rule to d^2 metals is complicated by other factors.

The structural manifestation of the *trans*-influence of the multiple bond—the lengthening of the bond with the *trans*-partner—can be conveniently characterised quantitatively by the parameter Δ, which is defined as the differences between the lengths of the bonds formed by the metal with the *trans*-partner and with the analogous ligand located in the *cis*-position relative to the multiple bond. In the absence of like ligands simultaneously in the *cis*- and

† The complexes of d^1 metals with multiple bond-linked ligands X usually have a dinuclear structure with a *cis*-disposition of the terminal and bridging ligands X, which is also characteristic of d^0 metals.

trans-positions, it is necessary to use the parameter Δ', defined as the difference between the length of the bond with the *trans*-partner and the standard (ST) mean statistical length of the bond with an atom of the same kind in the usual complexes (not containing multiple bond-linked ligands). In order to estimate such standard Mo–O, Mo–N, and Mo–S distances, we employed the structural data presented in a monograph‡.[5] On their basis, one can postulate the following typical ranges of bond lengths: $Mo-O_{trans}$ = 2.11–2.38 Å, $Mo-O_{ST}$ = 1.94–2.08 Å (Δ_{av}' = 0.25 Å), $Mo-N_{trans}$ = 2.26–2.45 Å, $Mo-N_{ST}$ = 2.11–2.26 Å (Δ_{av}' = 0.20 Å); $Mo-S_{trans}$ = 2.63–2.80 Å, $Mo-S_{ST}$ = 2.42–2.51 Å (Δ_{av}' = 0.25 Å).

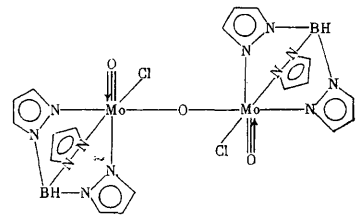
As already mentioned, the *trans*-influence diminishes in the sequence d^0 metals > d^1 metals > d^2 metals. We shall quote two examples. In the series of oxo-halogenometal complexes having the general formula $K_2[M^VOX_5]$, where M = d^0-Nb and X = F,[7] M = d^1-Mo and X = Cl,[8] and M = d^2-Re and X = Cl,[9] the quantity Δ diminishes correspondingly from 0.23 to 0.21 and 0.08 Å on passing from d^0 to d^1 and d^2 metals. Admittedly in the given instance, not only the electronic configuration but also the nature of the metal varies, so that this example is not entirely convincing. The comparison of compounds of heptavalent and pentavalent rhenium, namely $Re^{VII}O_3(ReO_4)(H_2O)_2$ [10] and $Re^VOI_2(ReO_4)(PPh_3)_2$, is much clearer.[11] At first sight, the difference between the lengths of the bonds with the *trans*-partner of the oxo-ligand—the oxygen atom of the perrhenate anion—is not very great: the decrease in the $Re-O_{trans}$ distance on passing from d^0-Re(VII) to d^2-Re(V) is only 0.07 Å (2.10 and 2.03 Å respectively). However, one should bear in mind that in the case of Re(VII) we are dealing with the trioxo-complex ReO_3^+, where the Re=O bonds are purely double bonds, while in the case of Re(V) we are dealing with a monoxo-complex ReO^{3+} formally containing a triple bond (Re≡O), which affects the Re–O (oxo) bond length (1.76 and 1.67 respectively). The increase in the multiplicity of the bond in the second compound enhances the *trans*-influence; therefore in the case of a pure Re=O double bond in the Re(V) complex, the $Re=O_{trans}$ distance should be significantly smaller than 2.03 Å.

II. The lability of the length of the M=O multiple bond in complexes of d^1 and d^2 metals

The vast majority of data concerning the structures of octahedral complexes with multiple bond-linked ligands refers to oxo-compounds. The the complexes of d^0 metals, the length of the metal–oxygen multiple bond is fairly stable and depends on the number of oxo-oxygen atoms in the complex (on the multiplicity of the bond). Thus, in the most numerous Mo(VI) compounds, the length of the formally triple Mo≡O bond (monoxo-complexes) is 1.61–1.68 Å, while the length of the bond having formally a multiplicity of 2.5 (dioxo-complexes) is 1.67–1.72 Å. In some of the trioxo-complexes investigated, the MoO=O double bonds have a length of approximately 1.74 Å.

‡Strictly speaking, in an estimate of this kind one should take into account in addition data obtained in recent years and a definite classification of O-, N-, and S-containing ligands (neutral-donor and acido-ligands, monodentate and polydentate ligands, ligands without multiple bonds in metallocycles and with multiple bonds, etc.) should be made.

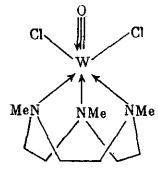
In the complexes of d^1 and especially d^2 metals, the length of the multiple bond is less constant regardless of the number of oxo-oxygen atoms. This is clearly seen from the data presented in Table 1. Depending on the nature of the outer-sphere cation and the number of molecules of water of crystallisation, the Mo–O distance in the three $[Mo^{IV}O(CN)_4(H_2O)]^{2-}$ complexes varies within the limits of 0.12 Å.[12,13] The Mo=O distances differ even more in two conformational isomers of the dinuclear complex $[Mo^VOCl\{HB(Pz)_3\}]_2(\mu\text{-}O)$ with a bridging oxygen atom.[14] The isomers differ in the local symmetry of the complexes: in the C_i isomer (I)



(I): isomer C_i

the bridging oxygen atom is located at the centre of inversion, while in the other isomer (C_2) it is located on the two-fold symmetry axis passing at right angles to the N–Mo–O–Mo–N axial coordinate. In the C_i isomer, the $Mo=O_{end}$ bond is longer by 0.109 Å than in the C_2 isomer.

The two crystalline modifications of the paramagnetic complex $[WOCl_2L](PF_6)$ (II), presented in Table 1, have different colours and are not geometrical isomers, but are almost identical as regards the conformation of the tridentate ligand L.[15]



(II)

These two forms differ mainly only by the length of the bond between the tungsten and oxygen atoms and the bond between the tungsten atom and the nitrogen atom (of the ligand L) in the *trans*-position. In the blue form, the first distance is smaller by 0.17 Å and the second distance is greater by 0.05 Å than in the green form (Δ = 0.13 and 0.17 Å respectively).

It is remarkable that these two forms persist also in solution: in anhydrous acetone they do not undergo a change in the colour characteristic of their solid state. One is therefore dealing not with crystalline modifications but with a special type of isomerism.

Table 1 shows that the range of variation of the M≡O bond lengths in the Mo complexes examined reaches 0.18 Å and, when account is taken of the compound of tungsten whose atomic radius differs little from that of molybdenum, the range increases to 0.29 Å. In all the compounds compared, a decrease in the stretching vibration frequency ν(M=O), accompanied by a change in the colour of the crystals from blue to green, corresponds to the increase in the length of the M=O bond.

Table 1. Geometrical parameters and vibration frequencies $\nu(M=O)$ of the complexes of d^2 and d^1 metals with a labile M=O double bond.

Formula	Colour of complex	Electronic configuration	Bond lengths, Å			Δ(Δ′)	$\Delta_{M=O}$*, Å	$\nu_{M=O}$, cm^{-1}	Refs.
			M=O	M−L_{trans}	M−L_{cis}				
$Kat_2[MoO(CN)_4(H_2O)]\cdot nH_2O$									
Kat=$AsPh_4$, n=4	Blue	d^2	1.60	2.48 (H_2O)	2.19 (CN)	(+0.39)	0.12	980	[12]
Kat_2=Pt(En)$_2$, n=2	Blue		1.668	2.271 (H_2O)	2.16 (CN)	(+0.18)	0.052	970	[13]
Kat=PPh_4, n=4	Green		1.72	2.96 (H_2O)	2.13 (CN)	(+0.87)	—	920	[12]
$(PPh_4)_3[MoO(CN)_5]\cdot 7H_2O$	Green	d^2	1.705	2.373 (CN)	2.168 (CN)	+0.205	—	920	[12]
$[WOCl_2L](PF_6)$ **	Blue	d^1	1.72	2.37 (NR_3)	2.24 (NR_3)	+0.13	0.17	980	[15]
	Green		1.89	2.32 (NR_3)	2.25 (NR_3)	+0.07	—	960	[15]
$[MoOCl\{HB(Pz)_3\}]_2(\mu\text{-}O)$	Brown (C_2)	d^1	1.670	2.313 (NR_2)	2.169 (NR_2)	+0.144	0.109	966	[14]
	Brown (C_i)		1.779	2.277 (NR_2)	2.179 (NR_2)	+0.098	—	960	[14]

*$\Delta_{M=O}$ is the difference between the M=O bond lengths in two isomers (green−blue or C_2-C_i).
**L = *N*, *N*′, *N*″-trimethyl-1,4,7-triazacyclononane.

The correlation between the M=O and M−L_{trans} bond length is also evident: the longer (weaker) the M=O bond, the weaker the *trans*-influence (the parameter Δ diminishes). Comparatively small variations in the lengths of the bonds between the metal and the *cis*-ligands are not regular in character.§

In the examples examined, the *trans*-ligand plays a relatively passive role: its bond with the metal is weakened to a greater or lesser extent in accordance with the requirements of the O−M multiple bond. The isomeric forms arising under these conditions can be naturally referred to as isomers of the metal−ligand multiple bond. Another very similar type of isomerism, in which the *trans*-ligand plays a more active role, is considered below in Section IV.

III. The choice of the *trans*-partner in complexes of d^0 and d^2 metals

The available structural data make it possible to establish series based on the preferential location in the *trans*-position relative to the oxo-ligand of ligands such as terminal halogen atoms, anionic *O*-organo-groups, water molecules, molecular *O*- and *N*-organo-donors, bridging halogen atoms, and asymmetric bridging oxygen atoms. For d^0 metals, the series assumes the following form:

$$Cl-,\ Br-,\ I-,\ RO-,\ R_2N-<H_2O\rightarrow,\ O_L\rightarrow,\ N_L\rightarrow,$$
$$-Cl_M\rightarrow,\ -R_2N\rightarrow<\rightleftarrows O_M\rightarrow,\ F-<-F_M\rightarrow,\ \rightleftarrows F_M\rightarrow.$$

The halogen atoms (Cl, Br, I), occupying the *trans*-position relative to the oxo-ligand, give way to water molecules and any neutral donor *O* and *N*-ligands; bridging donor oxygen atoms, forming a multiple bond with another metal atom, are even more preferable.

The exact position of the weakly polarisable F^- anion is not evident, since, so far as we are aware, the available structural data are restricted to only one example—the compound $(NH_4)[VO(O_2)\cdot F_2(bipy)]\cdot 2H_2O$.[16] In this complex, obtained by the reaction of $(NH_4)[VO(O_2)_2(bipy)]\cdot 4H_2O$ with HF, an inner-sphere rearrangement takes place in addition to the replacement of one peroxo-group in the initial compound by two fluorine atoms. The rearrangement consists in the migration of the axial N atom of the bidentate bipyridyl (bipy) ligand, in the *trans*-position to the oxo-ligand, to the equatorial position and the substitution of this position by one of the fluorine atoms. Thus in the given instance the fluoro-ligand in the *trans*-position to the oxo-ligand is preferable to the neutral donor nitrogen atom of bipy.

In addition, attention may be drawn to the fact that in the numerous hydrates of molybdenum oxide fluorides [not only Mo(VI) but also Mo(V) and Mo(IV)], the water molecules are not as a rule incorporated in the inner sphere of the complex and the inner sphere of a purely fluoride type. When the number of terminal fluorine atoms is insufficient, oligomerisation or polymerisation takes place more readily than the incorporation of a solvent molecule in the inner sphere. Of the two types of fluoride anions, the bridging

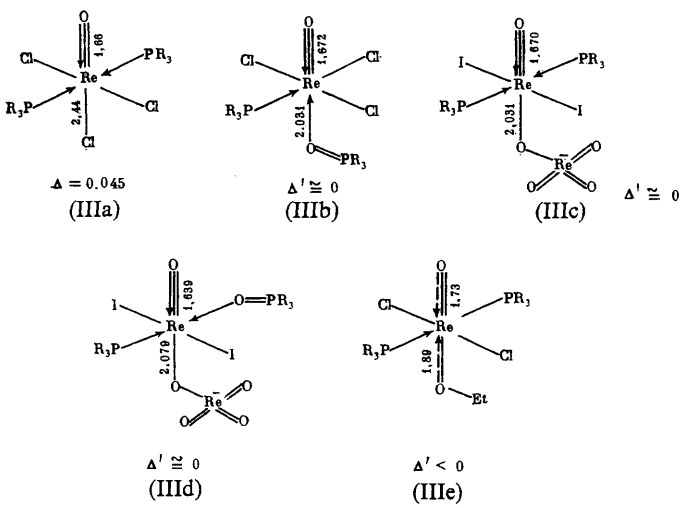
§The authors of a structural study of the green form of $(PPh_4)_2\cdot[MoO(CN)_4(H_2O)]\cdot 4H_2O$ [12] found that the Mo−$(H_2O)_{trans}$ bond length is 2.96 Å (this actually means that the coordination number of the metal is five). This result is very doubtful bearing in mind that the given compound is isotypical (pseudo-isostructural) with the compound $(AsPh_4)_2[MoO(CN)_4(H_2O)]\cdot 4H_2O$.[12] It is difficult to suppose that the difference between the Mo−H_2O distances, amounting to 0.5 Å, is caused by the different degrees of involvement of the water molecule in the hydrogen bonds or by the replacement of the cation PPh_4^+ by $AsPH_4^+$. It is apparently a result of the poor quality of the crystals employed and the low accuracy of the investigation, which was noted by the authors themselves.[12]

$-F_b\rightarrow$ or $\overleftarrow{=}F_b\rightarrow$ anion is preferable to the terminal F^- anion as the *trans*-partner of the multiple bond-linked ligand ($O\overleftarrow{=}$ or $-O\overrightarrow{=}$).

Overall, in the series presented above the trans-length parameter $\Delta(\Delta')$ increases from left to right and the self-consistency principle is satisfied:[17] the ligand whose σ-bond with a d^0 metal can be most readily weakened, i.e. the least polarisable [least "hard" according to Pearson[18]] donor among all the ligands present in the complex, enters most readily the *trans*-position relative to the multiple bond.

Initially it seemed that this principle is general and applies to not only d^0 metals but also to d^2 metals. Mixed halogeno-phosphine oxo-complexes are well known for Re(V) and Mo(IV). Structural studies have shown that phosphine, a powerful σ-donor, never occupies the *trans*-position relative to the multiple bond involving oxygen (the π-acceptor properties of PR_3 play no role) and gives way to a halogen (Cl, Br, I), for example, in the structure of *trans*-[$ReOCl(PEt_2Ph)_2$] (IIIa).[19]

It is just as natural that the halogen (Cl, Br) gives way to L_{trans}, which is a neutral oxygen-containing ligand—phosphine oxide in the complex [$ReOCl_3(OPPhEt_2)(PPhEt_2)$] (IIIb)[20]—and passes to the *trans*-position relative to PR_3. In the complex [$ReO(ReO_4).I_2(PPh_3)_2$] [11] containing two acido-ligands (iodine and perrhenate), ReO_4^- occupies the *trans*-position relative to the oxo-ligand [compound (IIIc)]. This can be regarded as evidence that the less-electron-donating ReO_4^- is preferred to the readily polarisable I^-, i.e. can be treated as a revision of the left-hand part of the series presented above. However, the perrhenate ligand occupies the same *trans*-position also in the complex [$ReO(ReO_4)I_2(OPPh_3)(PPh_3)$] (IIId),[11] containing also the neutral phosphine oxide ligand. Thus, in the case of Re(V) the singly-charged acido-ligand ReO_4 is preferable to the neutral phosphine oxide in the *trans*-position relative to O(oxo).



Furthermore, the *trans*-weakening Δ′ in the *trans*-preference series for d^2 metals does not increase from left to right, as for d^0 metals, but diminishes (regardless of the Re≅O multiple bond length). The *trans*-position relative to the oxo-ligand in the structure [ReO(OEt).$(PPh_3)_2Cl_2$] (IIIe)[20,21] is also occupied by an acido-ligand (the ethoxy-group) having one unpaired electron. Here Δ′ is altogether negative (it is smaller by 0.15 Å than the sum of Pauling's covalent radii of Re and O), i.e. the $M-L_{trans}$ bond is shortened (strengthened) and not lengthened (the Mo=O bond with the terminal oxo-ligand is simultaneously lengthened).

The reason for such "anomalous" choice of the *trans*-partner in the d^2 complexes becomes understood if one recalls that, in contrast to the complexes of d^0 metals, the multiple bond-linked ligands in these compounds always occupy opposite and not neighbouring vertices of the octahedron (see Fig. 1). Hence follows the conclusion that the ethoxy-group can also be regarded as a multiple bond-linked ligand¶.

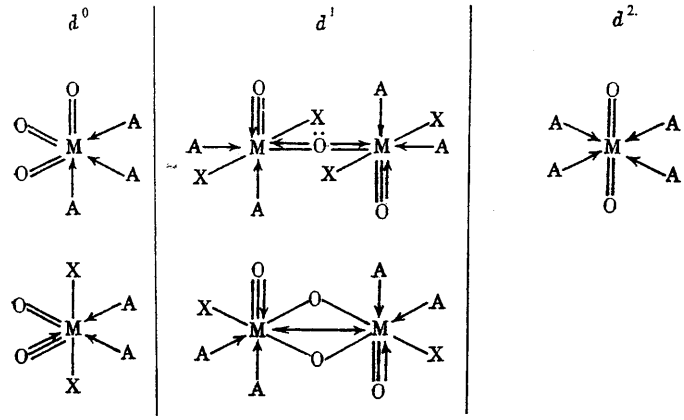
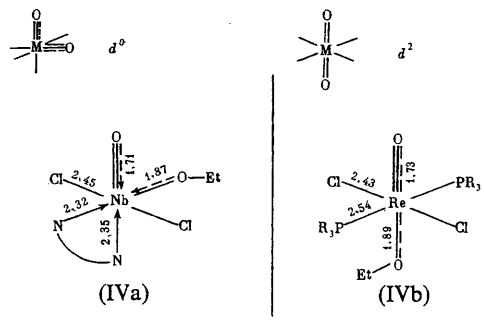


Figure 1. The disposition of multiple bond-linked ligands in the oxo-complexes of d^0 and d^2 Group V–VII transition metals.

This conclusion is well illustrated by the comparison of complexes of the d^0 metal Nb(V) and the d^2 metal Re(V): [NbO(OEt).(bipy)Cl_2] (IVa)[23] and [$ReO(OEt)(PPh_3)_2Cl_2$] (IVb).[20,21]



In complex (IVa), the ethoxy-group is in the *cis*-position relative to the O(oxo) atom and the Nb–O (OEt) distance (1.87 Å) is significantly smaller than the usual value, while in complex (IVb) the group is located in the *trans*-position relative to the O(oxo) atom at approximately the same distance from the metal. The Nb–O (OEt) and Re–O (OEt) distances are shorter by 0.20 and 0.13 Å

¶ The conclusion that the M–OEt bond is multiple was first reached from NMR data.[22]

respectively than the standard ("expected") M–OR bond lengths (2.07 and 2.02 Å respectively[4]). The increased multiplicity of the Nb–O (OEt) bond is also indicated by the Nb–N distances to the nitrogen atoms of bipyridyl: they are greatly lengthened (to approximately the same extent) in the *trans*-positions relative to both the multiple bond-linked oxygen and to the ethoxy-group (to 2.35 and 2.32 Å respectively).

The location of the ethoxy-group in the *trans*-position relative to the M=O bond and the shortening of the M–O(OEt) bond in the Re(V) complexes is not fortuitous, which is indicated by the geometrical parameters of the O≒Re⇄OEt fragment in all four structures investigated having the general formula $[ReO(OR)]X_2L_2$ (X = halogen)[20,21,24,25] (Table 2). In all these compounds, the OR^- (R = Et, Me) group is in the *trans*-position relative to the oxygen atom and in all cases the length of the bond between the Re atom and the methoxy- and ethoxy-groups is shortened (to 1.859 to 1.896 Å)‡. For comparison Table 2 presents the geometrical parameters of the O≒Re–$OReO_3$ linkage in two complexes with the perrhenate group in the *trans*-position relative to oxygen.[11] The Re–O (ReO_4) *trans*-bond in $[ReO(ReO_4)I_2(PPh_3)_2]$ and $[ReO(ReO_4)\cdot(OPPh_3)(PPh_3)I_2]$ is lengthened to 2.031 and 2.079 Å respectively. The difference between the Re–O (OEt) and Re–O (ReO_4) bond lengths is quite natural (Fig. 2). While the π-electrons of the oxygen of the OR^- group can participate in the formation of a bond with the central rhenium atom, the similar electrons of the oxygen in the perrhenate anion are involved to a considerable extent in the molecular orbitals of the ReO_4^- anion itself and participate to only a slight extent in the formation of a bond with the central atom.

If the *trans*-ligand is a pure σ-donor, then the self-consistency principle operates: the *trans*-position relative to the oxo-oxygen atom is occupied preferentially by the hardest donor with a simultaneous increase in the length of the *trans*-bond. However, if the complex contains a ligand capable of π-donation to the metal, then in the case of a d^2 metal precisely this ligand occupies preferentially the *trans*-position relative to the oxygen-ligand and the *trans*-shortening via the π-mechanism is then superimposed on the *trans*-lengthening via the σ-mechanism, and the former may predominate.

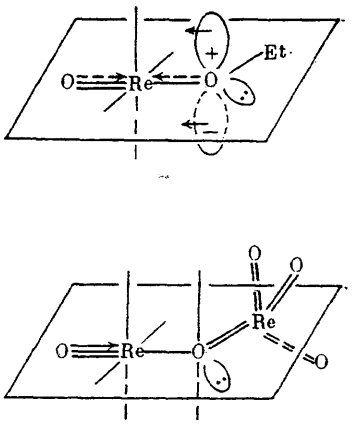


Figure 2. The structure of the ORe(OEt) and ORe(ReO_4) fragments in the mixed halogeno-phosphine monoxo-complexes of d^2-Re(V).

Table 2. Geometrical parameters of the MO(OR) (R = Me, Et, ReO_3) fragment in the Re(V) and Tc(V) d^2-complexes.

Compound	Bond lengths, Å		Refs
	O≒M	M⇄OR_{trans}	
$ReO(OEt)Cl_2(PPh_3)_2$	1.73	1.89	[16, 17]
$ReO(OEt)I_2(PPh_3)_2$	1.715	1.880	[20]
$ReO(OMe)I_2(PPh_3)_2$	1.698	1.859	[20]
$ReO(OEt)Cl_2(Py)_2$	1.684	1.896	[21]
$TcO(OEt)Br_2(NPy)_2$	1.684	1.855	[22]
$ReO(OReO_3)I_2(PPh_3)_2$	1.670	2.031	[11]
$ReO(OReO_3)(OPPh_3)I_2(PPh_3)$	1.639	2.079	[11]

The following hypothesis may be put forward on the basis of the characteristic features of the stereochemistry of the complexes of d^0 and d^2 metals examined. Two opposite tendencies may be superimposed in the selection of the *trans*-partner and in the structural manifestation of the *trans*-influence in the case of oxo-complexes of a d^2 metal.

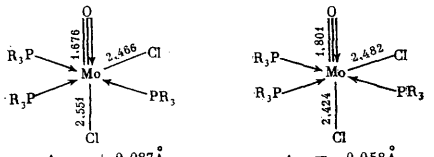
† The pentavalent technetium complex d^2-$[TcO(OEt)Br_2\cdot(NPy)_2]$ complex has a similar structure:[26] the Tc–O (OEt) bond in the *trans*-position relative to the Tc=O bond is shortened to 1.855 Å (the Tc=O bond length is 1.684 Å).

IV. The *trans*-influence isomerism in mixed halogeno-phosphine complexes of d^2 metals

In 1970, Butcher and Chatt[27] synthesised a series of diamagnetic mixed complexes of tetravalent molybdenum having the composition $MoOX_2(PR_3)_3$, where X is a halogen or a pseudo-halogen and PR_3 is a tertiary phosphine ligand. Depending on the individual characteristics of the ligand X and the nature of the substituents R, the two series of compounds obtained differed in colour. The series A complexes with X = NCO or NCS and PR_3 = $PPhMe_2$ or $PPhEt_2$ were blue, while the series B complexes with X = Cl, Br, or I and PR_3 = $PMePh_2$ or $PEtPh_2$ were green. As a rule, the stretching vibration frequency ν(Mo=O) in the series A complexes was higher by 5–10 cm^{-1} than in the series B complexes. Other characteristics, especially the ^1H NMR spectra[28] and the ^{95}Mo NMR spectra[29] of compounds of both series, were virtually indistinguishable. However, it was shown subsequently[30,31] that both the colour and the ν(Mo=O) frequency are not decisive parameters for the assignment of the compound to a particular series.

In two cases, for X = Cl and PR_3 = $PPhMe_2$ and for X = Cl and PR_3 = PMe_3, two isomers were obtained in each instance.[27] The isomers of the first of these compounds, $MoOCl_2(PPhMe_2)_3$, differed both in colour and in the μ(Mo=O) frequency [ν(MO=O) = 954 cm^{-1} for the blue isomer and 943 cm^{-1} for the green isomer]. The unstable green isomer was irreversibly converted into the stable blue isomer on heating in organic solvents. The authors[27] assumed that the different colours are due to the geometrical isomerism of the complexes: it was postulated that the *trans*-position relative to the oxo-oxygen atom is occupied by X in the series A complexes and by

PR_3 in the series B complexes. However, X-ray diffraction studies on the blue isomer of $MoOCl_2(PPhMe_2)_3$ (Va) [32] and on the unstable green isomer of $MoOCl_2(PPhEt_2)_3$ (Vb) [33,34] showed that they both have the *cis*-meridional geometry as regards to the disposition of the C atoms (one of the Cl atoms is in the *trans*-position relative to the oxo-oxygen atom).



(Va) (Vb)

However, the principal difference between the isomers consists in the unequal lengths of the bonds along the $O=Mo-Cl_{trans}$ coordinate: the multiple bond in the blue complex ($PR_3 = PPhMe_2$) is shorter than in the green complex ($PR_3 = PPhEt_2$) by 0.125 Å and instead of the *trans*-lengthening of the $Mo-Cl_{trans}$ bond in the blue complex, the bond undergoes *trans*-shortening in the green complex ($\Delta = +0.087$ and -0.058 Å respectively). The crystal structure of the green isomer $MoOCl_2(PPhMe_2)_3$ has been recently determined (at −160 °C [35]). As in the green $MoOCl_2(PPhEt_2)_3$, the Mo−O bond in this compound is greatly lengthened and its length is 1.80(2) Å. Other geometrical parameters of the complex are not quoted; only structural disorder, reducing the accuracy of the study, is noted.

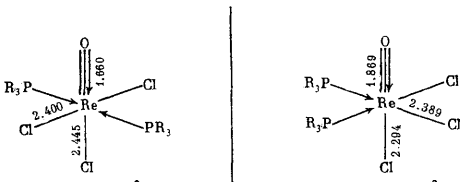
Thus, in compounds of this class the isomerism of the multiple metal−ligand bond is manifested in the sharpest and most clear-cut form: a shortening and not a lengthening of the *trans*-bond corresponds to the second isomer. It is quite evident that the bond with the *trans*-partner also plays an active role in the given instance in the formation of the second isomer. The negative parameter Δ ("*trans*-fixation") can be most naturally accounted for by the replacement of the pure $M-L_{trans}$ σ-bond by a multiple bond with a significant contribution by the π-donor component $M \rightleftarrows L_{trans}$, which is consistent with the tendency of the complexes of d^2 metals towards a *trans*-disposition of their multiple bond-linked ligands. This variety of the multiple bond isomerism can therefore be conveniently designated as the isomerism of the mutual influence of the ligands or the isomerism of axial π-bonding.

Some workers refer to differences of this kind between the structures of the complexes as "distortion isomerism". This name appears inappropriate: it is too indefinite and can include effects of a completely different nature [for example, the distortion of the Cu(II) octahedra induced by the Jahn−Teller effect or the distortion of the octahedra of the d^{10} metals Ag(I), Hg(II), Ga(III), and Sn(IV) caused by the hypervalence of the equatorial bonds].

Henceforth we shall refer to complexes with a short $Mo \equiv O$ bond and a greatly weakened $Mo-L_{trans}$ bond as A-isomers and to complexes with a longer Mo=O bond and a shortened $Mo=L_{trans}$ bond as B-isomers.

The crystal structures of a further two compounds of the class considered were determined in 1987: $MoO(NCO)_2(PPhEt_2)_3$ and $MoOCl_2(PMePh_2)_3$.[30] Although the former has a blue colour and the latter is green, it was found that both are A-isomers: their Mo=O distances are virtually the same (1.684 and 1.667 Å respectively), while the opposite $Mo-L_{trans}$ bonds are as usual lengthened as a consequence of the *trans*-influence ($\Delta_{av} = +0.085$ and $+0.043$ Å respectively).

We observed the *trans*-influence isomerism also in compounds of another d^3 metal, namely rhenium(V).[19,31] A structural study of two $ReOCl_3(PPhEt_2)_2$ isomers, having different colours, showed that they differ not only in the Re=O and $Re-Cl_{trans}$ bond lengths but also in the relative disposition of the Cl and PR_3 ligands in the equatorial plane. The green form (VIa)[19] is a meridional (with respect to Cl atoms) *trans*-isomer and at the same time a mutual *trans*-influence A-isomer, while the blue form (VIb)[31] is a facial (with respect to Cl atoms) *cis*-isomer and at the same time a mutual *trans*-influence B-isomer.



(VIa) (VIb)

The short Re=O bond is lengthened by 0.209 Å on passing from the first isomer to the second, while the $Re-Cl_{trans}$ bond is shortened by 0.151 Å ($\Delta = +0.045$ and -0.095 Å respectively). The equatorial $Re-Cl_{cis}$ bonds have similar lengths in both isomers (their average values are 2.400 and 2.389 Å).

A stronger $Re-Cl_{trans}$ bond in the blue isomer compared with the green isomer is consistent with their different behaviour in solution.[36] Refluxing of the green *trans*-$[ReOCl_3(PPhEt_2)_2]$ isomer in alcohol leads to the ready substitution of the chloride ion in the *trans*-position relative to the oxo-ligand and to the formation of the violet complex *trans*-$[ReO(OR)Cl_2(PPhEt_2)_2]$. On the other hand, refluxing of the blue *cis*-$[ReOCl_3(PPhEt_2)_2]$ in methanol even for several days does not lead to methanolysis—the strong $Re-Cl_{trans}$ bond is not ruptured and the chloride ion occupying the *trans*-position relative to the oxo-oxygen atom is not substituted by the OMe^- group. However, on heating to 160 °C in the crystalline state, the blue complex is irreversibly converted into the green complex (the *cis* → *trans* and B → A isomerisations take place simultaneously).

The authors[30] believe that the colour of the compounds of the class considered is determined by the basicity of the ligands X and PR_3: the blue complexes contain more basic ligands X and PR_3 ($X = NCS^-, NCO^-$, $PR_3 = PMe_3, PPhMe_2, PPhEt_2$), while the green complexes contain the less basic ligands ($X = Cl, Br, I$; $PR_3 = PMePh_2, PEtPh_2$). A combination of ligands of different basicity gives rise to the possibility of the coexistence of the blue and green isomers. This applies, in particular, to the combination X = Cl and $PR_3 = PPhMe_2$ or PMe_3.

The M−L bond lengths, the *trans*-influence parameters Δ, the differences between the M=O bond lengths in the two isomers $\Delta_{M=O}$, and the stretching vibration frequencies ν(M=O) for certain halogeno-phosphine complexes are listed in Table 3. It follows from these data that a complete correlation is not observed between the colour, the frequencies ν(M=O), and the parameter Δ. The colour and the frequencies ν(M−O) can be regarded as correlated for only two forms of the same compound: the higher and lower frequencies correspond respectively to the blue and green forms (the first two pairs in Table 3). On the other hand, if the complexes are different, then the absolute values of ν(M=O) even for compounds with similar compositions are not correlated with colour. In

Table 3. Geometrical parameters and vibration frequencies ν(M=O) of the *trans*-influence isomers of mixed halogeno-phosphine complexes of d^2 metals.

Compound	Isomer	Colour	Bond lengths, Å			Δ, Å	$\Delta_{M=O}$*, Å	$\nu_{M=O}$, cm^{-1}	Refs.
			M=O	$M-L_{trans}$	$M-L_{cis}$				
trans-$[ReOCl_3(PPhEt_2)_2]$ *cis*-$[ReOCl_3(PPhEt_2)_2]$	A B	Green Blue	1.660 1.869	2.445 (Cl) 2.294 (Cl)	2.400 (Cl) 2.389 (Cl)	+0.045 −0.095	0.209	975 986	[18, 19, 37] [31, 37]
cis-$MoOCl_2(PPhMe_2)_3$	A B	Blue Green	1.676 1.80	2.551 (Cl) — (Cl)	2.464 (Cl) — (Cl)	+0.087 —	0.124	954 943	[27, 32] [27, 35]
cis-$MoOCl_2(PPhEt_2)_3$	B	Green	1.801	2.424 (Cl)	2.482 (Cl)	−0.058	—	940	[27, 34]
cis-$MoOCl_2(PMePh_2)_3$	A	Green	1.667	2.509 (Cl)	2.466 (Cl)	+0.043	—	945	[27, 30]
cis-$MoO(NCO)_2(PPhEt_2)_3$	A	Blue	1.684	2.180 (NCO)	2.095 (NCO)	+0,085	—	940	[27, 30]

* $\Delta_{M=O}$ is the difference between the M=O bond lengths in the two isomers ["blue"−"green" for Re(V) and "green"−"blue" for Mo(IV)].

particular, ν(Mo=O) for the blue complex *cis*-$[MoO(NCO)_2.(PPhEt_2)_3]$ is located in the region characteristic of the green isomers of the mixed halogeno-phosphine complexes of molybdenum (IV).

The correlation between the colour and sign of Δ is still weaker. Not only the blue forms *cis*-$[MoOCl_2(PPhMe_2)_3]$ and *cis*-$[MoO(NCO)_2(PPhEt_2)_3]$ but also the green forms *cis*-$[MoOCl_2.(PPhMe_2)_3]$ and *trans*-$[ReOCl_3(PPhEt_2)_2]$ belong to type A (positive Δ), while type B (negative Δ) includes not only the green forms *cis*-$[MoOCl_2(PPhEt_2)_3]$ and *cis*-$(MoOCl_2(PPhMe_2)_3]$ but also the blue form *cis*-$[ReOCl_3(PPhEt_2)_2]$. In essence, the blue and green forms of the Re(V) complexes considered [and the ν(Re−O) frequency characteristics] change places: the green form with the lower ν(Re=O) frequency corresponds to the A-isomer and the blue form corresponds to the B-isomer.

The absence of a complete correlation between the length of the M=O double bond and its stretching vibration frequency, mentioned above, is somewhat unexpected. It shows that the ν(Mo=O) frequency is not characteristic: it clearly depends on fine nuances of the composition of the compound as a whole.

Furthermore, the type of the *trans*-influence isomer is determined not by the basicity of the entire set of ligands but by the basicity and capacity for π-donor interaction with the metal of the L_{trans} ligand: its relatively low donor capacity is due to the stability of the A-isomer and its tendency towards π-donation promotes the transition to the B-form. Chlorine satisfies both these requirements. Depending on the conditions, it can either virtually not participate or can significantly participate in π-donation to the metal.

Summarising the foregoing, we may note two factors. Firstly, the *trans*-influence isomerism is determined by the distribution of the σ- and π-interactions along the $O=M-L_{trans}$ coordinate. Within the framework of the limiting canonical forms, the A-isomer can be written as $O\overline{=}M-L_{trans}$, while the B-isomer can be formulated as $O=M\overline{=}L_{trans}$. In essence, the O−M bonds in the compounds $[MoOCl_2(PPhEt_2)_3]$ (Vb) and *cis* $[ReOCl_3(PPhEt_2)_2]$ (VIb) should be regarded as double bonds and not as triple bonds, while the $M-Cl_{trans}$ bonds should be regarded as double bonds and not as single bonds, i.e. the axial π-bonding isomerism obtains.

The above examples show that the chlorine atom can function also as the usual σ-acido-ligand and under certain conditions as a multiple bond-linked ligand (with a significant involvement in π-donation).

Secondly, the preferential formation of a particular *trans*-influence isomer (and the corresponding redistribution of electron density along the axial coordinate) depend under certain conditions not only on nuances in composition but also on the characteristic features of the disposition of the remaining ligands (Re complexes).

One cannot rule out the possibility that the transition from one isomer to another in the acido-phosphine anionic or cationic complexes, for example, $[Mo^{IV}OCl_3(PR_3)_2]^-$ or $[Re^{V}OCl_2(PR_3)_3]^+$, can be determined also by the nature of the outer-sphere ion or even by the presence or absence of the molecules of water of solvation, as in the case of the anionic Mo(IV) complexes $Kat_2[MoO(CN)_4.(H_2O)].nH_2O$ examined above.

V. Analysis of the disposition of the chelate organic ligands in oxo-complexes of d^0 and d^2 metals

We shall consider yet another important aspect of the choice of the *trans*-partner of the oxo-ligand in the complexes of d^0 and d^2 metals. This concerns the disposition in the oxo-complexes of anionic chelate ligands having acido- (X^-) and neutral-donor (A) coordinatively active atoms.

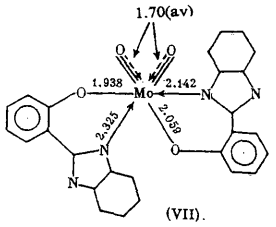
For d^0 metals, this problem has been solved unambiguously, fully in conformity with the principle of self-consistency. The *trans*-position relative to the multiple bond always contains the neutral-donor "end" of the chelate ligand A, whose lone electron pair "adjusts" readily to the requirements of the *trans*-active multiple bond-linked ligand. The structures of the molybdenum(VI) dioxo-complexes with hydroxamic acid anions containing different solvating molecules, i.e. $MoO_2L_2.A$, may serve as examples. Here HL = PhCoNHOH and A = MeCOEt,[38] $^2/_3$EtCOOH,[39] and Bu^nOH[40] or HL = HOC_6H_4CONH and A = $2H_2O$.[41] Their *trans*-positions relative to the oxo-ligands are occupied by the donor atoms of the

Table 4. Geometrical parameters of the d^2-M(V) (M = Re, Tc) monoxo-complexes with bidentate (O, N) and tridentate (O, N, O) organic ligands.

Compound*	Bond lengths, Å			Δ, Å	Refs.
	M=O	$M-O_{trans}$	$M-N(O)_{cis}$		
ReOCl (Me-Sal)$_2$	1.680	1.976	1.995 (O), 2.111(N)$_{av}$	−0.019	[45]
trans-[ReOCl$_2$(PPh$_3$)(Me-Sal)]	1.701	1.949	2.125 (N)	—	[47]
cis-[ReOCl$_2$(PPh$_3$)(Me-Sal)]	1.660	1.955	2.150 (N)	—	[47]
trans-[ReOBr$_2$(PPh$_3$)(Ph-Sal)] (tricl.)	1.680	1.972	2.141 (N)	—	[48]
trans-[ReOBr$_2$(PPh$_3$)(Ph-Sal)] (monocl.)	1.683	1.937	2.173 (N)	—	[49]
[ReOCl$_2$(PPh$_3$)]$_2$ (μ-Salen)·CHCl$_2$	1.680	1.925	2.150 (N)	—	[50]
TcOCl (Ph-Sal)$_2$	1.67	1.94	1.99 (O), 2.155(N)$_{av}$	−0.05	[46]
ReOCl$_2$(PPh$_3$){PhC (O)NNCMe$_2$}	1.685	2.013	2.130 (N)	—	[53]
TcOCl (ONC$_9$H$_5$Me)$_2$	1.649	1.994	1.947 (O), 2.197(N)$_{av}$	+0.047	[54]
TcO (ONC$_9$H$_6$) (O$_2$NC$_{13}$H$_{19}$)	1.659	2.014	2.007(O)$_{av}$, 2.130(N)$_{av}$	+0.007	[55]

Notation: Sal = salicylideneaminate; Salen = ethylenebis- (salicylideneaminate).

ligand O(C), while the *cis*-positions are occupied by the acido-atoms O(N). In all these and other oxo-complexes of d^0 metals‡ the *trans*-lengthening is as a rule 0.15−0.30 Å. We are aware of only one example of the infringement of this general rule governing the orientation of the acido-donor chelate ligand in d^0 metal complexes. In the structure of [Mo^{VI}O$_2$L$_2^{(2)}$].2EtOH (VII),[44] where $L^{(2)}$ = 2-*o*-hydroxyphenylbenzimidazole, the two chelate *O, N*-ligands $L^{(2)}$ are coordinated to the metal in different ways.

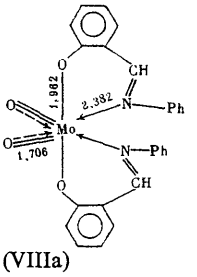


Δ_O = + 0.121Å
Δ_N = + 0.183Å

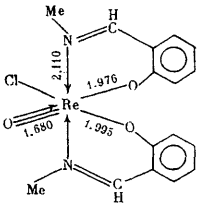
(VII).

One of them is coordinated in the usual way—the neutral donor N atom is located in the *trans*-position relative to the multiple bond, while the other ligand is "rotated", as a result of which the acido-"end" of $L^{(2)}$, i.e. the O atom, is in the *trans*-position relative to the second oxo-oxygen atom. Both ligand−metal bonds, occupying *trans*-positions relative to the M=O bonds, are weakened under these conditions albeit to different extents. The quantity Δ is +0.183 Å for the Mo−N bond and +0.121 Å for the Mo−O bond. The reason for the rotation of one of the ligands $L^{(2)}$ is not evident. Possibly it is associated with the way in which the complex is obtained. One should also draw attention to the fact that the M−L_L bond in the first of the two ligands, occupying the third *cis*-position relative to both M=O bonds, is also significantly shortened (to 1.938 Å), i.e. is in essence also multiple. Therefore the preference for one orientation over another possible orientation is not all that important for the second chelate ligand: at any rate, the N_L atom is in the *trans*-position relative to the M=O or M⇄O_L multiple bond.

We may quote yet another example of the disposition of the chelate ligand typical for the oxo-complexes of d^0 metals. In the silicylideneanilinato-complex [MoO$_2$(Ph-Sal)$_2$] (VIIIa) which we investigated[43] both chelate ligands are oriented in accordance with the requirements for self-consistency: the *trans*-positions relative to the multiple bonds contain the donor "ends" of the chelates (the imine N atoms), while the *cis*-positions contain the acido-"ends" (the hydroxyl O atoms). The *trans*-lengthening Δ′ is on average 0.21 Å.



(VIIIa)



(VIIIb)

This example is especially interesting when compared with the isotypical complexes of d^2 metals [Re(V) and Tc(V)]:[ReOCl.(Me-Sal)$_2$] (VIIIb)[45] and [TcOCl(Ph-Sal)$_2$].[46] Comparison of these complexes makes it possible to reveal clearly the differences in the coordination of chelate monoionic ligands in d^0 and d^2 complexes. Firstly, the chelate ligand is "rotated": the acido-O atom of the ligand R-Sal moves to the *trans*-position relative to the multiple bond in the d^2 complexes. Secondly, the *trans*-lengthening in the complexes of d^0 metals is replaced in the case of d^2 metals by a

‡A complete compilation of the geometrical parameters of monomeric octahedral molybdenum complexes with chelate ligands and Mo−O and Mo−N bonds occupying *trans*-positions relative to Mo=O has been published.[42,43]

slight but clearly manifested *trans*-shortening of the M–O(Sal) bonds [in the given instance by 0.019 and 0.05 Å respectively in the Re(V) and Tc(V) complexes].

This result is not fortuitous, since the same feature is characteristic of a whole series of monomeric octahedral d^2-Re(V) complexes of a similar composition incorporating R-Sal ligands[47–49] (Table 4). In all these structures the *O, N*-chelate ligands are coordinated to the metal in a similar manner (the acido-O atom occupies the *trans*-position, while the donor N atom occupies the *cis*-position relative to O_{oxo}), i.e. a "rotation" is observed compared with the complexes of d^0 metals. In particular, out of the seven theoretically possible isomers of [ReOCl(PPh$_3$)(Me-Sal)] (Fig. 3), only two have been isolated in the crystalline state—the *cis*- and *trans*-isomers (A) and (B)—and in the structures of both an O (and not N) atom of the Me-Sal ligand is in the *trans*-position relative to the oxo-oxygen atom.[47] Exactly the same situation is obtained in the conformational isomers of *trans*-[ReOBr$_2$(PPh$_3$)(Ph-Sal)],[48,49] where the *trans*-position relative to the O (oxo) atom is occupied by the O (Ph-Sal) atom, while the N (Ph-Sal) atom is in the *trans*-position relative to the phosphine ligand.

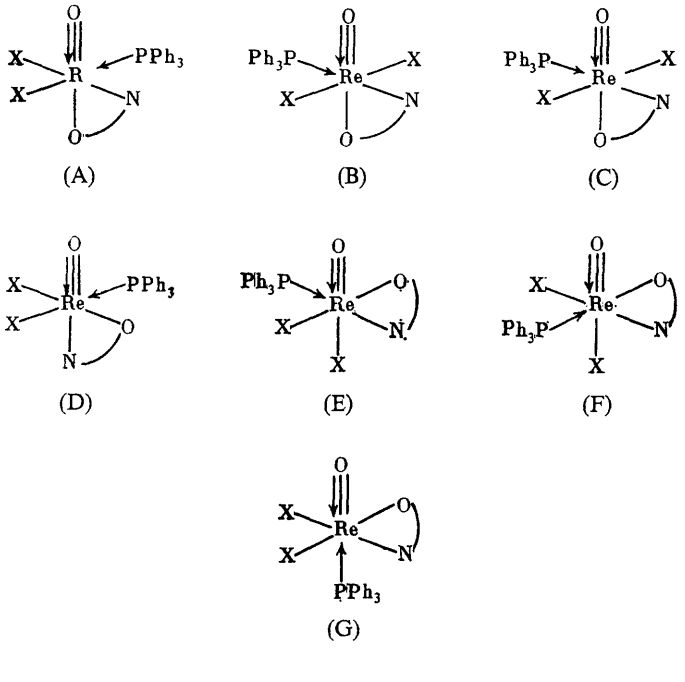
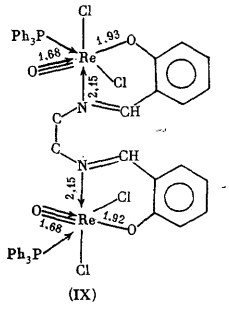


Figure 3. The theoretically possible geometrical isomers of the d^2-Re(V) complexes of the type ReOX$_2$(PPh$_3$)(R-Sal), where X = Cl or Br and R = Ph or Me.

The reason for this is fairly evident. The oxygen atom linked directly to the benzene ring is a conductor of the π-interaction from the ring to the metal, while the nitrogen atom, separated from the unsaturated group by the CH_2 group is not such a conductor. Accordingly, the M–O(Sal) bond in the complexes of d^0 metals is located in the *cis*-position, while in the complexes d^2 metals it is in the *trans*-position relative to the M=O bond.

It is seen from Table 4 that the R–O (chelate) bond, *trans* to Re=O, is on average shorter by 0.03 Å in six complexes than the only Re–O (chelate) bond *cis* to Re=O in the compound [ReOCl.(M-Sal)$_2$];[47] at the same time, the length of these bonds is smaller by the same amount than the standard Re–OH distance, which is 2.00 Å[4] (Δ' = 0.032 Å) and smaller by ~0.07 Å than the sum of the covalent radii of rhenium and oxygen (2.04 Å according to Pauling).

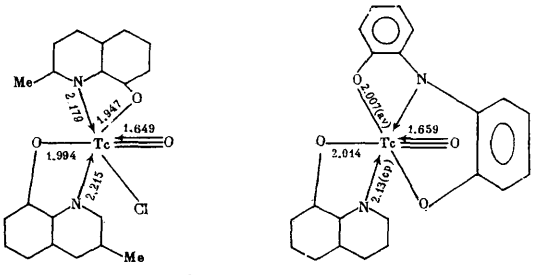
The Re–O (Sal) bond, in the *trans*-position relative to Re=O in the dimeric d^2-Re(V) complex [ReOCl$_2$(PPh$_3$)]$_2$(μ-Salen).CHCl$_2$ (IX), is shortened even more drastically.[50]



The length of this bond is on average 1.925 Å (Δ' = 0.075 Å). On the whole, the Re–O (Sal) distances (*trans* to Re-O) are in the range 1.925–1.976 Å (the mean is 1.963 Å) in the six d^2-Re(V) complexes containing salicylidene-aminato-ligands[45,47–50] and are on average somewhat shorter than the Re=O (Sal) distances (*trans* to Re–Cl) in the complexes *mer*-[Re^{IV}Cl$_3$(Ph-Sal)(PPhMe$_2$)] (1.970 Å)[51] and *cis*-[Re^{III}Cl$_2$(Ph-Sal)(PPhMe$_2$)$_2$] (1.990 Å).[52]

The same mode of coordination of the bidentate Ph-Sal with a similar shortening of the M–O (Sal) bond has been observed also in the pentavalent technetium compound TeOCl(Ph-Sal)$_2$:[46] the Tc–O (Sal) bond in the *trans*-position relative to Tc≡O (1.94 Å) is shorter by 0.5 Å than the analogous Tc–O (Sal) bond the second bidentate ligand.

In certain cases, the "rotation" of the ligand shifting the acido-centre to the *trans*-position relative to the multiple bond-linked ligand is not accompanied by a shortening of the M–L$_{trans}$ bond. This applies particularly to the complexes [ReOCl$_2$(PPh$_3$).{PhC(O)NNCMe$_2$}],[53] [TcOCl(ONC$_9$H$_5$Me)$_2$] (Xa),[54] and TcOL$^{(2)}$L$^{(3)}$ (Xb), where L$^{(2)}$ is the bidentate 8-hydroxyquinolinate ligand, while L$^{(3)}$ is the tridentate *N*-(2-oxidophenyl)salicylidenc-aminate ligand.[55]



In the first complex, the Re–O$_{trans}$ bond is 2.013 Å long, in the second complex (Xa) the Tc–O$_{trans}$ bond is 1.994 Å long (longer by 0.047 Å than the analogous Te–O$_{cis}$ bond of the second bidentate

ligand, while in the third complex (Xb) the Tc—O_{trans} bond is 2.014 Å long (on average longer by 0.007 Å than both Tc—O_{cis} bonds). However, in all three compounds the M—O_{trans} distances do not exceed the standard length of the single bond in the hexacoordinate and heptacoordinate complexes (for example, the Tc—O bond length is 2.02 Å according to the data of Bandoli et al.[56]).

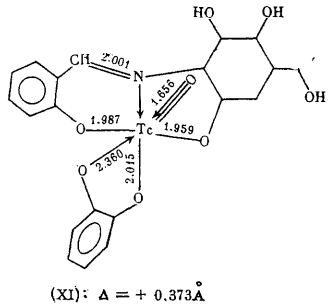
According to spectroscopic data (IR, ^{1}A NMR, and mass spectra), a further seven complexes having the general formula Mo($L^{(3)}$) (R-Sal), where M = Tc or Re and R = H, Me, or Ph, have structures similar to those described above:[55] the phenolic (charged) oxygen atom of the bidentate salicylideneaminate ligand R-Sal is located in the *trans*-position relative to the O (oxo) atom.

Thus it follows from the foregoing that, in contrast to complexes of d^0 of metals, the *trans*-partner of the oxo-ligand in the d^2 complexes of Re(V) and Tc(V) is the acido-"end" (and not the neutral-donor "end") of the chelate ligand.

The authors of the original investigations[45–50, 53–55] apparently missed the importance of this result. To us there seems to be no doubt that it is a consequence of the simultaneous manifestation of the two tendencies described above—the set of σ-donor and π-dative properties of the ligand§. Therefore it is not to be expected that the analogous "rotation" of the chelate ligands in the complexes of d^2 metals will occur in all cases; everything depends on the possibility and degree of involvement of the acido-"end" of the chelate in bonding to the metal. Evidently the "rotation" should be a characteristic feature of unsaturated chelate systems. The degree of involvement of the chelate ligand's π-electrons in the formation of a bond with the metal can be inferred from the disposition of the chelate ligand in the oxo-complexes of d^2 metals and from the degree of shortening of the M—O_L bond.

An example of a complex of a d^2 metal in which the *trans*-position relative to the M=O bond is occupied by the donor "end" of the chelate ligand may be provided by $TcOL^{(3)}L^{(2)}$, where $L^{(3)}$ is the dianion of *N*-salicylidine-D-glucosamine (Glusal) and $L^{(2)}$ is the monoanion of salicylaldehyde (Sla) (XI).[58]

In this compound, the carbonyl O atom of the Sla ligand is in the *trans*-position relative to the oxo-ligand, while the acidic phenolic O (Sla) atom occupies the *cis*-position relative to the Tc=O bond (in the *trans*-position relative to the N atom of the Glusal ligand).

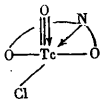


(XI): Δ = + 0.373Å

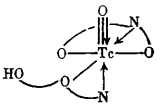
§One should recall the hypothesis that *trans*-dioxo-complexes of d^2 metals are formed only in the presence of ligands L which are pure σ-donors (weak π-donors), for example, in the presence of tetraazocyclotetradecane—the structure *trans*-$[Tc^VO_2(L)](ClO_4).H_2O$.[57] According to the authors,[57] the *trans*-TcO_2^+ compounds cannot be formed in the presence of salicyclidene-aminate ligands.

The Tc—O_{trans} = 2.360 Å bond is greatly lengthened compared with the Tc—O_{cis} bonds (1.959—2.015 Å): Δ = +0.373 Å. However, this example cannot be regarded as characteristic, since the phenolic oxygen atom is in principle a good conductor of the π-interaction and one may expect that it will in fact occupy the *trans*-position relative to the Tc=O bond.

The most probable cause of the reorientation of the ligand $L^{(2)}$ is believed[58] to be the specific features of the initial reaction occurring under the conditions of kinetic control. The complex [TcO(Glusal)(Sla)] was obtained by the reaction of $TcOCl_4^-$ with a fivefold excess of $GlusalH_2$ in methanol. The presence of the chelating ligand Sla in the final product is not the result of the hydrolysis of the ligand $Glusal^{2-}$ before coordination, since the direct reaction of $TcOCl_4$, $GlusalH_2$, and SlaH, taken in the stoichiometric proportions of 1:1:1, does not lead to the formation of [TcO(Glusal)(Sla)]. Furthermore, the initial reaction proceeds readily only in methanol (and also in ethanol but with a low yield), whereas in acetone, tetrahydrofuran (THF), and dimethyl sulphoxide (Me_2SO) it does not occur. According to the authors, the role of the solvent is very great: THF, Me_2SO, and actone promote the rapid hydrolysis of $GlusalH_2$ with formation of SlaH and glucosamine, whereas in methanol the ligand $GlusalH_2$ is stable for a long time. The authors suggest that the initial reaction can take place in stages with the successive addition of two $GlusalH_2$ ligands and the formation of two intermediates: the square-pyramidal [TcOCl(Glusal)] (XIIa) with the tridentate (O,N,O)-ligand $Glusal^{2-}$ in the plane of the base of the pyramid and the octahedral [TcO(Glusal)(GlusalH)] (XIIb) in which the bidentate ligand $GlusalH^-$ is coordinated to the acidic phenolic O atom in the *cis*-position and to the neutral N (imine) atom in the *trans*-position relative to the oxo-ligand.



(XIIa)



(XIIb)

This mode of coordination facilitates the direct addition of the ligand Sla^-, formed on hydrolysis of $GlusalH^-$, via the carbonyl O atom, since the Tc—N (Glusal) bond is weakened to the greatest extent.

Thus one can postulate that in the given instance the thermodynamically less favourable mode of coordination of the ligand Sla to the metal is determined by the reaction conditions.

- - -o0o- - -

The data presented permit the conclusion that the problem of the relative disposition of the ligands in complexes containing multiple bond-linked ligands is far from being exhausted and that further studies may reveal many new and unexpected nuances both in the overall structure of the complexes and in the geometrical parameters characterising the mutual influence of the ligands. In particular, this concerns the complexes of d^2 metals whose structure is determined, judging from all the available data, by the combined effects of several opposed tendencies, including kinetic factors.

References

1. M A Porai-Koshits, E A Gilinskaya *Kristallokhimiya* (Crystal Chemistry), Izd. VINITI, Moscow, 1966, p. 126 [Itogi Nauki i Tekhniki (Advances in Science and Engineering)]
2. Yu A Buslaev, V A Shcherbakov *Zh. Strukt. Khim.*, 1966, **7** 345
3. A Griffith, C Wicking *J. Chem. Soc., A*, 1968, 379
4. M A Porai-Koshits *Izv. Yugosl. Kristallogr. Tsentra*, 1974, **9** 19
5. M A Porai-Koshits, L O Atovmyan *Kristallokhimiya i Stereokhimiya Koordinatsionnykh Soedinenii Molibdena* (Crystal Chemistry and Stereochemistry of the Coordination Compounds of Molybdenum), Izd. Nauka, Moscow, 1974, 231 pp
6. E M Shustorovich, M A Porai-Koshits, Yu A Buslaev *Coord. Chem. Rev.*, 1975, **17** 1
7. G Z Pinsker *Kristallografiya* 1966, **11** 736
8. O N Krasochka, Candidate's Thesis in Chemical Sciences, Branch of the Institute of Chemical Physics of the USSR Academy of Sciences, Chernogolovka, 1972, 168 pp.
9. T Gloviak *Diss. Wroclaw*, Uniwersytet, 1967, 148 pp.
10. H Beyer, O Clemers, B Krebs *Angew. Chem.*, 1968, **80** 286
11. G Ciani, A Sironi, T Beringolli, et al. *Inorg. Chim. Acta*, 1986, **113** 61
12. K Weighardt, G Backes-Dahmann, W Holzbach, et al. *Z. Anorg. Allg. Chem.*, 1983, **499** 44
13. P R Robinson, E O Shlemer, R K Murmann *Inorg. Chem.*, 1975, **14** 2035
14. S Linkoln, S A Koch *Inorg. Chem.*, 1986, **25** 1594
15. K Weighardt, G Backes-Dahmann, W Holzbach, et al. *Angew. Chem.*, 1985, **97** 773
16. V S Sergienko, V K Borzunov, M A Porai-Koshits *Dokl. Akad. Nauk SSSR*, 1988, **301** 1141
17. M A Porai-Koshits, L O Atovmyan *Koord. Khim.*, 1975, **1** 1271
18. R G Pearson *J. Am. Chem. Soc.*, 1963, **85** 3533
19. V S Sergienko, M A Porai-Koshits *Koord. Khim.*, 1982, **8** 251
20. V S Sergienko, M A Porai-Koshits, V E Mistryukov *Koord. Khim.*, 1982, **8** 230
21. R Graziani, U Casellato, R Rossi, et al. *J. Cryst. Spectr. Res.*, 1985, **15** 573
22. Yu A Buslaev, Yu V Kokunov, V A Bochkareva, et al. *Dokl. Akad. Nauk SSSR*, 1971, **201** 355
23. B Kamenar, C K Prout *J. Chem. Soc., A*, 1970, 2379
24. G F Ciani, G d'Alfonso, P Romiti, et al. *Inorg. Chim. Acta*, 1983, **72** 29
25. C J L Lock, G Turner *Can. J. Chem.*, 1977, **55** 333
26. P H Fackler, M E Kastner, H J Clarke *Inorg. Chem.*, 1982, **21** 1941
27. A V Butcher, J Chatt *J. Chem. Soc., A*, 1970, 2652
28. E Carmona, A Galindo, L Sanchez, et al. *Polyhedron*, 1984, **3** 347
29. C G Yong, J H Enemark *Inorg. Chem.*, 1985, **24** 4416
30. F A Cotton, M P Diebold, W J Roth *Inorg. Chem.*, 1987, **26** 2848
31. M A Porai-Koshits, V S Sergienko, Kh T Sharipov *XVI Vsesyuznoe Chugaevskoe Soveshchanie po Khimii Kompleksnykh Soedinenii: Tezisy Dokladov* (The XVIth All-Union Chugaev Conference on the Chemistry of Complex Compounds: Abstracts of Reports), Krasnoyarsk, 1987, Vol. 2, p. 351
32. L Manojlovic-Muir *J. Chem. Soc., A*, 1971, 2796
33. J Chatt, L Manojlovic-Muir, K W Muir *J. Chem. Soc. Chem. Commun.*, 1971, 655
34. L Manojlovic-Muir, K W Muir *J Chem. Soc., Dalton Trans.*, 1972, 689
35. B L Haymore, W A Goddard, J C Alison *Proc. 23rd Intern. Conf. Coord. Chem.*, 1984, p. 535
36. K V Kotegov, Yu N Kukushkin, N K Kabilov, et al. *Zh. Neorg. Khim.*, 1977, **22** 1008
37. N K Kabilov, Candidate's Thesis in Chemical Sciences, Lensovet Leningrad State University, Leningrad, 1977, 154 pp.
38. Kh T Sharipov, N K Makhmudova, T S Khodashova, et al. *Koord. Khim.*, 1982, **8** 117
39. N K Makhmudova, Kh T Sharipov, T S Khodashova, et al. *Koord. Khim.*, 1986, **12** 846
40. Kh T Sharipov, N K Makhmudova, T S Khodashova, et al. *Koord. Khim.*, 1982, **8** 535
41. Kh T Sharipov, N K Makhmudova, T S Khodashova, et al. *Koord. Khim.*, 1983, **9** 266
42. V S Sergienko, A D Garnovskii, M A Porai-Koshits, et al. *Koord. Khim.*, 1985, **11** 1407
43. V S Sergienko, M A Porai-Koshits, V L Abramenko, et al. *Koord. Khim.*, 1985, **11** 1399
44. B Pigott, S D Thorpe, R N Sheppard *Inorg. Chim. Acta*, 1985, **103** L3
45. G Gilly, M Sacerdoti, V Bertolasi, et al. *Acta Crystallogr., Sect. B*, 1982, **38** 100
46. G Bandoli, U Mazzi, D A Clemente, et al. *J. Chem. Soc., Dalton Trans.*, 1982, 2455
47. V Bertolasi, V Ferretti, M Sacerdoti, et al. *Acta Crystallogr., Sect. C*, 1984, **40** 971
48. M Sacerdoti, V Bertolasi, G Gilli, et al. *Acta. Crystallogr., Sect. C*, 1984, **40** 968
49. V Bertolasi, M Sacerdoti, G Gilli, et al. *Acta Crystallogr., Sect. B.*, 1982, **38** 426
50. G Bambieri, U Mazzi, G Gilli, et al. *J. Organomet. Chem.*, 1978, **159** 53
51. V Bertolasi, V Ferretti, G Gilli, et al. *J. Chem. Soc., Dalton Trans.*, 1987, 613
52. V Ferretti, M Sacerdoti, V Bertolasi, et al. *Acta Crystallogr., Sect., C*, 1984, **40** 974
53. M B Hursthause, A S A Jayaweera, A Quick *J. Chem. Soc., Dalton Trans.*, 1979, **279**
54. B E Wilcox, M J Heeg, E Deutsch *Inorg. Chem.*, 1984, **23** 2962
55. U Mazzi, F Refosco, F Tisato, et al. *J. Chem. Soc., Dalton Trans.*, 1986, 1623
56. G Bandoli, U Mazzi, E Roncari, et al. *Coord. Chem. Rev.*, 1982, **44** 191
57. S A Zuckman, G M Freeman, D E Trutner, et al. *Inorg. Chem.*, 1981, **20** 2386
58. A Duatti, A Marchi, L Magon, et al. *Inorg. Chem.*, 1987, **26** 2182