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STEREOCHEMICAL ASPECTS OF REACTIONS OF COMPLEXES OF d^0 TRANSITION METALS WITH MULTIPLY BONDED LIGANDS

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CONTENTS

A. INTRODUCTION

Development of coordination chemistry was originally associated with compounds of platinum-group and other metals with the electronic configuration d^3–d^9. During the last several decades attention has been diverted to the problems of stereochemistry of complex compounds of transition metals with an incompletely filled *d*-shell which are situated in the central part of the Periodic Table. The large number of vacant orbitals on the central atom causes lability of the complexes and high coordination numbers (7, 8 and greater), and the complexing atom becomes capable of adding light atoms (O, N, S, and others) via a multiple bond. Such groupings ($M \overset{\leftarrow}{=} O$, $M \equiv N$, $M \overset{\leftarrow}{=} S$, and others) proved to be rather stable, and this provided a new branch in the chemistry of transition metals, namely, coordination chemistry of heteroatomic cations.

A problem of mutual influence of ligands arises in mixed complexes, when ligands of one sort experience perturbation by other ligands. Substitution of

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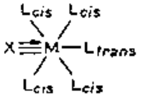
one ligand $\mathcal{L}_1$ by another ligand $\mathcal{L}_2$ in an inner sphere causes the appearance of non-equivalent positions for the ligands $\mathcal{L}_1$ and, hence, different rate of their substitution. The establishment by Chernyaev [1] of a regularity in the *trans* influence in square complexes of platinum(II) has given rise to the study of the mutual influence of ligands in complexes.

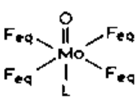
A multiply bonded ligand in a complex

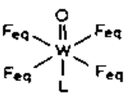


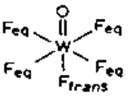
brings about non-equivalence of position in the octahedron due to a strong *trans* influence; the distance M–$\mathcal{L}_{trans}$ is considerably elongated relative to M–$\mathcal{L}_{cis}$. Such *trans* weakening is characteristic for complexes of transition metals with the electronic configuration d^0 and d^1 [2–10]. Elongation of the M–$\mathcal{L}_{trans}$ bond is manifest in activation of the $\mathcal{L}_{trans}$ ligand in substitution reactions and, indeed, substitution reactions of molecular ligands in the position *trans* to the multiply bonded atom proceed easily. In reactions with π-donor acidoligands the situation may change, since the vacant d_{xy}-orbital, capable of accepting electron pairs, will favour substitution in the equatorial plane. Therefore if the attacking ligand can form a covalent bond with a metal and is capable of donor–acceptor d_π–p_π interaction with a metal atom, there arise conditions for activation of *cis* positions.

B. *Cis*-EFFECT OF THE MULTIPLY BONDED LIGAND

Stereospecificity of substitution reactions becomes particularly apparent when interactions in solutions are studied by spectroscopic methods; this was decisive in the choice of subjects for investigations, namely, halide (mainly fluoride) complexes of d^0-elements, stable in non-aqueous media. First data on the substitution reactions in complexes with a multiply bonded ligand were obtained for oxofluoride complexes of molybdenum and tungsten [11–13]. The interaction of complexes with alcohol ROH (R = CH_3, C_2H_5, C_3H_7, C_4H_9 and Ph) can lead to the replacement of the molecular donor ligand $\mathcal{L}$, F_{trans}, or F_{eq}.







Upon addition of alcohol to a solution of $[WOF_5]^-$ in acetonitrile, the lines (a doublet and a quintet) in the ^{19}F NMR spectrum of $[WOF_5]^-$

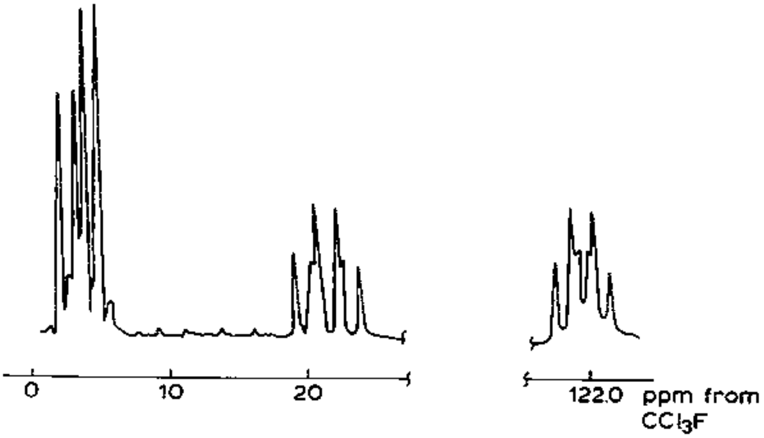
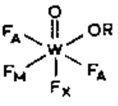
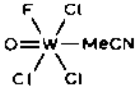


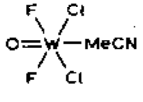
Fig. 1. ^{19}F NMR spectrum of complex $[WOF_4(OR)]^-$.

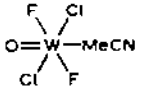
disappear. A new spectrum appears (two doublets and two pairs of triplets) of the A_2MX type (Fig. 1) due to the formation of a tungsten complex with four fluorine atoms occupying three non-equivalent positions in the octahedron, $[WOF_4(OR)]^-$, in which th OR group is in a *cis* position to the multiply bonded oxygen atom. In the reaction of $[MoOF_4 \cdot MeCN]$ and

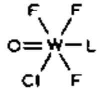


$[WOF_4 \cdot MeCN]$ with alcohols, first substitution of a fluorine atom takes place and formation of complexes $[MOF_3(OR) \cdot MeCN]$ (M = Mo, W) with the OR-group in the equatorial plane of the octahedron. Instead of singlets in the ^{19}F NMR spectrum due to $MOF_4 \cdot MeCN$ a spectrum of A_2B type is observed (Fig. 2). Subsequently a molecule of acetonitrile is displaced with the formation of complexes $[MOF_3(OR) \cdot ROH]$. In the case of phenol the reaction ends at the stage of $[MOF_3(OR) \cdot MeCN]$.









As a result of reaction of mixed fluorochlorooxo-compounds of tungsten with alcohols diverse complex oxohalides with an alkoxy group in the equatorial plane are formed with the exception of *trans*-$[WOF_2Cl(OR) \cdot MeCN]$, this being indicative of the stability of complexes with the coordinate F—W—OR [14].

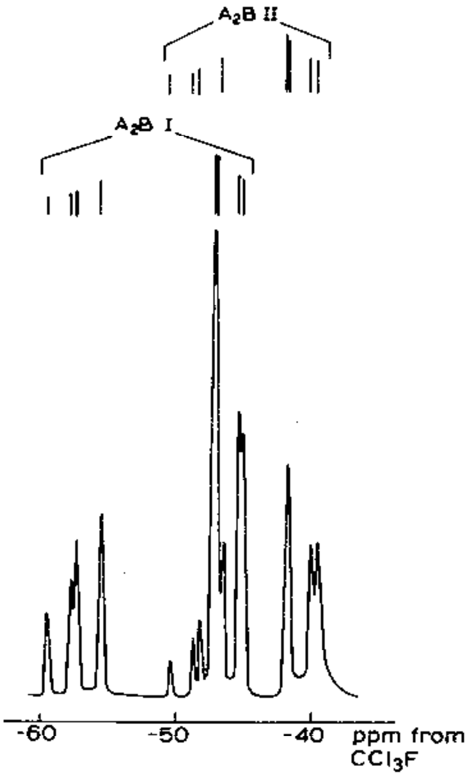
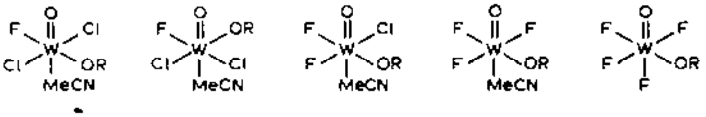
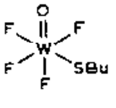


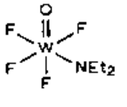
Fig. 2. ^{19}F NMR spectra of complexes [$MoOF_3(OR) \cdot MeCN$] (A_2B I) and [$MoOF_3(OR) \cdot ROH$] (A_2B II).



The *cis* effect of the multiply bonded oxygen atom manifests itself not only in reactions with oxygen-containing acidoligands, but also with sulphur- and nitrogen-containing ligands [15].

The interaction of WOF_4 with BuSH, even with a considerable excess of the latter, cannot be identified with the aid of ^{19}F NMR spectra. However, upon introduction of a base into this solution, substitution of one fluorine atom in WOF_4 takes place and formation of the complex [$WOF_4(SBu)$]$^-$ with a non-linear fragment O=W—SBu occurs.



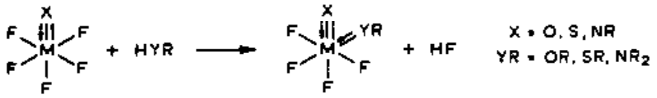


Upon adding diethylamine to WOF_4 in acetonitrile, two doublets and two pairs of triplets appear in the ^{19}F NMR spectrum of the solution with the intensity ratio 2:1:1 (A_2MX type of spectrum), assigned to the complex $WOF_4(NEt)_2^-$ with the group NEt_2 *cis* to the oxygen atom.

Similar reactions carried out with $[WSF_4 \cdot MeCN]$ and $[WSF_5]^-$ demonstrated the formation of complexes $[WSF_4(OR)]^-$, $[WSF_4(SR)]^-$ and $[WSF_4(NEt_2)]^-$ containing non-linear fragments S=W—OR, S=W—SR and S=W—NEt_2 [16]. The *cis* effect of multiply bonded imido-groups has been monitored with the aid of the ^{19}F NMR method in reactions of $[W(NBu)F_5]^-$ and $[W(NCONH_2)F_5]^-$ with ethyl alcohol and diethylamine. These reactions gave complexes $[W(NBu)F_4(OEt)]^-$, $[W(NBu)F_4(NEt_2)]^-$ and $W(NCONH_2)F_4(OEt)^-$, in which substituting ligands are *cis* to the imido-group [15].

It should be pointed out that the interaction of WOF_4 with acetic acid does not lead to substitution of the fluorine atoms, but only coordination of CH_3COOH *trans* to the multiple bond with formation of the adduct $WOF_4 \cdot CH_3COOH$ [17].

A feature common to the reactions of complexes with multiply bonded ligands is that oxygen-, sulphur- and nitrogen-containing acidoligands substitute first a fluorine atom in a *cis* position to the multiple bond. This can be regarded as a stereospecific reaction. Complexes were obtained with all kinds of combinations of X and YR in the non-linear fragment X=M—YR (except RN=M—SR)



In the reactions cited-above a specific feature can be noted: the substituting ligands contain groups —OR, —SR, —NR_2, i.e. groups which are capable of forming an additional donor–acceptor d_π—p_π bond. In compounds with one multiple bond the substituting ligand, occupying a *cis* position to the multiply bonded ligand, creates conditions for additional d_π—p_π interaction with a metal atom.

By now the structures of three complexes are known, containing a multiply bonded ligand and an OR-group: $[NbOCl_2(OEt) \cdot dipy]$ [18], $[VO(OiPr)(oxine)_2]$ [19], and $[WSeCl_3(OCH_2CH_2OMe)]$ [20]. In these compounds OR-groups occupy positions *cis* to the multiple bond. $[NbOCl_2(OEt) \cdot dipy]$ has a structure of an octahedron with *cis* arrangement of the OEt-group with respect to the multiply bonded oxygen atom and with distances Nb=O = 1.71 Å and Nb–OEt = 1.87 Å. A shortened Nb–OEt distance compared with the length of the ordinary Nb–O bond may be regarded as an attribute of participation of d_π–p_π interaction in the Nb–OEt bond. Alkoxygroups ($V{-}OiPr = 1.77$ Å) occupy a *cis* position with respect to the multiply bonded oxygen atom ($V{=}O = 1.6$ Å) in the oxyquinoline compound of vanadyl[$VO(OiPr)(oxine)_2$].

C. ON THE MUTUAL ARRANGEMENT OF TWO MULTIPLY BONDED LIGANDS

In octahedral compounds containing two or three multiply bonded ligands, these may be found either *cis* or *trans* to one another. The most extensive data on the mutual arrangement of multiply bonded ligands are available for complexes with multiply bonded oxygen atoms. The main information concerning the structure of dioxo-compounds was obtained by IR spectroscopy, X-ray crystallographic analysis and NMR techniques.

The relative arrangement of oxygen atoms in "-yl" groupings UO_2, VO_2, MoO_2 and WO_2 has received the attention of many authors [21–26].

The non-linearity of the groups MoO_2 and WO_2 was first pointed out in refs. 27–31. The appearance of intensive absorption bands of symmetric and antisymmetric vibrations of MO_2 groups at 850–1000 cm^{-1} in the IR spectra of compounds containing MoO_2 and WO_2 groups was interpreted as a direct proof of the non-linearity of the groups MoO_2 and WO_2. In the investigation of aqueous solutions of salts $RB_2MoO_2F_4$ and $K_2WO_2F_4$ by using ^{19}F NMR techniques two resonance signals of equal intensity were obtained, due to non-equivalence of fluorine atoms because of the *cis* arrangement of oxygen atoms.

On the basis of IR spectroscopy data [32,33], it is pointed out that in molybdenyl acetylacetonate and in chelate compounds of tungstyl $WO_2\mathcal{L}_2$ (HL = acetylacetone, benzoylmethane, oxyquinoline, etc.) the groups MO_2^{2+} have a *cis* structure.

Griffith and Wickins [34] carried out an investigation of a number of complex compounds with the anion $[MO_2X_4]^{n-}$ ($M = Mo^{VI}$, W^{VI}, V^{V}; $X = Cl$, F, 1/2 ox) by IR and Raman spectroscopy techniques. For complex anions $[MO_2X_4]^{n-}$ three vibrations associated with group MO_2 (ca. 950, 900 and 370 cm^{-1}) are expected. For the *cis* arrangement of the oxygen atoms (symmetry C_{2v}) all three vibrations will be active in the IR and Raman spectra; for a *trans* configuration (D_{4h}) only one vibration is active in the Raman spectra, while the two other vibrations are active in the IR spectra only. Comparing the IR and Raman spectra, the authors came to the conclusion that the anions $[VO_2F_4]^{3-}$, $[MoO_2F_4]^{2-}$, $[MoO_2Cl_4]^{2-}$, $[WO_2Cl_4]^{2-}$ and $[VO_2(C_2O_4)_2]^{3-}$ in the compounds have a *cis* structure. Later the *cis* configurations of MoO_2 and WO_2 groups in various complexes, both in the solid state and in solutions, were confirmed by IR, ^{19}F and ^{1}H NMR spectroscopy techniques. For instance, *cis*-MO_2 was found in complexes $[MO_2F_2 \cdot 2\mathcal{L}]$ ($M = Mo$, W; $\mathcal{L} =$ ROH, MeCN, DMSO, DMFA, 1/2 dipy, 1/2 phen) [35–38], $MoO_2Cl_2 \cdot 2\mathcal{L}$ ($\mathcal{L}$ = derivatives of pyridine-*N*-oxide) [39], $[Mo_2F_2(dicet)]^-$ (dicet = β-diketonates) [40], MO_2Q_2 (HQ = oxyquinoline, mercaptoquinoline) [41,42].

Only *cis* MO_2-groups were found in the X-ray crystallographic analysis of crystalline dioxo-complexes of transition d^0-elements. The compositions of complex compounds of transition d^0-elements with two multiply bonded oxygen atoms, the structures of which are now known, are given below: $K_2VO_2F_3$ [43], $(NH_4)_3[VO_2(C_2O_4)_2] \cdot H_2O$ [44], $NH_4[VO_2(H_2EDTA)] \cdot 3H_2O$ [45], $Na_3[VO_2(EDTA)] \cdot 4H_2O$ [46], $VO_2(acac) \cdot phen$ [47], $[VO_2F \cdot dipy]_2$ [48], $PPh_4[VO_2(C_{11}H_7N_3O_2)]$ [49], $K_2MoO_2F_4 \cdot H_2O$ [50], $K_2MoO_2F_4$ [51], $Rb_2MoO_2F_4$ [52], $RbMoO_2F_3$ [53], $(NH_4)MoO_2F_3$ [54], $[MoO(S_2CNEt_2)_3]_2 \cdot [Mo_2O_4F_6]$ [55], $MoO_2Cl_2 \cdot H_2O$ [56], $MoO_2Cl_2(H_2O)_2 \cdot 2KCl$ [57], $MoO_2Cl_2 \cdot H_2O \cdot KCl$ [58], $MoO_2Cl_2 \cdot (DMFA)_2$ [59], $MoO_2Br_2 \cdot dipy$ [60], $MoO_2(oxine)_2$ [61,62], $MoO_2(S_2CNEt_2)_2$ [63], $MoO_2(acac)_2$ [64,65], $MoO_2(O_2C_{15}H_{11})_2$ [66], $MoO_2(OC_2H_4OH)_2$ [67], $MoO_2(OC_2H_4CNMe)_2$ [68], $K_2[MoO_2(O_2C_6H_4)_2] \cdot 2H_2O$ [69], $H[MoO_2(OCH_2CH_2)_3N]$ [70], WO_2Cl_2 [71], $(C_{10}H_{13}O_2)^+ \cdot [WO_2Cl_2(acac)]^-$ [72], $[MoO_2(Hpin)(OMe)]_2 \cdot 2MeOH$ [73], $[MoO_2Cl_2(O_2C_{14}H_8)]$ [74], $Ba[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ [75], $[MoO_2Cl(DMFA)_2]_2O$ [69], $MoO_2Br_2(PPh_3O)_2$ and $MoO_2Cl_2(PPh_3O)_2$ [76].

Information on the structure of octahedral complexes with two multiply bonded sulphur atoms is absent. Only one paper is known [77], in which the structure of the compound $[Mo(NPh)_2(Et_2NCS_2)_2]$ with two multiply bonded imidogroups found *cis* to each other ($Mo{=}N_1 = 1.754$ Å and $Mo{=}N_2 = 1.789$ Å) is reported. Data on the structure of complexes with two different multiply bonded ligands are also limited. A *cis* WOS group was found in the compound $WOSCl_2(CH_3OCH_2)_2 \cdot WSCl_4$ [78] ($W{=}O = 1.72$ Å, $W{=}S = 2.10$ Å), and a *cis* MoONR group was found in the compounds $MoO(NH)Cl_2(EtPh_2PO)_2$ [79] ($Mo{=}NH = 1.70$ Å, $Mo{=}O = 1.66$ Å) and $MoO(NNMe_2)(S_2CNMe_2)_2$ [80] ($Mo{=}NNMe_2 = 1.685$ Å, $Mo{=}O = 1.71$ Å).

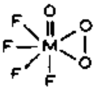
According to the data reported, the *cis* arrangement of two multiply bonded ligands in complexes of d^0-elements (V^V, Mo^{VI}, W^{VI}) has no exceptions. At the same time it is known that in complexes of elements with the electronic configuration d^2 (Mo^{IV}, Re^V, Os^{VI}) MO_2 groups are linear. The problem of the mutual arrangement of multiply bonded ligands has been treated in refs. 4, 31, 34, 81, 82. Attention has been paid to the dependence of the configuration of groups MX_2 (metal–multiply bonded ligand) on the character of d_π–p_π interaction [31,34,81].

In a qualitative scheme of octahedral molecular orbitals the orbitals of t_{2g} type formed due to the d_{xy}, d_{xz} and d_{yz} orbitals of metal are energetically found directly above the σ-bonding orbitals and according to their symmetry can be used by π-bonding electrons of the ligands. For dioxo-complexes of *d*-elements with a *cis* configuration each oxygen atom uses one orbital (d_{yz}

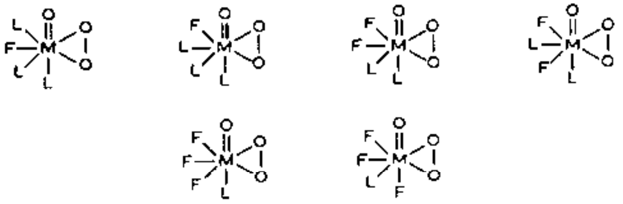
for O_z and d_{xy} for O_x), possessing the third orbital (d_{xz}) jointly. In the case of the structure of the MO_2 group being *trans*, two oxygen atoms together possess two *d*-orbitals (d_{yz} and d_{xz}), the third orbital (d_{xy}) being non-bonding. Therefore the *cis* form of the MO_2 group is preferred and the order of the metal–oxygen bond in this case is higher than in the *trans* arrangement.

D. COORDINATION OF n-DONOR TWO-CENTRE LIGANDS

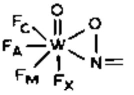
n-Donor two-centre ligands are those containing —O—O—, =N—O—, =N—N= and other groups and coordinating with a metal according to the η^2-type. According to X-ray crystallographic analysis data, in the compounds $K_2[MoO(O_2)F_4] \cdot H_2O$, $(NH_4)_3F[MoO(O_2)F_4]$ and $(C_9H_8NO)_2[WO(O_2)F_4] \cdot 3\,H_2O$, the complex anion $[MO(O_2)F_4]^-$ has the structure of a pentagonal bipyramid, in which the peroxogroup and three fluorine atoms are located in the equatorial plane, and the multiply bonded oxygen atom and the fourth atom of fluorine are *trans* to each other and occupy axial positions [83–85].



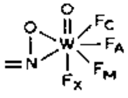
^{19}F NMR investigation of oxo-peroxo-fluoride complexes of molybdenum and tungsten in aqueous solutions showed that the resulting complexes having the composition $[Mo(O_2)F \cdot 3\,H_2O]$, $[MO(O_2)F_2 \cdot 2\,H_2O]$, $[MO(O_2)F_3 \cdot H_2O]$ and $[MO(O_2)F_4]$ are also pentagonal bipyramidal with the peroxogroup in the equatorial plane *cis* to the multiple bond [86,87]. In the investigation of the reaction of hydrogen peroxide with WOF_4 in acetonitrile by the ^{19}F NMR method oxo-peroxo-fluoride complexes of the composition $[WO(O_2)F_3 \cdot MeCN]$, $[WO(O_2)F_2(H_2O) \cdot MeCN]$, $[WO(O_2)F_2 \cdot (MeCN)_2]$ were obtained, the structures of which were similar to those cited above [88]. It should be emphasized that complexes containing one atom, two atoms, or three atoms of fluorine, both in an aqueous solution and in acetonitrile, exist in the form of various geometrical isomers differing in the arrangement of the fluorine atoms relative to the peroxo-group.



The interaction of tungsten oxotetrafluoride with some O,N-two-centre ligands (oximes and β-phenylhydroxylamine) in acetonitrile solution has been studied by the ^{19}F NMR technique [89,90]. Fig. 3 illustrates the ^{19}F NMR spectrum of the complex $[WOF_4(ON{=}CMe_2)]^-$. The spectrum is of the ACMX type with the ratio of integral intensities being 1 : 1 : 1 : 1, indicative of formation of a complex with four fluorine atoms occupying four non-equivalent positions. As oxo-peroxofluorides of molybdenum and tungsten, complexes of tungsten with O,N-two-centre ligands have a pentagonal bipyramidal shape in which the coordinated fragment —O—N = is in the equatorial plane.



Ia



Ib

With an increase of temperature the signals F_C and F_M in the ^{19}F NMR spectra of complexes with oximes become considerably broadened, and the multiplicity of the signal F_X changes (Fig. 3). The phenomenon may be due to the existence at low temperatures of two stereoisomers Ia and Ib, interconverting with an increase of temperature by way of rotation of the ligand about an axis passing through the centre of the O—N bond and lying in the equatorial plane.

In complexes of tungsten with oximes and phenylhydroxylamine the organic ligand uses for bonding with the central atom two unshared electron pairs located on the orbitals which to a considerable extent can be char-

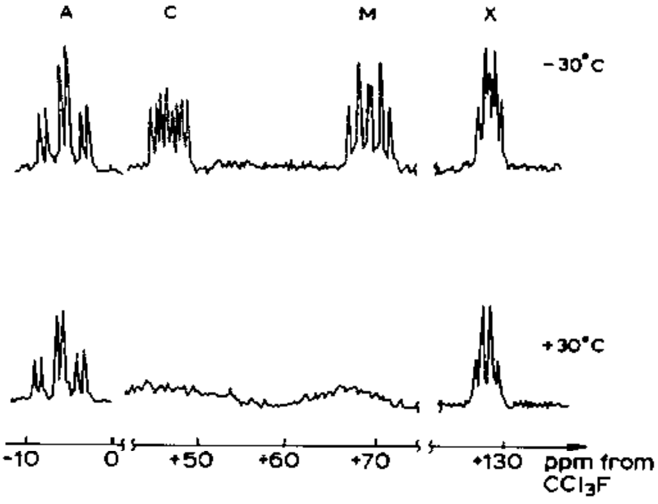


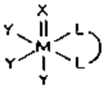
Fig. 3. ^{19}F NMR spectrum of complex $[WOF_4(ON{=}CMe_2)]^-$.

acterized as *p*-orbitals. Similarly to the case with ethylene, linear combinations of these orbitals lead to a bonding and anti-bonding MO. However, in contrast to ethylene where the anti-bonding orbital is vacant, in the molecule of the n-donor two-centre ligand both orbitals are populated by electron pairs. While in olefin complexes the metal accepts electrons from the bonding π-orbital and is a donor with regard to the anti-bonding orbital of the organic ligand, in complexes with oximes and related two-centre ligands the central atom, for the η^2-coordination to take place, must be capable of accepting electrons from both the bonding and antibonding π-orbital of the organic ligand. The tungsten atom in the configuration d^0 has (in addition to hybridized orbitals of the σ-type, located in the equatorial plane and fit for accepting electrons from the π-orbitals) vacant *d*- or *p*-orbitals which may be used for accepting electrons from π^*-orbitals. Thus, the structure of the complexes with O,N-two-centre ligands is similar to the structure of π-complexes of the Zeise salt type. The main difference is that while in the Zeise salt the central atom is at the same time a donor and an acceptor of electrons with regard to the ligand, in the complexes under consideration the central atom behaves only as an acceptor.

The coordination of O,N-two-centre ligands in complexes of d^0-transition metals of Groups V—VI was also shown to be of the η^2-type by X-ray crystallographic analysis and IR spectroscopy [91–94]. Thus, X-ray crystallographic analysis of $C_5H_3N(COO)_2MoO(ONPh)_2(HMPA)$ has shown this complex with a heptacoordinated Mo atom to have the form of a pentagonal bipyramid, in the equatorial plane of which O and N atoms of the tridentate ligand and O and N atoms of β-phenylhydroxylamine are located.

E. SPECIFIC FEATURES OF COORDINATION OF BIDENTATE LIGANDS IN COMPLEXES WITH MULTIPLE BONDS

In cases of a multiple bond being present in hexacoordination complexes, a bidentate ligand may be attached to the metal in two ways:

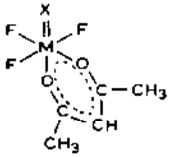


In the first case functional groups of the bidentate ligand are *cis* and *trans* to the multiple bond; in the second case the bidentate ligand occupies two coordination sites in the equatorial plane of the octahedron. Cases are also known when a bidentate ligand is bonded to metal via one functional group and exhibits the properties of a monodentate ligand.

Depending on the character in which bidentate ligands are attached to the central atom, they may be divided into three types: (1) both functional groups form donor—acceptor bonds with a metal; (2) both functional groups are attached to a metal via covalent σ-bonds (dibasic-bidentate ligands); and (3) one functional group forms a covalent bond with a metal, and the other, a donor–acceptor bond (monobasic bidentate ligands). It is natural to expect that the character of bonding of metal to bidentate ligands will determine its arrangement in complexes with a multiple bond.

According to the X-ray crystallographic analysis data, in $[WSeCl_3(OCH_2CH_2OMe)]$ [20] one oxygen atom of bidentate methoxyethane is *cis* to the group W=Se and is bonded to the W atom by a covalent bond, and the other oxygen atom forms a donor—acceptor bond with the metal and is *trans* to the W=Se group. In the oxyquinoline complex of vanadyl $[VO(Oi\text{-}Pr)(oxine)_2]$ [19], the oxygen atoms of oxyquinoline form a covalent bond with the metal and are *cis* to the multiply bonded ligand. Nitrogen atoms attached to the vanadium through a donor–acceptor bond are, respectively, *trans* to the oxygen atom and alkoxy-group. The structure of complexes $[MoO_2(OCH_2CH_2OH)_2]$ [67] and $[MoO_2(oxine)_2]$ [61,62] also confirms the fact that functional groups of the bidentate ligand which form donor—acceptor bonds with the metal, are *trans* to the multiply bonded oxygen atoms. The atoms of bidentate ligands, bonded to the metal via covalent bonds, are *cis* to the molybdenyl group.

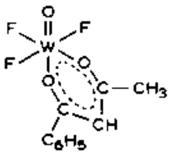
^{19}F and ^{1}H NMR techniques have also established that in complexes $[WOF_3(acac)]$, $[MoOF_3(acac)]$ and $[WSF_3(acac)]$ oxygen atoms of acetylacetonate occupy equatorial and axial positions in the octahedron [12,13,16,17,95,96].

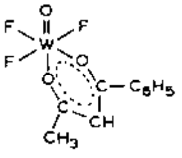


With such a structure of acetylacetonate complexes CH_3-groups must be in non-equivalent positions to the multiply bonded ligand, a fact established from the ^{1}H NMR spectra of complex $[WOF_3(CH_3COCHCOCH_3)]$ [17]. A similar conclusion about the coordination of acetylacetonate was made in the investigation of $Et_4N[NbOCl_3(acac)]$ by ^{1}H NMR [96].

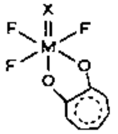
The compound $[MoO_2(acac)_2]$ was investigated [64] by ^{1}H NMR. Having found two non-equivalent CH_3-groups as displayed by the ^{1}H spectra, the authors suggested possible *trans*-isomerization. Taking into account the data on the structure of $MoO_2(acac)_2$ [65] and the results reported in [17], the non-equivalence of the CH_3-groups in $[MoO_2(acac)_2]$ may also be explained by their different arrangement with respect to the oxygen atoms in molybdenyl MoO_2^{2+}.

The interaction of WOF_4 with benzoylacetone $C_6H_5COCH_2COCH_3$ yields almost equal quantities of two isomeric complexes $[WOF_3(C_6H_5COCHCOCH_3)]$ which differ in the arrangement of the CH_3- and C_6H_5-groups relative to the multiply bonded atom of oxygen [97]. The ^{19}F NMR spectra of these complexes are shifted with respect to each other by as little as 30 Hz.



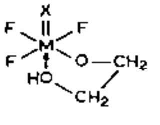


The reaction of tropolone with $MoOF_4$ and WSF_4 is accompanied by the formation of complexes $[MoOF_3(C_7H_5O_2)]$ and $[WSF_3(C_7H_5O_2)]$ [16,17]. According to the ^{19}F NMR spectra, two oxygen atoms of the tropolonate group in these complexes are *cis* and *trans* to the multiply bonded ligand.



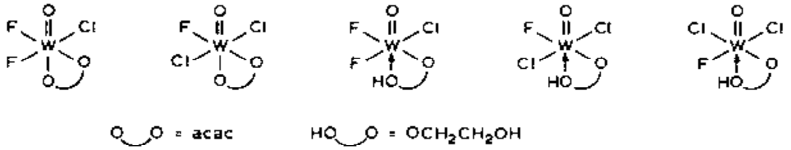
M = Mo, X = O
M = W , X = S

When carrying out reactions with ethylene glycol, one could suppose that the latter would be monobasic or dibasic, displaying, depending on the conditions, both mono- and bidentate properties. From the ^{19}F NMR data it appears that ethylene glycol reacts with $[WOF_5]^-$, $[W_2O_2F_9]^-$, $[W(NCONH_2)F_5]^-$ and $[W(NBu)F_5]^-$ as a monodentate monobasic ligand, giving complexes $[WXF_4(OCH_2CH_2OH)]^-$ ($X = O, S, NBu, NCONH_2$) with the group $—OCH_2CH_2OH$ *cis* to the multiple bond [12,15]. The interaction of $[MoOF_4 \cdot MeCN]$, $[WOF_4 \cdot MeCN]$ and $[WSF_4 \cdot MeCN]$ with ethylene glycol yields complexes $[MXF_3(OCH_2CH_2OH)]$ ($M = Mo, W$; $X = O, S$) in which two oxygen atoms of the ethylene glycol group occupy, respectively, *cis* (covalent σ-bond) and *trans* positions (donor—acceptor bond) relative to the multiply bonded ligand (ABX type of spectra) [12,16].



In such an arrangement the CH_2 groups become non-equivalent, and, therefore, fine structure may appear in the ^1H NMR spectrum. Indeed, in the ^1H NMR spectrum of the complex $[WOF_3(OCH_2CH_2OH)]$ there are two triplets of equal intensity due to the interaction of the non-equivalent CH_2-groups.

The reaction of tungsten oxo-chloro-fluorides with acetylacetone results in complexes having the composition [$WOF_2Cl(acac)$] and [$WOFCl_2(acac)$], [$WOF_2Cl(OCH_2CH_2OH)$] and [$WOFCl_2(OCH_2CH_2OH)$], in which two oxygen atoms of the acetylacetonate ion and of the deprotonated glycol group lie in the equatorial and axial planes in the octahedron [14].



1,2-Propanediol, $HOCH_2CHOHCH_3$, having two non-equivalent groups, reacts with WOF_4 as a monobasic bidentate ligand, giving two isomeric complexes [$WOF_3(OCH(CH_3)CH_2OH)$] and [$WOF(OCH_2CH(CH_3)OH]$) with a five-membered chelate ring (^{19}F NMR spectrum, Fig. 4).

These complexes differ in the character of oxygen atoms and hydroxo-groups attached to the tungsten atom, respectively, via a covalent and a donor—acceptor bond and occupying *cis* and *trans* positions to the multiply bonded

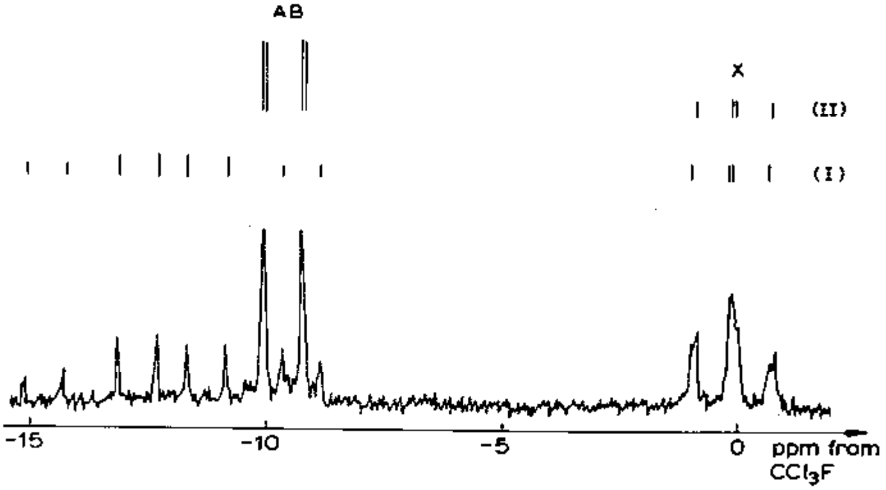
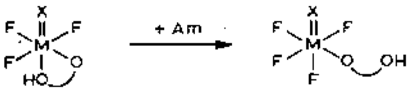


Fig. 4. ^{19}F NMR spectra of complexes [$WOF_3(OCH_2CH(CH_3)OH)$] and [$WOF_3(OCH(CH_3)CH_2OH)$].

ligand [97]. The above complexes may be termed chelate isomers with equal-membered rings, differing in the position of the primary and secondary oxygen atoms of the alcohol groups.

Interaction of WOF_4 in acetonitrile with 1,3-propanediol, $HOCH_2CH_2CH_2OH$, leads to the formation of complex $[WOF_3(OCH_2CH_2CH_2OH) \cdot MeCN]$, in which the diol group is *cis* to the multiple bond, and the *trans* position is occupied by the acetonitrile molecule. The reaction of WOF_4 with the aromatic diol, 1,2-benzenediol, gave a chelate complex with a five-membered ring of the composition $[WOF_3(1,2\text{-}OC_6H_4OH)]$ [97]. As a result of reaction of WOF_4 with 1,3-benzenediol and 1,4-benzenediol compounds with closed rings are not formed, and ^{19}F NMR spectra make it possible to identify only complexes with diols *cis* to the multiple bond: $[WOF_3(1,3\text{-}OC_6H_4OH) \cdot MeCN]$, $[MeCN \cdot WOF_3(1,4\text{-}OC_6H_4O)WOF_3 \cdot MeCN]$ and $[WOF_3(1,4\text{-}OC_6H_4OH) \cdot MeCN]$ [97].

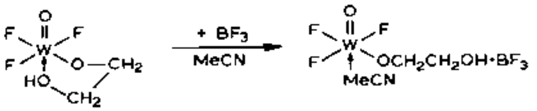
As is known, coordinated molecular donor ligands are bonded to the central atom in a complex less strongly than *cis* ligands, and can be easily displaced by ligands having a higher donor number [84]. Therefore, if a sufficient concentration of, say, fluoride ion is created in solution, it can displace the hydroxyl group of diol, found *trans* to the multiple bond. Indeed, in the case of adding, to solutions containing a chelate complex and HF, an amine which neutralizes HF and thus increases the concentration of the fluorine ion, coordination of F^- *trans* to the multiple bond and opening of the chelate ring occurs [15,97,98].



$O{-}OH \bullet O{-}CH_2CH_2OH$

Interaction of $[WOF_3(OCH_2CH_2OH)]$ with $[WOF_5]^-$ yields a dimeric anion with a bridging group $-OCH_2CH_2O-$, i.e. in this case opening of the chelate ring takes place, and one of the *cis* fluorine atoms in $[WOF_5]^-$ is substituted by the oxygen atom of the second functional group of ethylene glycol [15].

Opening of the chelate ring occurs when gaseous BF_3 is passed into a solution of $[WOF_3(OCH_2CH_2OH)]$. Boron trifluoride, being a stronger



acceptor, coordinates the second OH-group of deprotonated glycol and opens the chelate ring. *Trans* to the multiple bond in this case is the molecule of acetonitrile [15].

X-ray structure investigations showed that in complexes $Et_4N[NbOCl_3(CF_3COCHCOC_4H_3S)]$ [99] and $[ReOCl_2(acac) \cdot PPh_3]$ (d^2-configuration) [100] two oxygen atoms of the thionyltrifluoroacetone and acetylacetonate groups occupy *cis* and *trans* positions with respect to the multiple bonds Nb=O and Re=O. The difference in the distances $Nb—O_{cis}$ and $Nb—O_{trans}$ is 0.24 Å, and in the distances $Re—O_{cis}$ and $Re—O_{trans}$, 0.11 Å.

Thus, functional groups of bidentate oxygen-containing ligands, when the latter display monobasic properties, occupy *cis* (σ-bond) and *trans* (donor—acceptor bond) positions relative to the multiply bonded atom of oxygen, sulphur or nitrogen. The opening of the chelate ring through breakage of the donor—acceptor bond proceeds under the action of both strong bases and Lewis acids.

F. REACTIONS WITH REARRANGEMENT OF LIGANDS

In numerous publications devoted to the investigation of aquo- and amino-complexes of the platinum metals, cobalt, nickel, chromium and others, it was established that the mobility of hydrogen atoms in the molecules NH_3, H_2O and RNH_2 increases with their coordination. At the same time, data on protonic dissociation of hydroxyl in coordinated molecules of alcohol and diols are rather limited. It is shown, for example, that in the adduct $BF_3(ROH)_2$ the hydrogen atom forms a stable hydrogen bond with another molecule of alcohol [101]. Acidic dissociation of hydroxyl in the $=N—OH$ group was observed by Grinberg and Stetsenko in complexes with coordinated molecules of hydroxylamine [102]. ^1H NMR spectra showed the degree of dissociation to increase when acetic acid is coordinated to WOF_4. In our investigations [16,98] we studied the influence of nitrogen-containing

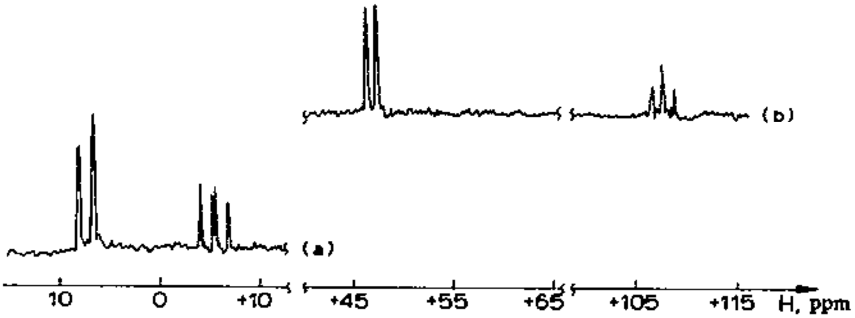
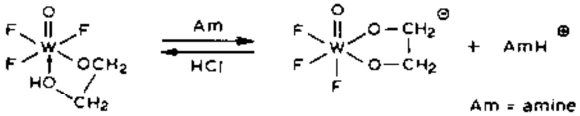


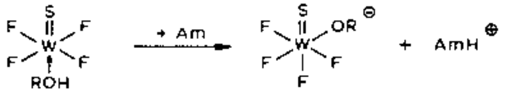
Fig. 5. ^{19}F NMR spectra of complexes (a) $[WOF_3(OCH_2CH_2OH)]$, and (b) $[WOF_3(OCH_2CH_2O)]^-$.

bases on protonic dissociation of alcohols and diols entering the inner sphere of tungsten, niobium and tantalum complexes.

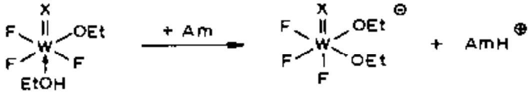
The introduction of an amine into a solution of $[WOF_3(OCH_2CH_2OH)]$ in acetonitrile, forms a complex anion $[WOF_3(OCH_2CH_2O)]^-$, in which two oxygen atoms of the glycol group are *cis* to the multiply bonded oxygen atom (^{19}F NMR spectrum in Fig. 5). The reaction is reversible, and $[WOF_3(OCH_2CH_2OH)]$ is formed again upon passing gaseous HCl through the solution.



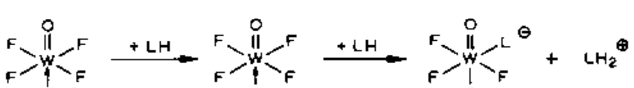
Addition of an amine into a solution of $[WSF_4 \cdot ROH]$ ($ROH = EtOH$, $HOCH_2CH_2OH$) leads to formation of complexes $[WSF_4 \cdot (OR)]^-$, in which the group OR forms a covalent σ-bond *cis* to the sulphur atom.



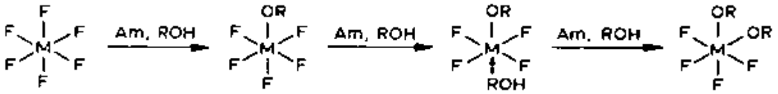
Complexes having the composition $WXF_3(OEt) \cdot EtOH$ ($X = O, S$) under the action of bases become converted into complex anions $[WOF_3(OEt)_2]^-$ and $[WSF_3(OEt)_2]^-$, in which two —OEt groups lie in the equatorial plane of the octahedron *cis* to each other.



Interaction of WOF_4 with imidazole and benzimidazole gives first a neutral complex $WOF_4 \cdot H\mathcal{L}$ ($H\mathcal{L}$ being imidazole and benzimidazole), in which the nitrogen-containing ligand is *trans* to the multiple bond. An increase in the basicity of the medium leads to deprotonation of the coordinated ligand, and shifting of $\mathcal{L}$ *cis* to the oxygen atom [103].



It is known that in alcoholysis of niobium and tantalum pentafluorides in solution, complexes $[MF_6]^-$, $[MF_5(OEt)]^-$ and *trans*-$[MF_4(OEt) \cdot (EtOH)]$ ($M = Nb, Ta$) are formed simultaneously. Introduction of a small amount of an amine into an alcoholic solution containing these complexes leads to the appearance in the ^{19}F NMR spectrum of two triplets of equal intensity indicative of the formation of the complex *cis*-$[MF_4(OEt)_2]^-$. This means that in the presence of a base the complexes $[MF_6]^-$ and $[MF_5(OEt)]^-$ undergo further alcoholysis and are transformed into *trans*-$[MF_4(OEt)_2]^-$ [16,98].



In the results presented here on the conversion of neutral complexes into anionic complexes in the presence of amines, one common reaction may be traced, namely, protonic dissociation of the coordinated molecular ligand or of the hydroxyl group of bidentate ethylene glycol. Dissociation is accompanied by the formation of a covalent σ-bond between the atom of metal and the atoms of oxygen or nitrogen of the acidoligand; the character of the ligand bonding to the central atom changes as the acidoligand shifts into the equatorial plane of the octahedron. In addition one of the *cis* fluorine atoms shifts *trans* to the multiply bonded ligand. Such a reaction of complex isomerization with proton dissociation we describe as a reaction of deprotonation with rearrangement of the ligand. One possible reason for the ligand rearrangement, evidently, resides in the fact that strengthening of the bonds of the central atom with the multiply bonded and π-donor ligands (= O, = S, —OR, —NR) takes place only in the case of their *cis* arrangement. Therefore the change from the donor—acceptor to covalent σ-bond as a result of proton dissociation can be realized only by way of a shift of the *trans* ligand into the equatorial plane. In the case of two ligands, whose oxygen atoms are *cis* to each other, already being present in a complex, a third oxygen-containing ligand may form a σ-bond in the equatorial plane only *cis* to another oxygen-containing ligand in this plane. Reactions with ligand rearrangement occur in transition element complex compounds, which differ in the nature of the atom that forms a bond of higher multiplicity ($\overset{\leftarrow}{=}$O, $\overset{\leftarrow}{=}$S, $\overset{\leftarrow}{-}$OR, $\underline{\leftarrow}$NR) with the metal, in the character of the ligand participating in the rearrangement, and in the number of oxygen-containing groups in the equatorial plane.

G. DIASTEREOMERS AND CHELATE ISOMERISM OF TUNGSTEN COMPLEXES WITH A MULTIPLE BOND

Dibasic alcohols of the 2,3-butanediol type, in contrast to ethylene glycol, contain two asymmetric carbon atoms and exist in the form of three stereoisomers: two optically active antipodes (enantiomers) and one optically inactive meso-form. Such ligands may form two diastereomeric complexes with a metal which must have different nuclear magnetic resonance spectra.

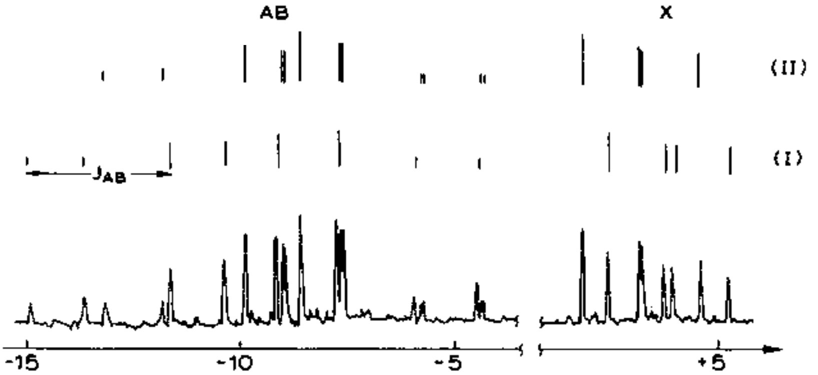
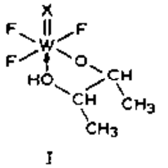


Fig. 6. ^{19}F NMR spectra of diastereomers [$WOF_3(OCH(CH_3)CH(CH_3)OH)$] (I and II).

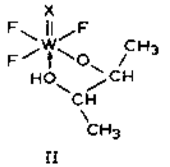
For instance, by ^{13}C NMR techniques the existence of two diastereomers for *cis*-[$Mo(CO)_4C_6H_4(AsMePh)_2$] was established [104]. For the octahedral complex anion *trans*-[$WO_2F_2(CH_3CH_2CH(CH_3)COCHCOCF_3$]$^-$ diastereotopic character of the fluorine atoms was also revealed [96].

Kokunov et al. [105] upon studying the reaction of WOF_4 and 2,3-butanediol obtained the ^{19}F NMR spectrum presented in Fig. 6. This spectrum is a superposition of two spectra of ABX type and is indicative of formation of two complexes with three non-equivalent fluorine atoms in the equatorial plane of the octahedron. The fact that the parameters of the spectra are close is an indication of considerable similarity in the structure of the complexes.

The spectra obtained are assigned to diastereomeric complexes of the composition [$WOF_3(OCH(CH_3)CH(CH_3)OH)$] differing from each other in the arrangement of the H atoms and CH_3 groups. In complex I the CH_3 groups lie in one plane, and in complex II they lie in different planes. Diastereomer II is a racemate, and diastereomer I is formally similar to a meso-form. Diastereomers of similar composition and structure were also obtained via interaction of 2,3-butanediol with WSF_4.

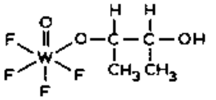


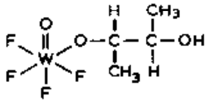
I



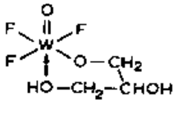
II

Introduction of an amine into a solution containing diastereomers [$WOF_3(OCH(CH_3)CH(CH_3)OH$] and HF results in an opening of the chelate ring, coordination of the fluorine ion and formation of two diastereomeric complex anions $[WOF_4(OCH(CH_3)CH(CH_3)OH]^-$ differing from each other in the arrangement of substituents at the carbon atoms.

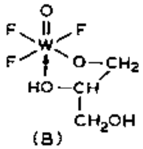




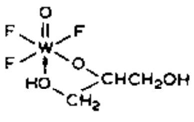
In the interaction of WOF_4 with glycerol, as followed by ^{19}F NMR spectra (Fig. 7), there are two isomeric complexes with three fluorine atoms in three non-equivalent positions and a bidentate glycerol in which oxygen atoms lie *cis trans* to the multiple bond. Since glycerol has three functional OH groups, two of the three possible isomers may correspond to the spectra obtained:



(A)



(B)



(C)

Isomer (A) has a six-membered ring and isomers (B) and (C) have five-membered rings. It was shown that reaction of WOF_4 with glycerol gave isomers (A) and (B) having 6- and 5-membered rings.

Glycerol derivatives monothioglycerol($CH_2OHCHOHCH_2SH$) and 3(*o*-methoxyphenoxy)-1,2-propanediol($CH_2OHCHOHCH_2OC_6H_4OCH_3$), inter-

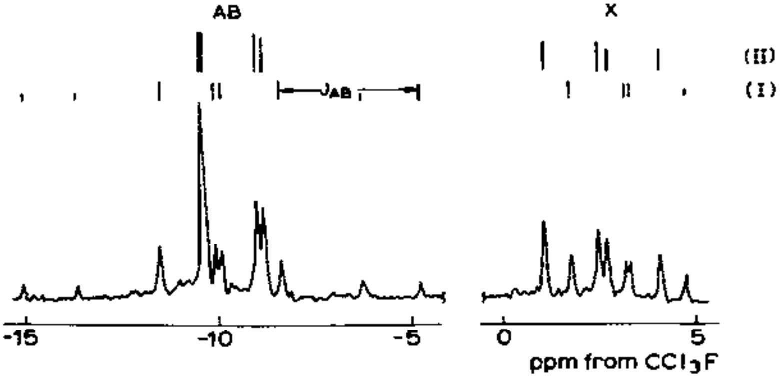
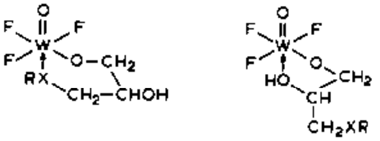


Fig. 7. ^{19}F NMR spectra of the chelate isomers of $[WOF_3(OCH_2CH(OH)CH_2OH)]$ (I and II).

acting with WOF_4, also give two isomers:

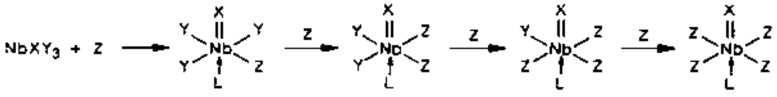


XR = SH and $OC_6H_4OCH_3$

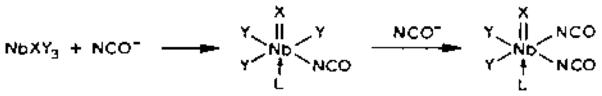
The isomers obtained with the complexes $[WOF_3(OCH_2CHOHCH_2OH)]$, $[WOF_3(OCH_2CHOHCH_2SH)]$ and $[WOF_3(OCH_2CHOHCH_2OC_6H_4OCH_3)]$ differ from each other in the size of the chelate ring. In both types of isomers the added ligands are bidentate, and *cis* to the multiply bonded oxygen atom there is the oxygen atom of the end alcohol group $—CH_2—O—$ (σ-bond with the metal atom). In the first isomer either the second end alcohol group $—CH_2—OH$ of glycerol, or the group $—CH_2—SH$ of monothioglycerol, or the ether atom of oxygen of phenoxy-substituted glycerol are attached to the tungsten atom *trans* to the multiply bonded ligand due to the donor-acceptor interaction. As a result of this a six-membered chelate ring is formed. In the other isomer the *trans* position is occupied by the middle alcohol group $(=CH—OH)$ and a five-membered chelate ring is formed.

H. EXCHANGE REACTIONS OF ACIDOLIGANDS

The presence of a multiply bonded atom in a complex favours exchange reactions in which mainly the acidoligands found in the equatorial plane participate. Buslaev et al. [106] showed with the aid of ^{51}V NMR that upon interaction of $VOCl_3$ in acetonitrile with HF and KF various vanadium oxochlorofluoride anions having the composition $[VOCl_nF_{4-n}\cdot MeCN]^-$ ($n = 0–4$) are formed. The ratio of concentration of *cis* and *trans* isomers $[VOCl_2F_2\cdot MeCN]^-$ is close to statistical. Reactions of $NbXCl_3$, $NbXBr_3$ ($X = O, S$) and of $NbSeCl_3$ with HF, KF, KNCS and KNCO in acetonitrile solution were studied by ^{93}Nb NMR [107,108]. As a result, successive substitution of the ions (Cl^-, Br^-) found in the equatorial plane of the octahedron with groups NCS^-, NCO^- and F^- ion takes place with the formation of anionic complexes with mixed ligands



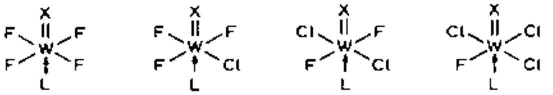
X = O, S, Se; Y = Cl^-, Br^-; Z = F^-, NCS^-



X = O, S, Se
Y = Cl^-; Br^-

A *cis*-configuration is more preferable for anionic complexes $[NbXY_2Z_2 \cdot MeCN]^-$. This complex is rather stable, and further substitution of planar ligands was observed only at high concentrations of the attacking ligand.

Buslaev and co-workers [109–111] have investigated ligand exchange reactions in systems WOF_4–$TaCl_5$, $WOCl_4$–WOF_4, WSF_4, $TaCl_5$, HF and $WSCl_4$–WSF_4, HF. In all cases the solvent was acetonitrile. In systems $WXCl_4$—WXF_4—MeCN (X = O, S) complexes of the composition $[WXF_nCl_{4-n} \cdot MeCN]$ ($n = 0$–4) are formed, and when HF acts upon $WXCl_4$, the anions $[WXF_nCl_{5-n}]^-$ ($n = 1$–5) are formed. Considering ligand exchange between $WOCl_4$ and WSF_4 in solution, the existence of oxo- and thiochlorofluorides was found. It is peculiar that in the interaction of WOF_4 with $TaCl_5$ fluorine atom pass on to tantalum and chlorine atoms to tungsten forming tantalum chlorofluorides and $[WOCl_4 \cdot MeCN]$.



X = O, S
L = MeCN, Cl⁻

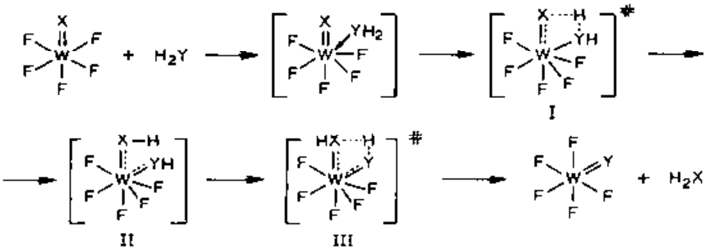
I. DIMER FORMATION

Formation in solution of stable dimeric anions with bridged fluorine atoms is highly characteristic of fluoride complexes with multiply bonded ligands. Thus, dimeric anions $[M_2O_2F_9]^-$ (M = Mo, W) were obtained from reaction of WF_6 with dimethylsulphoxide [112], $WOCl_4$ with HF in acetonitrile solution [109] and MOF_4 with acetylacetone [95]. In the reactions of solvolysis of tungsten hexafluoride, dimeric anions $[W_2X_2F_9]^-$ (with X = O, S, NR) with a bridged fluorine atom [113] are also obtained. In the interaction of $MoOF_4$ with $[WOF_5]^-$ the mixed dimeric anion $[WOF_4FMoF_4O]^-$ is formed, in which a bridged fluorine atom bonds two different metals [114]. The ^{19}F NMR data show that in dimeric anions the bridged metal—fluorine bond is of noticeably ionic character and the bridged fluorine atom is further from the metal atom than the equatorial fluorine atoms. A greater ionic character of the bridged fluorine atom bond as compared with the axial fluorine atom in $[MOF_5]^-$ was confirmed by IR spectroscopy with the complexes $NO[MOF_5]$ and $NO[M_2O_2F_9]$ (M = Mo, W) [115]. X-ray investigation of the dimeric $M[Mo_2O_2(O_2)_2C_7H_3NO_4)_2F]$ with bridged fluorine atoms (F_{bridge} *trans* to two groups Mo=O) and monomeric $NH_4[MoO(O_2)(C_7H_3NO_4)F]$ (F *trans* to M=O) showed that the difference in Mo—F distances in groups O=Mo—F—Mo=O and O=Mo—F is 0.05 Å [116].

J. SUBSTITUTION OF MULTIPLY BONDED LIGANDS

So far we have considered reactions of complexes with multiply bonded ligands, in which substitution occurred with atoms and molecules attached to the metal atom via a single bond. Substitution reactions of one multiply bonded atom by another in complex compounds of transition elements are rather rare. Thus, the interaction of compounds $[ReOCl_3(PPh_3)_2]$ and $[MoOCl_2(PMe_2Ph)_3]$ containing multiply bonded oxygen atoms with hydrazine derivatives in methyl alcohol leads to breakage of the N—N bond, substitution of the oxygen atom and formation of complexes with the multiply bonded imino-group (= NR). Buslaev et al. [119] studied reactions of WOF_4 with primary amines, of WSF_4 with amines and water, and of $[W(NBu)F_5]^-$ with water. These reactions proceed at room temperature at a high rate and are accompanied by substitution of multiply bonded ligands of one kind by multiply bonded ligands of another. Thus, in the interaction of tungsten oxofluorides with primary amines various iminofluoride complexes containing the W=NR group are formed; the multiply bonded sulphur atom in WSF_4 is easily substituted with an imino-group (=NR) and oxygen atom (=O); the reaction of $[W(NR)F_5]^-$ with water gives the complex $[WO_2F_4]^{2-}$.

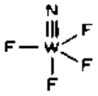
The groups M=X (metal–multiply bonded ligand), in particular, groups MO^{3+} ($M = V, Nb, Ta$), M^IO^{4+} ($M^I = Mo, W$) and $M^{II}O_2^{2+}$ ($M^{II} = Mo, W, U$) are very stable and oxygen is not displaced by acidoligands. On the other hand, the fact that multiply bonded ligands of one kind easily substitute multiply bonded ligands of another kind is worthy of attention. That reactions of substitution of multiply bonded ligands proceed in neutral or in weakly acidic and weakly basic solutions indicates that non-protonated complexes participate in these reactions. We believe that substitution of multiply bonded ligands follows one of the types of associative mechanism.



The first stage of the reaction is the formation of a seven-coordinate intermediate with *cis* arrangement of the substituting ligand which labilizes the multiply bonded ligand by protonation. Enhancement of the ability of H_2Y to proton elimination favours the transfer of H^+ from H_2Y to the atom X in the four-centre transition state (I and III). The formation of four-membered rings in I and II provides a possibility for both hydrogen atoms to be transferred from the attacking ligand to the multiply bonded ligand X with subsequent removal of H_2X. For the substitution of multiply bonded ligands X it is necessary that the attacking compound should have strong donor properties and that its composition should comprise a group containing at least two hydrogen atoms.

Kokunov et al. [120] found a reaction which leads to the substitution of a ligand forming a triple bond with a metal for a ligand with a higher multiplicity of the bond (← OR). In the interaction of tungsten alkoxy(phenoxy) fluorides with diethylamine a complex having the composition [$WF_4(OR)^+NHEt_2$] is first formed, the position of the resonance signal of which in the ^{19}F NMR spectrum is strongly dependent on the basicity of the medium.

Further introduction of an amine results in disappearance of the complex and in the ^{19}F NMR spectrum of the solution a doublet and a quartet are identified with the intensity ratio 3:1 (A_3X type of spectrum), pertaining to the complex anion $[WNF_4]^-$.



This complex contains a triple bond $W \equiv N$ and is built as a trigonal bipyramid in which three equivalent fluorine atoms lie in the equatorial plane and the fourth fluorine atom is *trans* the triple bond $W \equiv N$.

The light atoms (N, O, S) in heteroatomic groupings of d^0-transition metals have a differentiating effect on the strength of bonding of equatorial and axial ligands, which is the basis of their stereospecific behaviour.

In the stereochemistry of complexes with the multiple bond a number of specific features are manifest, which have no analogies in the chemistry of complex compounds with the partially filled *d*-shell.

Further investigation will reveal different reactivity of organic ligands and will establish kinetic characteristics of substitution reactions in such complexes.

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