Reviews

Mutual influence of metals and ligands in the complex formation of oxo anions of d-elements with chelating ligands

G. M. Larin

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117907 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: Lagema@ionchran.msk.ru

The complex-formation processes between ions of d-elements having multiple M=O bonds with bidentate monoanions, mainly 1,1-ditiolates, are considered. The data of ESR spectroscopy and X-ray diffraction analysis for this type of complexes are analyzed. Owing to the strong *trans*-effect of the M=O group, M—ligand valence bonds are not formed in the *trans*-position to the M=O group, and only donor-acceptor M—ligand bonds are realized. The valence M—ligand bonds can arise only in the equatorial plane, in *cis*-positions with thespect to the multiple M=O bond.

Key words: complexation in solutions, ESR, HFS, electronic and geometric structures, coordination compounds, oxo ions, diethyl phosphodithioate, diethyl dithiocarbamate.

Introduction

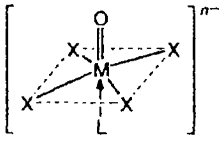
The Chernyaev *trans*-effect rule[1,2] has opened up ways for target-directed synthesis of compounds and has spurred the creation of a more general theory, the theory of mutual influence of ligands (MIL).[3–6] The problem of mutual influence can be discussed not only for ligands; it can be extended to other objects including mutual influence of ligands and the central metal atom.[7] Consideration of the MIL for transition and nontransition metals and the *trans*-effect series for various elements demonstrate that the character of this influence depends substantially on the central atom.

The mutual influence of metals and ligands is clearly manifested in the interaction of monobasic bidentate ligands with oxo ions of d-elements, which is discussed in this paper.

General items

The strongest *trans*-effect is known to be exerted by ligands forming multiple bonds with metal atoms, M=O, M=NR, M= S, *etc.*

Let us consider characteristic features of complexation of metals linked by a double bond to an oxygen atom, *i.e.*, M=O groups, where M = V^{IV}, Cr^{V}, Mo^{V}, and Re^{VI}, with monobasic bidentate organic ligands. The electronic configuration of all these metal ions is d^1 but their oxidation states are different. The unpaired electron occupies the d_{xy} orbital, which is arranged in the equatorial plane and whose lobes are directed between the ligand atoms. The coordination compounds are shaped as tetragonal pyramids or bipyramids with C_{4v} symmetry.



The central atom deviates somewhat from the equatorial plane toward the doubly bound oxygen atom. For example, the molybdenum atom in the compound $[AsPh_4][MoOCl_5]$ deviates[8] from the equatorial plane of the four chlorine atoms by 0.61 Å. The M=O distances are appreciably shortened compared to other distances and are equal to (Å): V=O, 1.62;[9] Cr=O, 1.64;[10] Mo=O,

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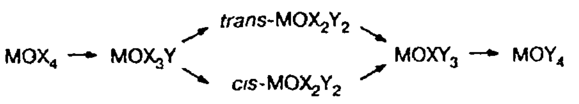
1.61;[8] Re=O, 1.62.[11] Although the M=O double bond is fairly strong, its lengths in various compounds are slightly different. Normally, the Mo=O bond lengths in coordination compounds lie in the range 1.61—1.72 Å.[8]

Replacement of monodentate acido ligands of one sort by those of another sort is a well-studied type of reaction. In particular, for coordination compounds VO^{II} and MoO^{III}, substitution of ligands Y^- for the ligands X^- in the complex MOX_n is known to occur *via* stepwise complexation during which all the $n + 2$ possible complexes are formed in solutions.[12—14]



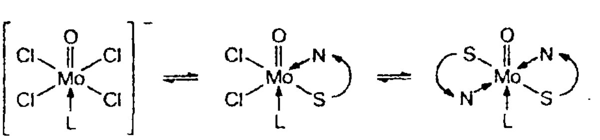
The stereochemistry of these complexes is entirely determined by the nature of the metal.

Based on the ESR data, it was found that the change in the spin Hamiltonian (SH) parameters during these substitution reactions obeys the additivity rule: upon every replacement of ligand X by ligand Y in the equatorial plane, the magnitudes of *g*-factors and the constants of the hyperfine splitting (HFS) at the central metal atom change by the same constant value.[12—14] The nature of the ligand located in the *trans*-position in relation to the oxygen atom has only a slight effect on the SH parameters.

Interaction of the oxo ions of d-elements with 1,1-dithiolates

The situation becomes somewhat more complicated on passing to the replacement of monodentate acido ligands by bidentate monobasic organic ligands. These complications are caused by several reasons. First, in the substitution reactions, bidentate ligands can be coordinated in both bidentate and monodentate ways. Second, functional groups in bidentate ligands can be represented by different atoms; therefore, it cannot be predicted *a priori* which of the two atoms would be more prone to complex formation, especially when a tautomeric equilibrium is involved. Third, the nature of the solvent can also be significant for complexation in various media.

In a study dealing with replacement of halogen atoms in $[MoOX_4]^-$ by 8-thioquinoline (tox^-) or by diethyl dithiocarbamate (ddc^-), the following stepwise complexation scheme was suggested:[15—18]



However, the structure proposed for $MoO(tox)_2Cl$ is at variance with X-ray diffraction data[19] (Fig. 1) and also with our results on the structure of complexes $MoOX_{n-m}Lg_m$, where $n = 3$, $m = 1, 2, 3$; Lg is a bidentate monobasic ligand.[20—22]

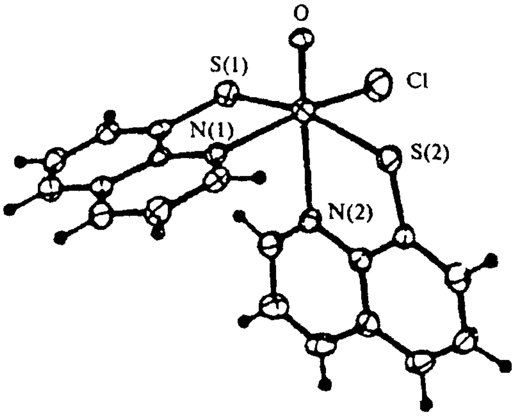


Fig. 1. Molecular structure of $MoOCl(tox)_2$.

We shall consider the substitution of a bidentate ligand for the ligands X^- in the complex $[MOX_4L]^{n-}$ based on the results obtained by ESR spectroscopy and using a particular ligand as an example. As the bidentate monobasic ligand, we chose the diethyl phosphodithioate anion $[(EtO)_2P(S)SH]$ (ddfH); this was due to several reasons. First, ddf^- links to a metal atom through one or two sulfur atoms; the introduction of sulfur atoms into the coordination sphere results in increased degrees of covalence of the metal—ligand bonds, narrowing of ESR lines, and, as a consequence, the additional HFS (AHFS) at the ligand atoms becomes better resolved. Second, the AHFS at the phosphorus atoms can be used to determine unambiguously how many bidentate ligands and in what manner are coordinated to the metal atom.

It is known[21—24] that a doublet with a ratio of component intensities of 1 : 1 and with a large AHFS constant in the spectra of complexes formed by d-element oxo ions and ddf^- (Table 1) is due to the coupling of the unpaired electron spin with the nuclear spin of the ^{31}P atom ($I = 1/2$) in the phosphodithioate anion, bound to the metal in the bidentate manner and arranged in the equatorial plane. The triplet with a similar AHFS constant and with an intensity ratio of 1 : 2 : 1 results from coupling of the unpaired electron spin with the nuclear spins of the two equivalent phosphorus atoms, which belong to two phosphodithioate anions, bound to the metal atom as bidentate ligands and arranged in the equatorial plane. It has been suggested[25] that delocalization of the unpaired electron from the metal atoms to the phosphorus atoms occurs *via* the M—S—P sequence; other researchers[26] believe that the pronounced splitting at the phosphorus atoms is largely due to the direct overlap of the $|nd_{xy}\rangle$ orbital ($n = 3, 4, 5$), which carries the unpaired electron, with the $|3s\rangle$ orbitals of the phosphorus atoms. In the case where ddf^- is coordinated bidentately, so that one sulfur atom is arranged in the equatorial plane, and the other sulfur atom occupies

Table 1. SH parameters of coordination compounds formed by oxo ions with 1,1-dithiolates

Compound	$<g>$	$<a_M>$	a_P	a_{Cl}	Ref.
			G		
$VO(ddf)_2$	1.982	92	52	—	28
$VO(ddtf)_2$	1.973	92	28	—	28
$VOCl_2(ddf)L$	1.976	100	24	—	29
$VO(ddf)_2L$	1.980	95.0	40.0	—	29
$VO(ddf)_2$	1.981	95.5	51.0	—	38
$VO(ddf)Py$	1.976	95.5	37.0	—	38
$VO(ddf)_22Py$	1.974	96.0	—	—	38
$CrOCl_2(ddf)$	1.9897	18.1	12.2	1.5	31
$CrOCl_2(ddc)$	1.9887	19.4	—	1.4	32
$CrOCl(ddc)_2$	1.9863	—	—	1.6	32
$MoOCl_2(ddc)$	1.9698	46.0	—	2.62	32
$MoOCl(ddc)_2$	1.9651	42.5	—	2.95	32
$MoOCl_2(ddf)$	1.971	45.0	46.0	2.5	22
$MoOCl_2(ddf)L$	1.964	49.0	47.0	2.9	22
$MoOCl(ddf)_2$	1.962	46.0	43.0	3.5	21
$[ReOCl_5]^-$	$g_\parallel = 1.970$, $g_\perp = 1.732$	$A^a = 638.0$, $B^a = 340.0$	—	—	40
$ReO(ddc)_4$	$g_\parallel = 2.058$, $g_\perp = 1.961$	$A^a = 406.0$, $B^a = 214.0$	—	—	35

[a] HFS constants in the parallel (A) and perpendicular (B) orientations are expressed in 10^{-4} cm^{-1}.

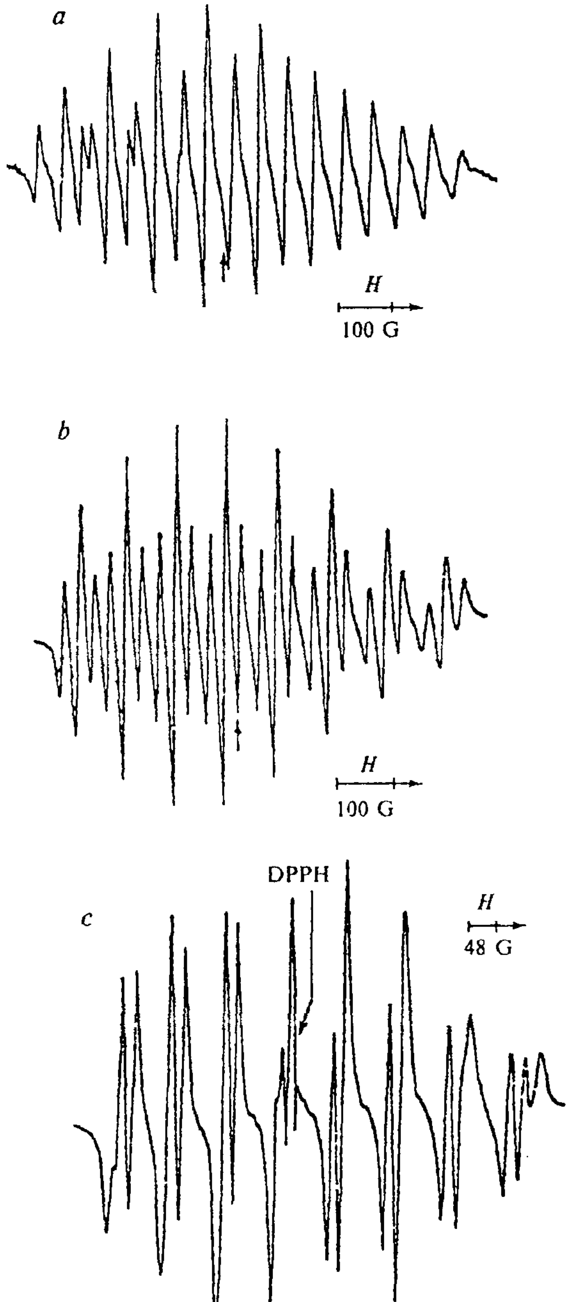


Fig. 2. ESR spectra of $VO(ddf)_2$ (a), $VO(ddtf)_2$ (b), and $[VOCl_2(ddf)]^-$ (c). The vertical arrows in all figures show the positions of the DPPH radical.

the *trans*-position to the doubly bound oxygen, or in the monodentate manner in the equatorial plane, the AHFS at the phosphorus atom is not observed.

Below we shall see that the interaction of ddf$^-$ with oxo ions depends not only on the nature of the metal and the solvent but also on whether the ligand is added as ddf$^-$ anion or as the corresponding acid.

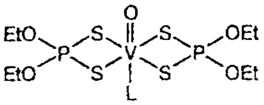
Let us consider in detail experimental data on the interaction of ddf$^-$ with the oxo ions of some d-elements.

Reaction of VO^{II} with diethyl phosphodithioate

When slightly acidified aqueous solutions of $VOSO_4$ are treated with the sodium salt ddfNa, and then the product is extracted with toluene, the extract exhibits an ESR spectrum consisting of eight triplets, which result from splitting of eight lines of the HFS due to the ^{51}V nucleus ($I = 7/2$) into three AHFS lines due to the two equivalent phosphorus atoms (Fig. 2, *a*).[24,27,28] This spectral pattern is observed irrespective of the initial VO^{II} : ddf$^-$ ratio. Due to the partial overlap of lines caused by the fact that the constant of the AHFS at the phosphorus atoms is almost half the constant of HFS at the vanadium atoms (see Table 1), the number of components decreases from 24 to 19. If diethylphosphinodithioic acid $[HS(S)PEt_2]$ (ddtfH) is used instead of the ddf$^-$ anion, the constant of the AHFS at the phosphorus atoms proves to be much smaller than half the constant of the HFS at the vanadium atoms, and the eight triplets become well resolved in the ESR spectra for solutions (Fig. 2, *b*).[28]

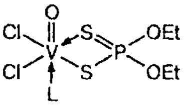
The ESR data make it possible to claim that extraction from aqueous solutions leads to the formation of only one compound, whose composition is $VO(ddf)_2L$

and whose structure is represented by formula **A**.[24,27,28] The nature of the ligand L that occupies the *trans*-position with respect to the doubly bound oxygen atom cannot be elucidated unambiguously from the ESR spectra; more likely, it is the polar solvent.



A

When the conditions of the reaction between VO^{II} and ddf^- are changed, the outcome of the reaction also changes. Thus when $[VOCl_2(MeCN)_2]$ reacts with ddfK in 1 : 1 molar ratio in acetonitrile, a complex of the composition $[VOCl_2(ddf)]^-$ (g = 1.976) appears in the solution, in addition to the initial complex (g = 1.972).[29] This is indicated by splitting of each of the eight lines of the HFS at the vanadium nucleus into two AHFS lines due to one phosphorus atom of the phosphodithioate group (Fig. 2, *c*). The presence of this set of bands and the value g = 1.976 imply that one phosphodithioate anion is coordinated as a bidentate ligand in the equatorial plane of the resulting complex, whereas two acetonitrile molecules are displaced, to give the complex $[VOCl_2(ddf)]^-$ with structure **B**.[29]



B

When the ligand : metal ratio is 2 : 1, the solution contains only vanadyl phosphodithioate $VO(ddf)_2L$. In this case, the ESR spectrum of the solution consists of eight triplets (g = 1.980) caused by the AHFS at two equivalent phosphorus atoms. Thus, the second ddf^- anion displaces two chlorine atoms from the coordination sphere of the vanadyl ion and is coordinated in the bidentate manner, being arranged in the equatorial plane; this yields a type **A** compound.

The reaction of $[VOCl_2(MeCN)_2]$ with ddfH occurs in the same way as that with ddfK but at other ligand : metal ratios. Even in the presence of a tenfold excess of the acid, the initial complex $[VOCl_2(MeCN)_2]$ predominates in the solution. At a 20-fold excess of ddfH, three complexes coexist: $[VOCl_2(MeCN)_2]$, $[VOCl_2ddf]^-$, and $[VO(ddf)_2]$. Only when the reactant ratio is 50 : 1, does the ESR spectrum indicate the presence of only $[VO(ddf)_2]$. This means that the reaction of $[VOCl_2(MeCN)_2]$ with ddfK occurs much more easily than that with ddfH.

This difference is apparently due to the following reasons: precipitation of KCl from the solution (which shifts the equilibrium toward the formation of the vanadyl phosphodithioate complex) and the higher degree of dissociation of the potassium salt in acetonitrile compared to that of the acid.[29]

Reactions of CrO^{III} with 1,1-dithiolates

When ddfH or ddfNa is added to solutions of CrO_3 in hydrochloric acid of various concentrations, and then the products are extracted with toluene, identical isotropic ESR spectra are recorded.[30,31] They consist of an intense central doublet, resulting from splitting of lines corresponding to even chromium isotopes giving an AHFS at one phosphorus atom of ddf^- bound in the bidentate manner and arranged in the equatorial plane, and less intense components on the sides, due to the ^{53}Cr isotope (I = 3/2, natural abundance 9.54%), which are also split into doublets. When the temperature decreases to 220 K, each line is additionally split into seven components with an intensity ratio of 1 : 2 : 3 : 4 : 3 : 2 : 1; this is due to the AHFS at the two equivalent chlorine atoms (Fig. 3). This spectrum permits the conclusion that a compound with the composition $CrOCl_2(ddf)L$ and structure **C** is formed in the solution.

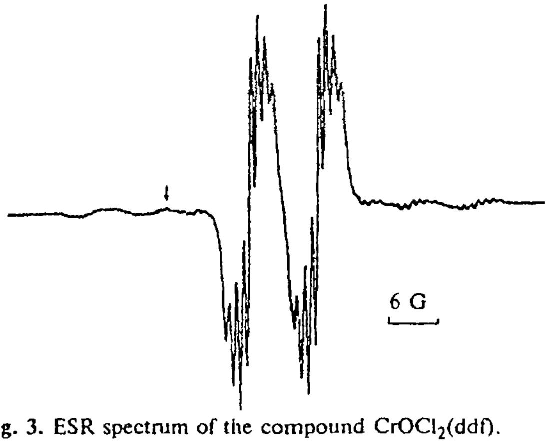
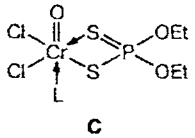


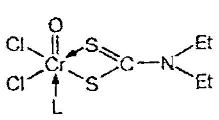
Fig. 3. ESR spectrum of the compound $CrOCl_2(ddf)$.



C

Since no other compounds of Cr^V with ddf^- could be obtained, a special study was undertaken[32] dealing with the reaction of CrO_3 with ddcNa in hydrochloric acid of various concentrations followed by extraction with toluene; this was done, because ddc^- tends to form stronger complexes than ddf^-. Decoding of the ESR spectra and determination of the SH parameters were carried out on a computer using the procedure of minimization of theoretical spectrum according to the experimental one.[33]

The product extracted from concentrated HCl in the presence of CrO_3 and ddcNa (ratio 1 : 1) is a type **C** compound of the composition $[CrOCl_2(ddc)]$. The ESR spectrum of this compound is described by an isotropic SH and contains an intense singlet, corresponding to even isotopes of chromium, and four less intense lines of the HFS at the ^{53}Cr isotope, supplemented by the resolved AHFS as a septet with an intensity ratio of 1 : 2 : 3 : 4 : 3 : 2 : 1 (Fig. 4, *a*) due to the two equivalent chlorine atoms. This compound is built as a tetragonal pyramid (structure **D**), whose base contains two Cl atoms and two S atoms of the bidentately bound ddc^- ligand. The vertex of the pyramid is occupied by the doubly bound oxygen.



D

In the range of HCl concentrations from 15 to 5% and in the

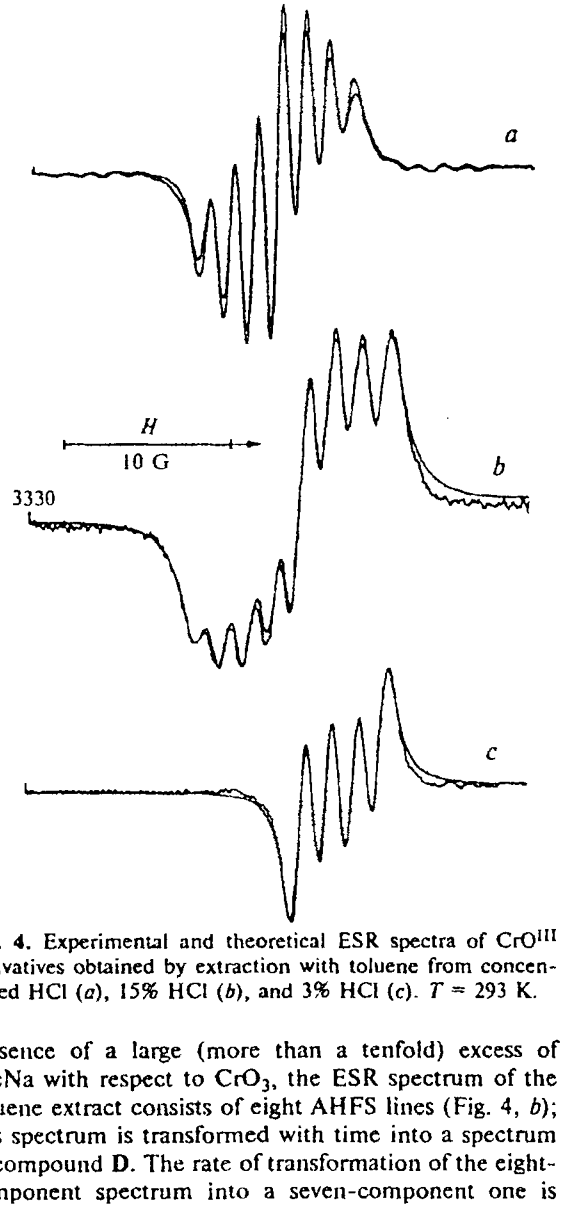
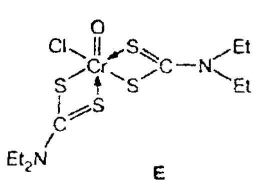


Fig. 4. Experimental and theoretical ESR spectra of CrO^{III} derivatives obtained by extraction with toluene from concentrated HCl (*a*), 15% HCl (*b*), and 3% HCl (*c*). T = 293 K.

presence of a large (more than a tenfold) excess of ddcNa with respect to CrO_3, the ESR spectrum of the toluene extract consists of eight AHFS lines (Fig. 4, *b*); this spectrum is transformed with time into a spectrum of compound **D**. The rate of transformation of the eight-component spectrum into a seven-component one is proportional to the concentration of HCl. The change in the spectral pattern indicates that at least two complexes are formed and that one of them is compound **D**. When the concentration of HCl is further decreased to 3% and the excess of ddcNa is increased, the ESR spectrum of the corresponding toluene extract consists of four AHFS lines with an intensity ratio of 1 : 1 : 1 : 1 (Fig. 4, *c*). The AHFS observed is due to the coupling of the unpaired electron spin with the nuclear spin of one of the chlorines. Thus, a decrease in the concentration of HCl and an increase in the excess of ddcNa promotes the formation of complex **E** with one Cl atom and three S atoms in the equatorial plane.



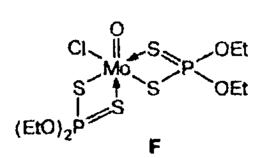
E

It is known that replacement of a Cl atom by an S atom results in a more covalent metal—ligand bond.[34] Simultaneously the *g*-factor approaches the value typical of a free electron, *viz.*, 2.0023. The smaller *g*-factor of complex **E** compared to that of compound **D** (see Table 1) indicates that one S atom of the second ddc^- ligand is coordinated in the *trans*-position to the doubly bound oxygen.[34] Thus, complex **E** is shaped like a tetragonal bipyramid.

Compound **E** is relatively unstable; its ESR spectrum disappears almost entirely over a period of 15 min. To interpret the spectrum consisting of eight lines, we constructed a theoretical spectrum as a superposition of the spectra of compounds **D** and **E**. It can be seen from Fig. 4, *b* that the theoretical and experimental spectra are identical. Therefore, in solutions in 5—15% HCl, reaction of CrO_3 with ddcNa yields simultaneously two compounds, **D** and **E**. The relative concentrations of these compounds depend on the concentration of HCl; in more dilute solutions, the initial proportion of compound **E** in the extract is higher, but as time passes, only compound **D** remains in the solution. This is apparently due to the higher stability of compound **D**. The attempts to substitute ddc^- for the last chlorine atom were unsuccessful: excess ddcNa reduced Cr^V to Cr^{III}.

Reaction of MoO^{III} with diethyl phosphodithioate

The ESR spectra of samples obtained by addition of ddfH or ddfNa to solutions of Mo^{VI} salts in hydrochloric acid of various concentrations and subsequent extraction with toluene are identical and isotropic.[21,24] They contain an intense central doublet, caused by splitting of lines due to even molybdenum isotopes into an AHFS at one phosphorus atom of the bidentately bound ddf^- ligand arranged in the equatorial plane; in addition, the spectra contain less intense components on both sides of the doublet caused by the odd $^{95,97}Mo$ isotopes (I = 5/2; natural abundance ~25%), which are also split into doublets. When the temperature is lowered to 250 K, each line is additionally split into four components with an intensity ratio of 1 : 1 : 1 : 1; these are caused by the SH splitting at the chlorine nucleus (Fig. 5, *a*). Figure 5, *c* shows one component of the doublet, which contains four clear-cut AHFS lines due to one chlorine atom. Based on this spectrum, the compound formed can be identified as $MoOCl(ddf)_2$ with structure **F**.



F

Figure 5, *b* shows the ESR spectrum of the complex of oxomolybdenum with ddf^-, prepared in the medium of concentrated HBr and extracted with toluene. The spectrum consists of an intense seven-component HFS and less intense components located on its both sides. This spectral pattern can be explained by assuming that each of the lines of the doublet caused by coupling of

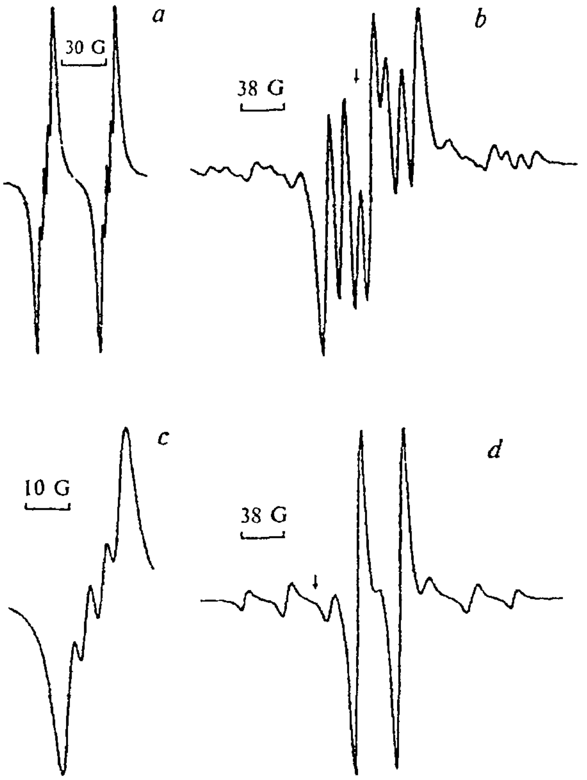
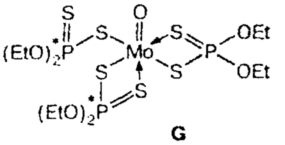


Fig. 5. ESR spectra of toluene solutions of MoO^{III}: $MoOCl(ddf)_2$ at 250 K (*a*); $MoOBr(ddf)_2$ at 293 K (*b*); a part of the doublet for $MoOCl(ddf)_2$ with the AHFS at the Cl atom (*c*); $MoO(ddf)_3$ at 293 K (*d*).

the unpaired electron with the phosphorus nucleus is split into four lines resulting from the AHFS at one nucleus of the $^{79,81}Br$ isotopes (I = 3/2; total natural abundance 100%). Thus, in this case, too, the extractable compound contains one bromine atom in the coordination sphere and has the composition $MoOBr(ddf)_2$ and a structure similar to complex **F**.

When ddf^- reacts with MoO^{III} in concentrated HF, HI, and H_2SO_4, extraction with toluene gives complex **G**. It can be seen from its ESR spectrum (Fig. 5, *d*) that AHFS at only one phosphorus atom is observed. Complex **G** can also be prepared from molybdenum compounds of type **F** by shaking their toluene solutions with solid ddfNa for several minutes. These findings, together with the fact that no AHFS at halogen atoms is manifested in the spectrum of complex **G**, make it possible to conclude that during the formation of complex **G**, the Cl^- and Br^- anions are replaced by the ddf^- anion, *i.e.*, complex **G** has the composition $MoO(ddf)_3$ and the following structure:[21]



G

The phosphorus atoms marked by asterisks do not lie in the equatorial plane; therefore, the d_{xy} orbital occupied by the unpaired electron cannot efficiently interact with them, and no corresponding AHFS is observed.[25,26] Extraction of molybdenum complexes with ddf^- from aqueous solutions never gives compounds of type **C** or **D** with one ddf^- anion and two halogen atoms in the equatorial plane.

Comparison of the results of studies of the interaction of CrO^{III} and MoO^{III} with ddc^- and ddf^- (Lg) in concentrated and dilute HCl demonstrates some difference between the chemical properties of these elements. In the case of CrO^{III}, the complex $CrOCl_2Lg$ is the most stable; the compound $CrOCl(Lg)_2$ is extremely unstable, and $CrO(Lg)_3$ is not formed at all. On going to MoO^{III}, the situation changes: $MoOCl(Lg)_2$ and $MoO(Lg)_3$ are the most stable complexes, and $MoOCl_2Lg$ exists only in nonaqueous solutions.

The compound $MoOCl_2ddf$ was obtained in the following way. When $MoOCl_3$ reacts with ddfNa in the metal : ligand molar ratio of 1 : 1, a solution in preliminary dehydrated toluene exhibits an isotropic ESR spectrum, which consists of an intense signal corresponding to the even isotopes of molybdenum and low-intensity HFS components due to odd isotopes. At room temperature, the spectrum of the solution exhibits an AHFS consisting of two lines with 1 : 1 intensity ratio, which is due to the SH coupling of the unpaired electron spin with the spin of the phosphorus nucleus in one ddf^- anion, bidentately coordinated to the Mo atom and located in the equatorial plane. At 240 K, each of the SH components due to the phosphorus atom is split, in its turn, at two equivalent Cl atoms giving seven AHFS lines (Fig. 6, *a*). The spectral pattern implies formation of a complex, whose equatorial plane contains two chlorine atoms and two sulfur atoms (complex **H**).[22]

Notice that the $<g>$ value does not conform to the rule of additive variation of g-factors for electron-donating atoms in the equatorial plane (see Table 1). This

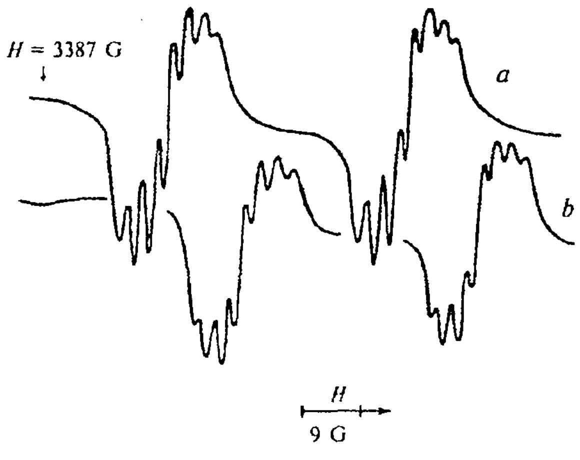
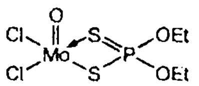
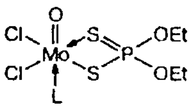


Fig. 6. ESR spectra of the complexes $MoOCl_2(ddf)$ (*a*) and $MoOCl_2(ddf)L$ (*b*) in anhydrous toluene at 240 K.

deviation is due to the influence of the off-plane ligand. Since the initial $MoOCl_3$: ddf^- ratio in the solution studied was not greater than 1 : 1 and, according to the ESR spectrum, ddf^- was coordinated in the bidentate manner in the equatorial plane, it can be inferred that in dry toluene, the *trans*-position in relation to the doubly bound oxygen atom in complex **H** remains vacant. In fact, when some ligands such as Ph_3P, Ph_3PO, $(NH_2)_2CO$, $(NH_2)_2CS$, and C_5H_5N are added to a toluene solution of complex **H**, a new ESR signal appears; this signal resembles the signal of compound **H** with an AHFS at one P atom and two equivalent Cl atoms (a doublet of sextets) but is characterized by different SH parameters, *g* and *a* (see Table 1, Fig. 6, *b*) (complex **I**). The presence of the AHFS at two equivalent chlorine atoms and a ddf^- phosphorus atom in both ESR spectra indicates that the equatorial planes of complex **H** and complex **I**, which is formed from **H** upon addition of L, contain identical ligand atoms (2 Cl, 2 S), *i.e.*, the new electron-donating ligands are not coordinated in the equatorial plane. The change in the *g*-factor observed upon the addition of a neutral ligand is due to coordination of the latter in the *trans*-position in relation to the doubly bound O atom thus giving complex **I**.


H

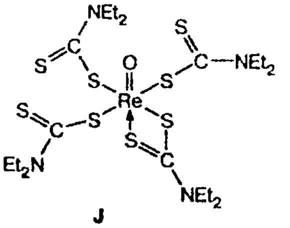

I

When the $MoOCl_3$: ddf^- ratio is 1 : 1, solutions in polar organic solvents such as ethanol, acetone, acetonitrile, *etc.*, capable of forming coordination bonds with metal atoms, exhibit only ESR signals corresponding to complex **I**.

When the ratio of the reactants, $MoOCl_3$: ddf^-, is 1 : 2 or smaller, a type **F** complex with the coordination sphere Cl3S is not formed in polar organic solvents; instead, two Cl atoms are simultaneously displaced by two anions of the acid, giving a complex of the composition $MoO(ddf)_3$. Conversely, in nonpolar solvents, a complex with the coordination sphere 4S and the composition $MoO(ddf)_3$ is not formed irrespective of the metal : ligand ratio.[22]

Reaction of ReO^{IV} with diethyl dithiocarbamate

Since the ddf^- anion reduces Re^{VI} to lower oxidation states and the ESR spectrum cannot be recorded, we had to use ddcNa instead of ddf^-. The reaction of $ReOCl_4$ with ddcNa is quite peculiar. In this case, no successive replacement of the chlorine atoms by the ddc^- anions is observed. Even at very low metal : ligand ratios (1 : 0.1), all the four Cl^- atoms are removed at the same time from the coordination sphere of rhenium, and their sites are occupied by four ddc^- anions.[35] Apparently, three of these anions are coordinated as monodentate ligands, and the fourth is bound bidentately; one sulfur atom of the latter lies in the equatorial plane, and the other one is located in the *trans*-position with respect to the doubly bound oxygen atom (compound **J**).


J

Thus, the mechanism of replacement of monodentate ligands by bidentate ligands during the reaction of $MOCl_4^{n-}$ ($M = V^{IV}, Cr^V, Mo^V, Re^{VI}$, $n = 2, 1, 0$) with bidentate monobasic organic ligands, the mode of coordination of the ligand, and the order in which the acido ligands are displaced depend, first of all, on the oxidation state of the central metal atom. However, the nature of the organic solvent also has an effect on the complexation.

Characteristic features of complexation of oxo ions

The foregoing experimental data allow the following general conclusions to be made: owing to the strong *trans*-effect of the M=O group, M—ligand valence bonds cannot be formed in the *trans*-position to the doubly bound oxygen; instead, only donor-acceptor M—ligand bonds are realized. The M—ligand valence bonds are formed only in the equatorial plane, *i.e.*, they occupy *cis*-positions with respect to the M=O double bond. Yet another specific feature of the complexation of organic ligands with d-elements is that the way of coordination of a particular chelating ligand to the metal depends on the oxidation state of the central atom. This has two consequences. First, depending on the oxidation state of the central metal atom, the equatorial plane can contain two, one, or no monobasic ligands coordinated bidentately. In some cases, an additional ligand is coordinated to the metal in the bidentate manner, one M—S bond being arranged in the equatorial plane and the other M—S bond being located in the *trans*-position with respect to the doubly bound oxygen. On the other hand, in some cases, one or three molecules of a bidentate monobasic ligand are coordinated to the metal in a monodentate manner, and the M—S bond is arranged only in the equatorial plane. Bidentate monobasic ligand never forms a single M—ligand bond located in the *trans*-position to the doubly bound oxygen.

Second, when the intermediate heteroligand complexes of the composition $MOCl_2Lg$ are formed, the geometric structure of the coordination polyhedron depends substantially on the nature of the solvent: in nonpolar solvents, pentacoordination complexes can exist, whereas in polar solvents, only hexacoordination complexes are possible.

It can be suggested that the ligand atoms that form donor-acceptor bonds with the metal cannot displace the acido ligand from the equatorial plane; in other words, the metal atom distinguishes a valence bond from a donor-acceptor bond.

It has been shown previously[2,7] that, in coordination compounds, ligand atoms bound to a metal through its common valence cannot be distinguished from those bound to the metal using its secondary valence. Thus in K_2PtCl_6, there is absolutely no difference between the four chlorine atoms bound to Pt by covalent bonds and the two atoms bound by a donor-acceptor bond. All six Cl atoms are fully equivalent. In the context of quantum chemistry, there is also no difference between these two types of bonding. For a bond to be formed between two atoms, an orbital must be possessed by each of them and a pair of electrons must be present. It makes no difference whether this pair of electrons belongs to one of these atoms or each atom has one electron. However, apparently, this rule does not hold for coordination compounds of oxo ions with organic ligands, in which the strong *trans*-effect of a doubly bound oxygen atom is manifested. If we assume that a stronger covalent bond should be formed in the equatorial plane, while a weaker (or more disperse) donor-acceptor bond can be weakened and arranged in the *trans*-position with respect to the M=O bond, it is easy to explain why in the VO^{II} complex, the equatorial plane contains two bidentate ligands, whereas in the case of MoO^{III}, there is only one bidentate ligand, and in the case of ReO^{IV}, there is none.

VO^{II} possesses two unpaired electrons for the formation of two valence bonds in the equatorial plane; the two remaining coordination sites can be occupied by ligands only due to formation of donor-acceptor bonds; therefore, two bidentate ligands are arranged in the equatorial plane.

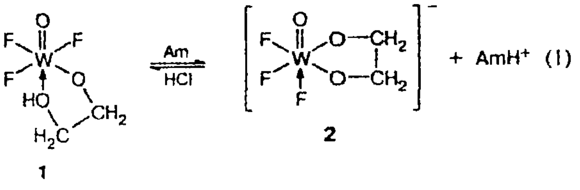
MoO^{III} has three unpaired electrons to form three valence bonds in the equatorial plane. The remaining coordination site can be occupied by a ligand only as a result of formation of a donor-acceptor bond; therefore, only one bidentate ligand can be arranged in the equatorial plane.

ReO^{IV} has four unpaired electrons, which can form four valence bonds in the equatorial plane. Thus no vacant sites for ligands to be bound to the Re atom according to the donor-acceptor pattern remain in the equatorial plane. Therefore, in the case of ReO^{IV}, the equatorial plane contains no bidentately bound ligands.

This explanation of the specific features of interaction of d-element oxo ions with monobasic bidentate chelating ligands, caused by the strong *trans*-effect of the doubly bound oxygen atom, is supported by several more experimental findings.

Let us consider the structure of the compound $MoOCl(tox)_2$ (see Fig. 1). Two identical monobasic bidentate ligands (8-thioquinoline) occupy two dissimilar positions in the coordination sphere of molybdenum. One of the tox^- ligands is coordinated through two functional atoms in the equatorial plane. The other tox^- anion is coordinated through the sulfur atom forming a valence bond in the equatorial plane and through the nitrogen atom, which occupies the *trans*-position with respect to the doubly bound oxygen atom and forms a donor-acceptor type bond. The metal—ligand distances are the following: Mo=O 1.716, Mo—Cl 2.342, Mo—S(1) 2.403, Mo—S(2) 2.411, Mo—N(1) 2.201, and Mo—N(2) 2.408 Å.[19] Thus, two tox^- ligands, coordinated to the molybdenum atom in different modes, are characterized by appreciably different lengths of the two bonds with two identical nitrogen atoms: the donor-acceptor Mo—N(2) bond located in the *trans*-position with respect to the doubly bound oxygen is more than 0.2 Å longer than the similar donor-acceptor Mo—N(1) bond arranged in the equatorial plane. This confirms the above-stated opinion that the donor-acceptor bonds can be characterized by different strengths and M—Lg distances.

Regarding the difference between valence and donor-acceptor bonds, particular interest is aroused by a study[36] in which a bidentate ligand in the coordination spheres of molybdenum and tungsten was found to be coordinated in different ways, depending on the conditions of the medium. Ethylene glycol reacts with $MoOF_4$ and WOF_4 to give a series of complexes in which it acts as a monobasic mono- or bidentate ligand. In the compound $[MOF_3(OCH_2CH_2OH)]$ (M = Mo, W), the two oxygen atoms of ethylene glycol occupy *cis*- (σ-bond) and *trans*-positions (donor-acceptor bond), respectively, in relation to the doubly bound oxygen atom.[37] Consequently, the CH_2 groups become nonequivalent: the ^1H NMR spectrum of a solution of $[WOF_3(OCH_2CH_2OH)]$ in acetonitrile exhibits two triplets with equal integrated intensities at δ 3.93 and δ 5.18; both are characterized by the splitting J = 5.5 Hz, caused by coupling of nonequivalent CH_2 groups. The signal occurring at δ_H 6.85 corresponds to the exchange between the hydrogen ion and the hydroxyl group of ethylene glycol. When an amine (Am) is added to an acetonitrile solution of $[WOF_3(OCH_2CH_2OH)]$ (**1**), the ^{19}F NMR spectrum of **1** consisting of a doublet (−8.0 ppm) and a pseudo-triplet (5.5 ppm) disappears being replaced by a new doublet at 47.0 ppm and a triplet at 107.0 ppm, both of which are characterized by the splitting J_{F-F} = 62 Hz with a ratio of intensities of 2 : 1 (Fig. 7); these signals are due to the complex *cis*-$[WOF_3(OCH_2CH_2O)]^-$ (**2**) in which two oxygen atoms of the glycol group occupy *cis*-positions with respect to the doubly bound oxygen atom.



1 **2**

Reaction (1) is reversible; when gaseous HCl is passed through the solution, complex **1** is restored. The spectra of these two complexes differ sharply from each

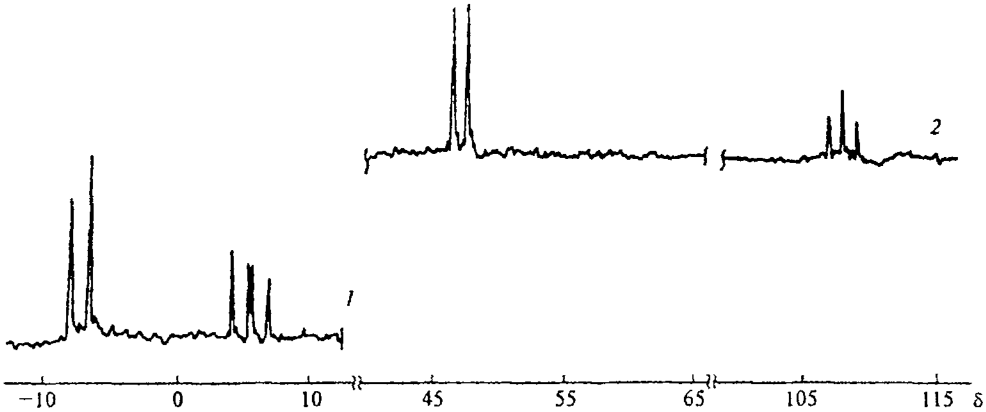
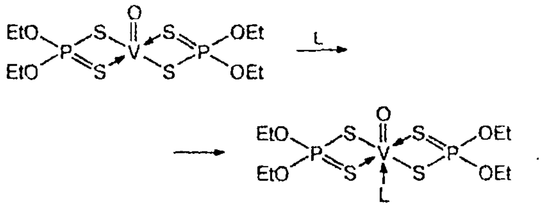


Fig. 7. ^{19}F NMR spectrum of the compound [$WOF_3(OCH_2CH_2OH)$] (*1*) and [$WOF_3(OCH_2CH_2O)$]$^-$ (*2*).

other in the chemical shifts of the triplets corresponding to the fluorine atoms that occupy the *trans*-position in relation to the O atom of the glycol ligand (complex **1**) or to the doubly bound oxygen atom (complex **2**).

Finally, the most amazing results were obtained in a study[38] of the reaction of pyridine with the complex VO(ddf)$_2$.

It is generally believed that tetragonal-pyramidal vanadyl complexes, whose equatorial planes contain two monobasic bidentate ligands, react with electron-donating bases according to the following scheme:[39]



The reactions of pyridine, 4-methylpyridine, and 4-cyanopyridine with VO(ddf)$_2$ have been studied[38] by ESR spectroscopy. It was found that two ligand molecules add to the vanadyl complex. This reaction can be schematically represented as follows:

$$VO[(RO)_2PS_2]_2 + Py \longrightarrow$$
$$\longrightarrow VO[(RO)_2PS_2]_2Py + Py \longrightarrow VO[(RO)_2PS_2]_2 \cdot 2Py.$$

It might appear that the first pyridine molecule should be coordinated to the vanadium atom in the *trans*-position with respect to the doubly bound oxygen atom. However, it is not clear what coordination site at the hexacoordinated vanadium atom could be occupied by the second pyridine molecule.

The ESR data have shown that the addition of a monobasic ligand to the vanadyl bis-phosphodithioate complex follows a different pathway. The use of ddf$^-$ as a ligand made it possible to elucidate definitely the sites of coordination of bases to the vanadium atom, because the AHFS at the phosphorus atoms of the ddf$^-$ anions can be used to check unambiguously the localization of a bidentate ligand in a solution. When VO(ddf)$_2$ is

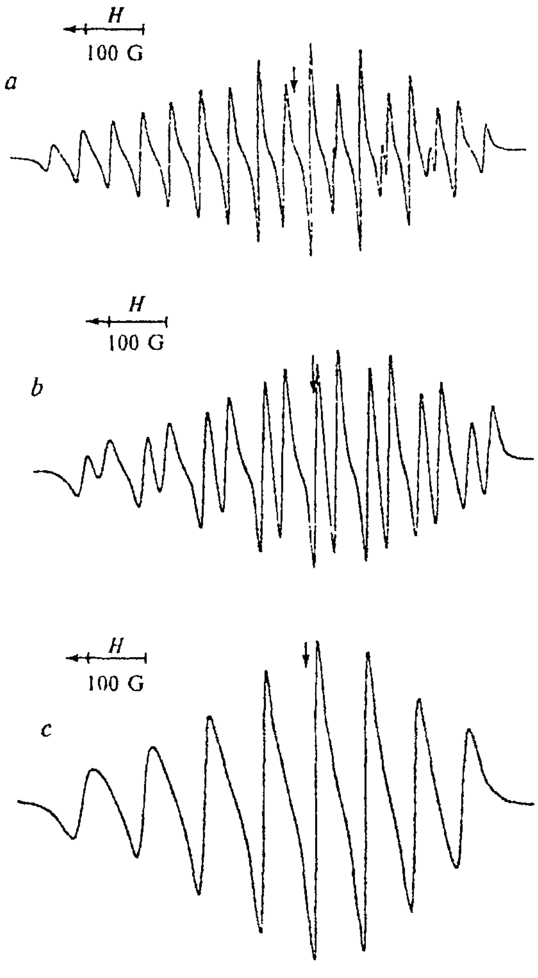
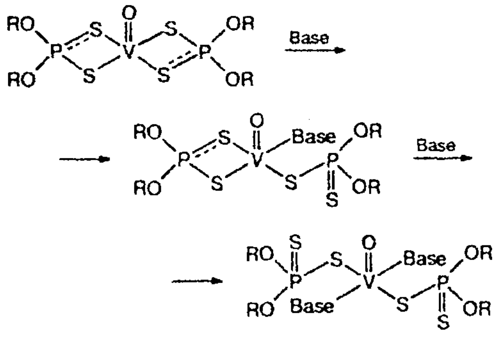


Fig. 8. ESR spectra of VO(ddf)$_2$ in toluene—pyridine solutions at 293 K: VO(ddf)$_2$ in toluene, [VO(ddf)$_2$] = 0.012 mol L^{-1} (*a*); VO(ddf)$_2$Py in toluene, [VO(ddf)$_2$] = 0.018 mol L^{-1}, [Py] = 0.36 mol L^{-1} (*b*); VO(ddf)$_2$ in pyridine, [VO(ddf)$_2$] = 0.024 mol L^{-1} (*c*).

dissolved in toluene, the resulting solution exhibits a well-known 24-component spectrum (Fig. 8, *a*), which is due to the splitting of each of the eight HFS lines corresponding to the vanadium atom into a triplet at two equivalent phosphorus atoms belonging to the two ddf$^-$ ligands. When pyridine is added, one more spectrum appears. When the concentration of pyridine increases, the intensity of the 24-component spectrum declines, and at the Py : V = 10 : 1 ratio, it entirely disappears, and the new spectrum contains eight doublets (Fig. 8, *b*): eight HFS lines due to the vanadium nucleus are split into a doublet at one phosphorus atom. When the Py : V ratio increases to above 100, the 16-component spectrum also disappears, and a new spectrum consisting of eight HFS lines due to the vanadium atom appears instead (Fig. 8, *c*). A similar spectrum is also observed for a solution of VO(ddf)$_2$ in pyridine. Similar results have been obtained for other bases.

Thus, during the reaction of VO(ddf)$_2$ with pyridine in toluene, one V—S bond of the donor-acceptor type is cleaved first, and a stronger V—N bond of the same type is formed instead. Since one ddf$^-$ ligand is bound to vanadium according to a monodentate pattern, the AHFS at one of the phosphorus atoms disappears. In the presence of a large excess of pyridine, the V—S donor-acceptor bond with the other ddf$^-$ ligand is cleaved, and this ligand also gets linked to vanadium in a monodentate manner. The AHFS at the second phosphorus atom also disappears, and the spectrum now exhibits only the HFS due to the vanadium nucleus; this can be explained in terms of the following scheme.[38]



It can be seen from the above that during the reactions of d-element oxo ions with monobasic bidentate ligands, the mutual influence of the ligands is manifested in the fact that a ligand can enter the *trans*-position to the doubly bound oxygen atom only if it forms a donor-acceptor bond. The mutual influence of metals and ligands is manifested in the fact that the manner of coordination of a monobasic bidentate ligand is determined by the nature or the valence capacity of the metal.

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