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STUDY OF EQUILIBRIA AND KINETICS OF LIGAND EXCHANGE REACTIONS OF COORDINATION COMPOUNDS IN SOLUTION BY ELECTRON SPIN RESONANCE

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The dependences of the g-factors and HFS constants upon atomic numbers, charges and effective charges of the ligands are discussed. The main results of the investigations of ligand substitution reactions in coordination compounds of Cu(II), Mo(V), V(IV), Co(II), Ni(III) and other paramagnetic ions by ESR are reviewed. The mechanisms of the substitution reactions of the bidentate ligands in the planar complexes of Cu(II), Pd(II) are discussed.

One of the central problems of coordination chemistry is the behaviour of coordination compounds in solution. This problem determines the development of some theoretical and practical aspects of coordination, inorganic and analytical chemistry. Successful solution of this problem is connected with direct detection of the various species of a given metal ion coexisting in solution and their mutual interchange. Nuclear magnetic resonance and electron spin resonance give new possibilities for the solution of this problem. Beginning from 1964, the principles of an ESR method for studying complex formation in solution and for determination of the electronic structure of coordination compounds have been developed in our Laboratory. The dependence of ESR parameters upon the nature of metal and ligands is a basis for the investigation of complex formation. Such data were obtained for coordination compounds with a d^1 electron configuration of the metal ion. As the atomic number of the ligand increases, the g-factor increases and the hyperfine coupling constant decreases (Table 1).

TABLE 1. ESR parameters of the complexes $MeOX_4Y'$

$MeOX_4Y'$	g	$g_{\parallel}$	$g_{\perp}$	$A\cdot10^4$ cm^{-1} A	$A_{\parallel}$	$A_{\perp}$
1	2	3	4	5	6	7
$CrOF_4Y'$	1.9646	1.959	1.968	23.1	-	-
$CrOCl_4Y'$	1.9877	2.0085	1.977	18.5	36.1	9.7
$MoOF_4Y'$	1.907	1.874	1.918	62	100	48
$MoOCl_4Y'$	1.948	1.970	1.940	47.0	75.0	33
$MoOBr_4Y'$	1.994	2.090	1.945	41.7	66.0	29.6
$MoOI_4Y'$	2.058	2.274	1.953	-	50	-

1	2	3	4	5	6	7
$MoO(HSO_4)_4Y$	1.921	1.898	1.938	57.5	92	40
$MoO(thio)_4Br$	1.975	2.0144	1.955	36	58	26
$MoO(HD_2)Y'$	1.974	1.943	1.990	37.8	-	-
$MoO(NCS)_4Y$	1.937	1.931	1.939	43	69.5	30

The charges are omitted.
Thio = Thiourea, H_2D = dioxime.

This dependence was explained by an extended theory of g-factor, taking into account spin-orbit coupling on the metal ion, spin-orbit coupling on the ligands and charge transfer from the filled orbitals. The expression for $g_{\parallel}$ is

$$g_{\parallel} = g_e - g_{\parallel}^{\xi m} + g_{\parallel}^{\xi l} + g_{\parallel}^{\varkappa \xi m} + g_{\parallel}^{\varkappa \xi l}$$

where g_e - g-factor of the free electron

$g_{\parallel}^{\xi m}$ - contribution to $g_{\parallel}$ from spin-orbit coupling on the metal ion

$g_{\parallel}^{\xi l}$ - contribution to $g_{\parallel}$ from spin-orbit coupling on the ligands

$g_{\parallel}^{\varkappa \xi m}$ and $g_{\parallel}^{\varkappa \xi l}$ - the corresponding contributions from charge transfer.

As the atomic number of a ligand increases, the values of $g_{\parallel}^{\xi l}$, $g_{\parallel}^{\varkappa \xi m}$, $g_{\parallel}^{\varkappa \xi l}$ increase. The dependences of the g-factor upon the ligand type were obtained also for Ni(III) and Co(II) dioximates (Tables 2 and 3).

TABLE 2. ESR parameters of mixed complexes of Ni(III) (A values in 10^4 cm units)

Complex	$g_{\parallel}$	$g_{\perp}$	g calc	$A_{\parallel}^{A}$	$A_{\perp}$	Nucleus
$Ni(Hdpg)_2X_2^+$	2.026	2.210	-	-	-	-
$Ni(Hdpg)_2XCl$	2.024	2.188	2.195	31	-	$^{35,37}Cl$
$Ni(Hdpg)_2Cl_2$	2.022	2.180	-	29	-	$^{35,37}Cl$
Ni(Hdpg)BrX	2.022	2.177	2.175	161,170	47	$^{79,81}Br$
Ni(Hdpg)BrPy	2.022	2.148	-	157,170, 21	41	$^{79,81}Br$ ^{14}N
$Ni(Hdpg)_2Br_2$	2.020	2.139	-	147,159, 154	34	$^{79,81}Br$
$Ni(Hdpg)_2XI$	2.015	2.232	-	191	70	^{127}I
$Ni(Hdpg)_2IPy$	2.014	2.216	-	189,20	64	^{127}I, ^{14}N

H_2dpg = dipropylglyoxime
X = CH_3CH_2OH

TABLE 3. ESR parameters of cobalt(II) dimethylglyoximetes(H_2dmg)

Complex	$g_{\parallel}$	$g_{\perp}$	$A \cdot 10^4$ cm^{-1}		
			A_{av}	$A_{\parallel}$	$A_{\perp}$
$Co(Hdmg)_2Cl^{2-}$	2.009	2.346	118	61	18
$Co(Hdmg)_2Br^{2-}_2$	2.009	2.326	124	107	93
$Co(Hdmg)_2I^{2-}_2$	2.007	2.246	117		117
$Co(Hdmg)_2O_2I^{-}$	2.006	2.345	132	99	88
$Co(Hdmg)_2(SeCN)^{2-}$	2.005	2.243	110	35	78
$Co(Hdmg)_2(SCN)^{2-}$	2.005	2.242	120	26	-
$Co(Hdmg)_2(ClO_4)^{2-}_2$	2.008	2.305	113	46	

The dioximates of Ni(III) and Co(II) have d^7 electron configuration and the unpaired electron is in a d_{z^2} ground state. For this case the $g_{\perp}$ and $A_{\perp}$ depend strongly upon the nature of the ligand.

An important regularity is the dependence of ESR parameters upon the number of the given ligands. This permits a direct determination of the various forms of a given metal in solution. The g-factors and HFS constants A of mixed complexes of oxocations having C_{4V} symmetry can be calculated using the following expressions

$$g_{MeOX_{4-j}Y_jY'} = (4-j)/4 \quad g_{MeOX_4Y'} + (j/4)\ g_{MeOY_jY'}$$

$$A_{MeOX_{4-j}Y_jY'} = (4-j)/4 \quad A_{MeOX_4Y'} + (j/4)\ A_{MeOY_jY'}$$

The same formulas were obtained for $g_{\parallel}$ and $A_{\parallel}$. The g-factor and A-constant of mixed complexes with bidentate ligands were calculated by the equations

$$g_{MLL'} = (g_{ML_2} + g_{ML'_2})/2$$

$$A_{MLL'} = (A_{ML_2} + A_{ML'_2})/2$$

In most cases the calculated and experimental g-factors and A-constants are in good agreement (Table 4).

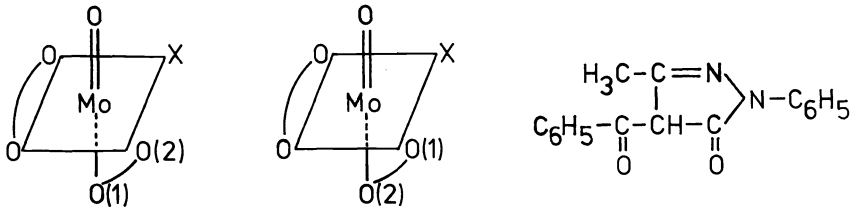
TABLE 4. The experimental and calculated $g_{\parallel}$ and g values of $MoOX_4Y$ complexes

Complex	g		$g_{\parallel}$	
	exper.	calc.	exper.	calc.
1	2	3	4	5
$MoOCl_4Y'$	1.949	-	1.970	-
$MoOCl_3BrY'$	1.960	1.960	2.000	2.000
$MoOCl_2Br_2Y'$	1.970	1.971	2.030	2.030
$MoOClBr_3Y'$	1.983	1.983	2.060	2.060
$MoOBr_4Y'$	1.994	-	2.090	-
$MoOF_4Y'$	1.908	-	1.882	-

1	2	3	4	5
$MoOF_3BrY'$	1.930	1.930	-	1.934
cis-$MoOF_2Br_2Y'$	1.954	1.951	2.007	1.986
trans-$MoOF_2Br_2Y'$	1.944			
MoOFBr3Y'	1.974	1.973	2.042	2.038

The rule of additivity cannot predict the ESR parameters for the cis- and trans-isomers. However, besides this restriction rules of additivity are extremely useful for prediction of the ESR parameters of mixed complexes.

For the same donor atom, having different charges, the ESR parameters are different. This dependence gives a possibility to identify by ESR the mixed complexes having in the coordination sphere the same donor atoms with different charges. The mixed complexes of Mo(V) with phenylmethylbenzylpyrazolone (HPMBP) having the composition $MoO(PMBP)_2Cl$ are an interesting example. It was stated that in the solutions there are two isomers having different ESR parameters



The superhyperfine structure (SHFS) of the ESR spectrum gives direct information about the complex composition. It is possible to determine the nature and number of ligand atoms, from which the SHFS is observed from the number of SHF lines and their intensity ratio. A SHFS of the ESR spectrum of a mixed complex is observed when there is a SHFS in the ESR spectrum of the parent complex (Tables 2 and 3). This is a very important and useful rule. It is interesting to note that the SHFS constant depends on the number of ligands (Table 5).

TABLE 5. Dependence of the SHFS constant on the number of ligands

Complex	SHFS constant $A \cdot 10^4$ cm^{-1}
$MoOF_4Y'^{2-}$	$11(^{19}F)$
$MoOF(Thio)_3Y'^{2+}$	$19(^{19}F)$
$MoOF(Tox)_2Y'^{o}$	$25.6(^{19}F)$
$MoO(H_2PO_4)_3(Thio)Y'^{o}$	$3.7(^{31}P)$
$MoO(H_2PO_4)(Thio)_3Y'^{2+}$	$4.1(^{31}P)$
$MoO(H_2PO_4)(Thio)_2Y'^{2+}$	$16.6(^{14}N)$
$Cu(Tox)_2$	$14(^{14}N)$
$Cu(Tox)\ (mnt)^-$	$11.5(^{14}N)$

H Tox = mercaptoquinoline

This indicates that the covalency of a metal ligand bond changes when the number of the given ligands changes.

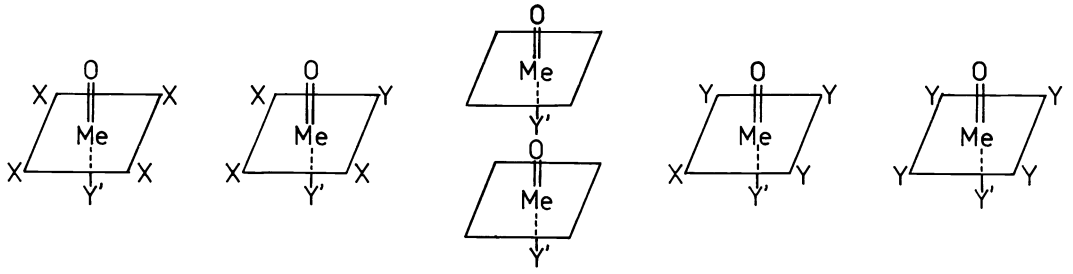
These regularities determine the role of ESR as a new method of investigation of the properties and structure of coordination compounds in solution. These regularities were applied for the investigations of the equilibria and mechanisms of stepwise substitution of ligands in the paramagnetic coordination compounds of Cr(V), Mo(V), W(V), V(IV), Re(VI), Cu(II), Ag(II), Ni(III), Co(II) and others.

One of the classes of compounds for which the substitution of monodentate ligands was studied, were coordination compounds of oxocations of Mo(V), Cr(V) and V(IV) with inorganic ligands. The mixed complexes formed in the reactions

$$MeOX_4Y'^{2-} + Y^- \rightleftharpoons MeOX_{4-j}Y_jY'^{2-} + jX^- \qquad (1)$$

(Y' - out-of-plane ligand)

were studied. It was shown that for these coordination compounds all of the possible mixed ligand complexes are formed according to the scheme.



All these compounds are labile. In such systems there exist labile cis- and trans-isomers. This interesting fact was new not only in the chemistry of Mo(V), but in ESR-spectroscopy as well. The equilibrium constants of reactions (1) were determined from ESR data (Table 6).

TABLE 6. The successive constants κ_j and the constants K_M of the reactions

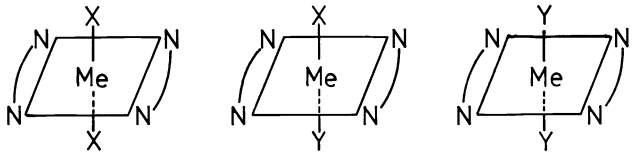
$4-j/4\ MeOX_4Y'^{2-} + j/4\ MeOX_4Y'^{2-} \rightleftharpoons MeOX_{4-j}Y_jY'^{2-}$;

$\log K_s = \log K_m - \log K_{stat}$

Complex	κ_j	K_m	$\log K_s$
1	2	3	4
$MoOCl_4Y'$			
$MoOCl_3BrY'$	0.36	2.3	-0.16
$MoOCl_2Br_2Y'$	0.28	4.3	-0.15
$MoOClBr_3Y'$	0.12	3.4	-0.07
$MoOBr_4Y'$	$4.5\cdot10^{-2}$		
$MoOCl_4Y'$			
$MoOCl_3(H_2PO_4)Y'$	1.9	5.03	+0.10
$MoOCl_2(H_2PO_4)_2Y'$	0.6	7.75	+0.11
$MoOCl(H_2PO_4)_3Y'$	$3\cdot10^{-1}$	5.55	+0.14
$MoO(H_2PO_4)_4Y'$	$0.7\cdot10^{-1}$		

For many systems the distribution of mixed ligand complexes is close to statistical. For all systems the ESR parameters calculated by the rule of additivity are in good agreement with the experimental parameters.

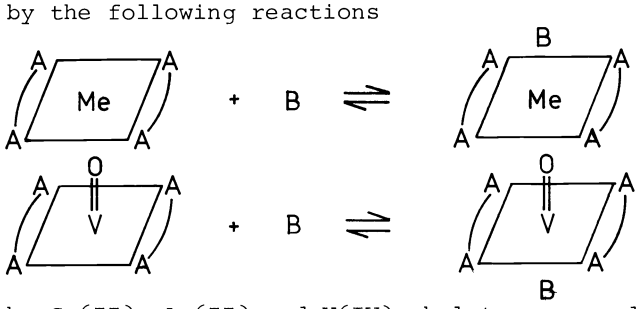
Other interesting coordination compounds for which the substituion reactions of monodentate ligands were studied are the dioximates of Co(II) and Ni(III) having the compositions $Co(HD)_2X_2^{2-}$ and $Ni(HD)_2X_2^-$ (Tables 2 and 3). The groups $Co(HD)_2$ and $Ni(HD)_2$ are very stable and do not change by the substitution reactions of the axial ligands.



(3)

(the hydrogen bonds are omitted).

The adducts were other coordination compounds studied by ESR. The adduct formation occurs by the following reactions



(4)

(5)

Many adducts of the Cu(II), Ag(II) and V(IV) chelates were determined by ESR. The thermodynamic regularities of their formation and the correlations between the ESR parameters and pK of the chelating ligand and pK_a of the donor base were established. The stability of the chelate adducts decreases from $Cu(O,O)_2$ to $Cu(N,O)_2$ and $Cu(S,S)_2$ (Table 7).

TABLE 7. The formation constants of the complexes CuA_2B in a chloroform + toluene mixture

T, K	$Cu(dtc)_2py$	$Cu(oxin)_2py$	$Cu(Dbm)_2py$
333	0.15	3.0	3.9
323	0.20	5.0	5.7
313	0.21	5.2	7.0
303	0.27	-	-
273	-	-	25

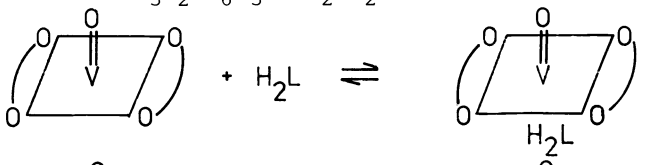
H oxin = hydroxyquinoline

The β-diketonates of VO(II) in DMF solution form the adducts $VO(\beta\text{-dik})_2 \cdot DMF$. The HFS constant decreases and the g-factor increases in comparison with the ESR parameters of $VO(\beta\text{-dik})_2$ (Table 8).

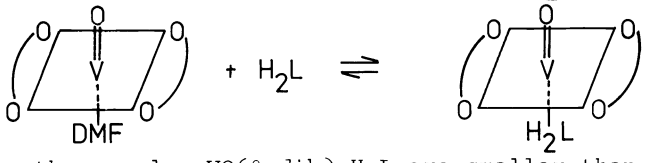
TABLE 8. The values of $g_{\parallel}$ and $A_{\parallel}$ for β-diketonates of oxovanadium (IV) and their adducts

β-diketone	$VO(\beta\text{-dik})_2$		$VO(\beta\text{-dik})_2$ DMF		$VO(\beta\text{-dik})_2 \cdot H_2$ xydt	
	$g_{\parallel}$	$A_{\parallel} \cdot 10^4$ cm^{-1}	$g_{\parallel}$	$A_{\parallel} \cdot 10^4$ cm^{-1}	$g_{\parallel}$	$A_{\parallel} \cdot 10^4$ cm^{-1}
HAcac	1.942	171	1.946	169	1.942	174
HDbm	1.941	174	1.941	171	1.938	176
HBA	1.947	170	1.947	167	1.942	174

The compounds $VO(\beta\text{-dik})_2$ and $VO(\beta\text{-dik})_2DMF$ form with the dithiols $CH_3C_6H_3(SH)_2(H_2bdt)$ and $(CH_3)_2(C_6H_3(SH)_2(H_2xydt)$ the adducts



(6)

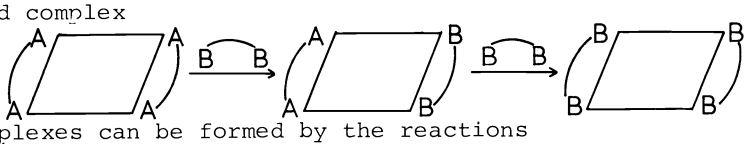


(7)

The $g_{\parallel}$-factors for the complex $VO(\beta\text{-dik})_2H_2L$ are smaller than the $g_{\parallel}$-factor for $VO(\beta\text{-dik})_2$. Probably, this is due to spin-orbit coupling on the sulphur atom and charge transfer.

We have studied other aspects of complex formation in solution, which are connected with specific substitution of the monodentate ligands by bidentate and bidentate by bidentate ligands. The planar complexes of Cu(II), pyramidal and octahedral complexes of VO^{2+} and MoO^{3+} were studied.

A scheme of a substitution of the bidentate ligands includes a formation only one mixed complex



(8)

The mixed complexes can be formed by the reactions

$$Cu(AA)_2 + Cu(BB)_2 \rightleftarrows 2Cu(AABB) \quad (9)$$

$$VO(AA)_2 + VO(BB)_2 \rightleftarrows 2VO(AABB) \quad (10)$$

or by the reactions (8).

These mixed complexes of copper (II) are usually formed in solution. There are three types of reactions:

(1)The formation constant of a mixed complex is close to the statistical value. This is true for ligands forming chelate rings of the same size (Table 9).

(2) The formation constant of a mixed complex is much greater than the statistical value. This stabilization effect for the Cu(II) complexes is observed when the ligands form four- and five-membered rings.

$$Cu(mnt)_2^{2-} + Cu(Et_2dsc)_2 \rightleftarrows 2Cu(mnt)(Et_2dsc)^-$$

$$Cu(Dmt\text{-}i)_2^{2-} + Cu(Et_2dsc)_2 \rightleftarrows 2Cu(Dmt\text{-}i)(Et_2dsc)^-$$

$$Cu(Dmt)_2^{2-} + Cu(Etdsc)_2 \rightleftarrows 2Cu(Dmt)(Et_2dsc)^-$$

$$Cu(acac)_2 + Cu(cupf)_2 \rightleftarrows 2Cu(acac)(cupf)$$

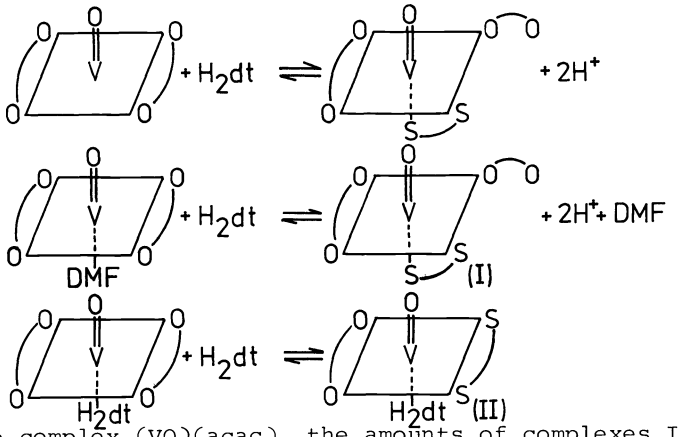
$$Cu(mnt)_2^{2-} + Cu(tox)_2 \rightleftarrows 2Cu(mnt)(tox)^-$$

TABLE 9. ESR parameters of mixed complexes of Cu(II) and their equilibrium constants in acetonitrile (1), acetone (2), benzene (3) and $CHCl_3$+acetone (4)

Complex	g		$A\cdot10^4 cm^{-1}$		K
	exp.	calc.	exp.	calc.	
$Cu(Et_2dtc)_2$	2.046		74.2		3.2±0.7 (1)
$Cu(Etdsc)_2$	2.021		75.1		3.4±0.3 (2)
$Cu(Et_2dtc)(Et_2dsc)$	2.033	2.034	74.6	74.8	3.7±0.6 (3)
$Cu(i\text{-}mnt)_2^{2-}$	2.047		73.8		6.1±0.7 (1)
$Cu(Et_2dsc)_2$	2.022		74.1		6.5±1 (4)
$Cu(i\text{-}mnt)(Et_2dsc)^-$	2.034	2.035	73.2	73.9	8.8±1.9 (3)
$Cu(Ced)_2^{2-}$	2.045		73.1		
$Cu(i\text{-}mns)_2^{2-}$	2.021		75.2		3.8±0.6 (1)
$Cu(Ced)(i\text{-}mns)^{2-}$	2.033	2.033	73.5	74.1	5.1±0.3 (2)

(3) The formation constant of a mixed complex is smaller than the statistical value. This is a destabilization effect. A destabilization effect is observed when the properties of the donor atoms are very different.

The substitutions of the bidentate ligands were studied for the complexes $VO(\beta\text{-dik})_2$ and $H_nL=H_2tdt$, H_2xydt, Htox, H_2mnt. It is interesting to note that aromatic dithiols form adducts by reactions (3) and (4). The following reactions take place in parallel to reactions (3) and (4)



In case of the complex $(VO)(acac)_2$ the amounts of complexes I and II are small, but in the general case the amounts of complexes I and II depend on the β-diketone. A weak destabilization of VO(PMBP)(tox) takes place by the reaction

$$VO(PMBP)_2 + HTox \rightleftarrows VO(PMBP)(Tox) + HPMBP \qquad (14)$$

$k=1.8\pm0.5$

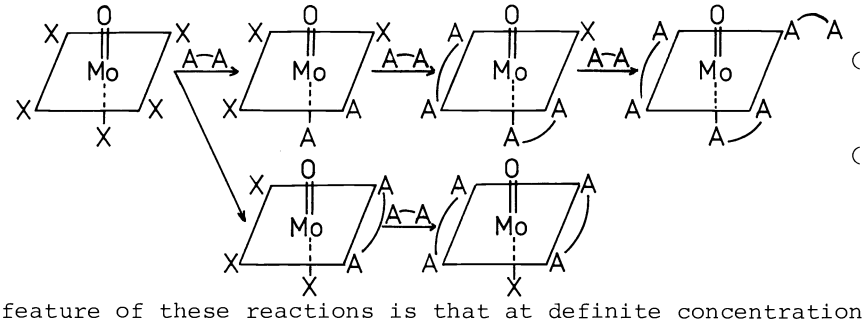
A strong destabilization of a mixed ligand complex occurs in the reaction

$$VO(acac)_2 + mnt^{2-} \rightleftarrows VO(acac)(mnt) + acac^- \qquad (15)$$

$$k=(5\pm1)\cdot10^{-2}$$

The substitution reactions of monodentate by bidentate ligands were studied for $MoOX_4Y'^{2-}$ complexes with H_nL=H -dik, HTox, H_2mnt, H_2D and others. All these reactions are very complicated and specific. It is interesting to note that the first bidentate ligand occupies both in-plane and out-of-plane positions.

The full scheme of these reactions is



(16)

(16a)

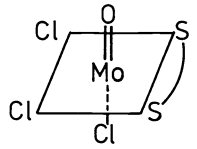
A specific feature of these reactions is that at definite concentrations of ligand A-A, there exists in solution only one complex I or III and the amounts of the others complexes are small. In Table 10, ESR data for Mo(V) mixed β-diketonates in acetone are given.

TABLE 10. ESR parameters of mixed complexes of $MoOI_5^{2-}$ with β-diketones

β-dik	Complex						
	I		II	III	$MoO(\beta\text{-dik})_2(\beta\text{-dik})$		
	g	$g_{\parallel}$	g	g	g	$g_{\parallel}$	$g_{\perp}$
HAcac	2.038	2.190	-	1.973	1.935	1.921	1.945
HBA	2.041	2.183	1.997	1.971	1.935	1.922	1.944
HDbm	2.040	2.188	1.998	1.972	-	-	-
HTTA	2.044	2.208	2.000	1.975	1.936	-	-
HDPM	2.040	-	1.996	1.970	-	-	-
HPMBP	2.042	2.207	1.993	1.975	1.935	1.921	1.945
		2.186		1.968			

The substitution of monodentate ligands by HTox occurs in general according to scheme (16). But the real substitution scheme can be more complicated due to the unequivalent donor atoms.

The scheme (16a) is valid for H_2mnt. It was observed the formation of the complex



(k = 2.0±0.5, acetonitrile).

The kinetics of substitution reactions was much less studied by ESR. In

connection with the investigation of copper (II) mixed complexes, the kinetics of reactions (9) were studied. It is necessary to note that reactions (9) for Cu(II) complexes are very fast. But the reactions between the paramagnetic complexes of copper (II) and the diamagnetic complexes and Ni(II), Pd(II) and Pt(II) are quite slow. This gives a possibility to study the kinetics of the reactions

$$Cu(mnt)_2^{2-} + M(i\text{-}mns)_2^{2-} \rightleftarrows Cu(mnt)(i\text{-}mns)^{2-} + M(mnt)(i\text{-}mns)^{2-} \quad (17)$$

$$Cu(Et_2dsc)_2 + M(mnt)_2^{2-} \rightleftarrows Cu(Et_2dsc)(mnt)^- + M(Et_2dsc)(mnt)^- \quad (18)$$

It is very interesting that the kinetic curve of the accumulation of the mixed complex in reactions (17) and (18), where M=Pd, in acetonitrile at temperatures below 50°C are S-shaped and hence cannot be described by kinetic equations for second order reactions. The following facts are very substantial for the mechanism of reactions (17) and (18):
1. The addition of free ligands L or L′ strongly decreases the rates of reactions (17) and (18); 2. The addition of free solvate ions of copper (II) strongly enhances exchange reactions; 3. The lower the temperature, the longer the first part of the kinetic curves. These results cannot be described by a four-center mechanism.

The following mechanism is suggested

$$CuL_2 \rightleftarrows CuL + L \quad (19)$$

$$PdL'_2 \rightleftarrows PdL' + L' \quad (20)$$

$$CuL + PdL'_2 \rightleftarrows CuLL' + PdL' \quad (21)$$

$$PdL' + CuL_2 \rightleftarrows PdL'L + CuL \quad (22)$$

$$CuL + L' \rightleftarrows CuLL' \quad (23)$$

$$PdL' + L \rightleftarrows PdLL' \quad (24)$$

List of ligands

R_2dtc = Dialkyl-dithiocarbamate
R_2dsc = Dialkyl-diselenocarbamate
R_2tsc = Dialkyl-thioselenocarbamate
i-mnt = Iso-maleonitrile-dithiolate
i-mns = Iso-maleonitrile-diselenolate
i-mnts = Iso-maleonitrile-thioselenolate
ced = 1-Cyano-1-carboethoxyethelene-2,2′dithiolate.