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X-Ray Photoelectron Study of *Trans*-Influence of the Re–Re Multiple Bond

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In Refs. [1–3] the metal–metal bond in d^7–d^7 complexes of Rh(II) and Pt(III) compounds was shown to weaken the bonding of axial ligand with Rh or Pt atom, this effect, in turn, leading to decrease in inner shell electrons binding energies of axial ligands. In Tables I and II [1–3] some data are presented illustrating this point. In the case of neutral donor ligands (Table I) the weakening of metal bonding with axial ligand is manifested by decrease in electron density transfer from ligand to metal. For this reason the inner electrons binding energies for ligand atom, which is the donor, are lower for Rh(II) and (Pt(III) complexes than for compounds where the *trans*-influence is absent. In the case of acidoligands (Table II) the ionic character of metal–axial ligand bond is enhanced, the binding energies of ligand inner electrons decrease and tend to values which are characteristic of ionic salts.

In Rh(II) and Pt(III) binuclear complexes of d^7–d^7 configuration the metal–metal bond is a simple σ-bond [4]. In the Re(III) complexes of $Re_2ac_4L_2$ or $Re_2ac_2Hal_4L_2$ type (Table III) with d^4–d^4 configuration there is Re≡Re quadrupole bond*. It is of interest to study the Re–Re bond *trans*-influence as manifested by X-Ray photoelectron spectral of axial ligands L.

Experimental data are presented in Table III. The C1s line of 285.0 eV binding energy was used as standard. By analysis of Table III data the following conclusions can be derived.

1. The binding energies for acidoligands in axial position to Re–Re bond are lower than these for equatorial acidoligands in *cis*-position, this fact indicating the noticeable *trans*-influence of Re–Re bond. The Cl2p and Br3d values for axial ligands in Re(III) compounds coincide practically with the same quantities for Rh(II) and Pt(III) compounds (Table II). This means that the manifestation of *trans*-influence by photoelectron characteristics of Cl-type acidoligands is insignificantly affected by the differences between Rh–Rh, Pt–Pt and Re–Re bonds. Furthermore, the $(Re–Cl)_{ax}$ distances are known to exceed the $(Re–Cl)_{eq}$ distances (Table III), that is X-Ray photoelectron data on *trans*-influence agree with the X-Ray structure analysis.

2. The binding energies for neutral donor ligands in axial position are somewhat higher compared to free ligands (Tables I and III), but lower than in the usual case of coordination through metals (*e.g.*, see Table I), showing the weakening of Re–L bonds due to Re–Re bond *trans*-influence.

Finally, it will be noted that for all compounds with Re–Re bond the formal oxidation number is 3. The change in Re $4f_{7/2}$ value for compounds in consideration is due to variation of ligands capacities to withdraw the electron density and, as well, reveal some structural distinctions of these compounds. For example, the decrease in Re $4f_{7/2}$ binding energy for compounds Nos. 10 and 11 (Table

TABLE I. Binding Energies (eV).

Compound	Ligand L and energy level		
	Py N1s	DMSO S2p	Thio S2p
Free ligand	399	165.7	162.3
Ligand in Rh(III) complex	400.2	167.1*	163.1
$Rh_2(HCOO)_4L_2$	399.7	166.5*	162.4
$Rh_2(CH_3COO)_4L_2$	399.8	166.5*	162.4
$Re_2(CH_3COO)_2Cl_4L_2$	399.4	166.7**	
$Re_2(CH_3COO)_2Br_4L_2$		166.5**	

*Coordinated through S atom. **Coordinated through O atom.

TABLE II. Binding Energies (eV).

Compound	Ligand L and energy level		
	Cl Cl2p	Br Br3d	NO_2 N1s
Ligand L coordinated in the complex of			
Rh(III)	198.8	69.4	404.3
Re(III)	199.2	69.5	
Pt(II) and Pt(IV)	198.9	69.6	404.4
$M^*_2Rh_2(CH_3COO)_4L_2$	198.1	68.9	403.6
$Re_2(CH_3COO)_4L_2$	198.2	68.8	
$Pt_2(CH_3CONH)_4L_2$	198.2	68.9	403.7
M*L	198.2	68.5	403.9

M* = Cs, K.

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*To simplify the notation this bond will be denoted as Re–Re.

TABLE III. Binding Energies (eV) and Interatomic Distances (A).

Compound	Re $4f_{7/2}$	Cl2p	Br3d	N1s S2p P2p	r(Re–Cl) r(Re–Br)
1. $Re_2(HCOO)_4Cl_2$	44.4	198.5(ax)			
2. $Re_2(CH_3COO)_4Cl_2$	44.0	198.2(ax)			2.52[a]
3. *trans*-$Re_2(CH_3COO)_2Cl_4$	44.1	199.3(eq)			2.58; 2.35[b]
4. *cis*-$Re_2(CH_3COO)_2Cl_4 \cdot 2H_2O$	43.7	199.0(eq)			2.28–2.32[c]
5. *cis*-$Re_2(CH_3COO)_2Cl_4 \cdot 2DMA$	43.7	199.0(eq)		400.2	
6. *cis*-$Re_2(CH_3COO)_2Cl_4 \cdot 2DMF$	43.8	199.1(eq)		400.6	2.30–2.32[d]
7. *cis*-$Re_2(CH_3COO)_2Cl_4 \cdot 2Py$	43.5	198.9(eq)		399.4	
8. *cis*-$Re_2(CH_3COO)_2Cl_4 \cdot 2DMSO$	43.7	199.0(eq)		166.7	2.31[e]
9. *cis*-$Re_2(CH_3COO)_2Cl_4 \cdot 2OPPh_3$	43.6	198.9(eq)		132.9	2.35f
10. $(NH_4)_2Re_2Cl_8 \cdot 2H_2O$	43.5	199.0(eq)		402.0	2.31–2.35[g]
11. $(NH_4)_2[Re_2Cl_6(HCOO)_2]$	43.8	198.9(eq)		401.9	2.31[h]
12. $Re_2(CH_3COO)_4Br_2$	44.0		68.8(ax)		
13. *trans*-$Re_2(CH_3COO)_2Br_4$	43.7		69.5(eq)		2.45; 2.48[i]
14. *cis*-$Re_2(CH_3COO)_2Br_4 \cdot 2H_2O$	43.7		69.5(eq)		
15. *cis*-$Re_2(CH_3COO)_2Br_4 \cdot 2DMA$	43.7		69.4(eq)		
16. *cis*-$Re_2(CH_3COO)_2Br_4 \cdot 2DMF$	43.5		69.4(eq)	400.4	
17. *cis*-$Re_2(CH_3COO)_2Br_4 \cdot 2DMSO$	43.5		69.4(eq)	166.5	
18. $OPPh_3$				132.7	
19. $Re(CO)_5Cl$	42.2	198.1			
20. K_2ReCl_6	44.2	199.2			
21. K_2ReBr_6	43.7		69.6		

[a] Ref. [5], [b] ref. [6], [c] ref. [7], [d] ref. [8], [e] ref. [9], [f] ref. [10], [g] ref. [11], [h] ref. [12], [i] ref. [13].

III) as compared to Nos. 1 and 3 can be attributed both to difference in coordination spheres (the consideration of Re $4f_{7/2}$ values for compounds Nos. 10 and 11 shows the formiate ion to be more capable of withdrawing electron density than the chloride ion) and to the fact of Re atoms entering the negatively charged anion part of compounds Nos. 10 and 11. To complete the picture, the data on some Re(I) and Re(IV) compounds are included in Table III. The interconnection of oxidation state and binding energy has been discussed in Ref. [2].

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