Axial *versus* equatorial metal—ligand distances in transition metal compounds
I. Hexafluoro complexes

R. BOČA

Department of Inorganic Chemistry, Slovak Technical University, 880 37 Bratislava

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X-ray structural data of the first-row transition metal hexafluorides were analyzed. It was recorded that mean equatorial, R_e, and mean axial, R_a, metal—ligand distances exhibit an R_a *vs.* R_e correlation realized in the fact that with increasing R_a the distance R_e decreases and *vice versa*. The studied complexes cover elongated and compressed tetragonal bipyramids having in their octahedral configuration three classes of electronic ground states: the nondegenerate — A_{1g}, the doubly degenerate — E_g, and the triply degenerate — T_{2g} ground state.

Были анализированы рентгеноструктурные данные гексафторидов первого ряда переходных элементов. Было отмечено, что среднее экваториальное R_e и аксиальное R_a расстояния металл—лиганд проявляют корреляцию в виде уменьшения расстояния R_e при увеличении расстояния R_a и наоборот. Изученные комплексы включают удлиненные и сжатые тетрагональные бипирамиды, обладающие октаэдрической конфигурацией трех классов основных электронных состояний: невырожденного A_{1g}, дважды вырожденного E_g и трижды вырожденного T_{2g} основных состояний.

The rarity of regular octahedral structures in Cu(II) complexes was the subject of some reviews [1, 2] and it was found that elongations in tetragonal bipyramids or *o*-rhombic distortions appear to be typical for this central atom surrounded by six ligands. It was also demonstrated that the statistical analysis of X-ray structural data for Cu(II) complexes with certain chromophores yields some dependences [3, 4] which enrich modern stereochemistry of coordination compounds. The tetragonal distortions of coordination polyhedra with CuN_6, CuO_6, and CuN_4O_2 chromophores [2, 5] and also in CuF_6^{4-} ion [6] are not arbitrary but they exhibit certain correlations between the mean axial, R_a, and mean equatorial, R_e, metal—ligand distances (for the coordination number 4 + 2, 6, and 2 + 4). These

correlations are realized in the way that with increasing R_a the distance R_e decreases and *vice versa*. In the large statistical set of X-ray data (this is, for example, the case of the CuO_6 chromophore) the R_a *vs.* R_e dependence becomes practically continuous and it is well represented by a smooth curve. The lower limit of R_e^{min} corresponds to the upper limit of R_a^{max}, where the chemical interactions may be ruled out and thus the complex becomes rather a square-planar. Analogically, the lower limit of R_a^{min} corresponds to the upper limit of R_e^{max} (coordination number 2+4) and the linear geometry is approached.

The questions under study in the present communication concern two fields:

i) the formulation of general validity of R_a *vs.* R_e dependences for square-bipyramidal (quasi-octahedral) transition metal complexes (to be cleared up by analyzing the X-ray structural data of the first-row transition metal fluorides);

ii) the manifestation of the central atom influence (the metal effect) on the observed correlations especially from the point of view of the Jahn—Teller theorem. The metal effect means here not only the influence of the proton number but also that of oxidation and spin states of the central atom.

Results and discussion

The known X-ray structural data, namely the metal—ligand interatomic distances in the first-row transition metal fluorides, are collected in Tables 1 and 2 separately for the oxidation states of M(II) and M(III). Three parameters describe the systems with *o*-rhombic symmetry: R_L (long), R_M (medium), and R_S (short) metal—ligand distances. For coordination polyhedra with D_{4h} symmetry following relations hold: $R_L = R_M > R_S$ (compressed tetragonal bipyramid) or $R_L > R_M = R_S$ (elongated form). Four identical (or nearly equal) interatomic distances define the equatorial plane of the complex and their average value was marked as R_e. The remaining two distances, after averaging if necessary, yield the axial, R_a, value. Some experimental data presented in Tables 1 and 2 were deleted by the next considerations because there exist later reinvestigations or because their little reliability was shown (some powder data belong here).

The mean distances R_a were plotted *vs.* the mean values R_e in dependence on the formal d^n configuration of the central atom (Fig. 1). This means that R_a *vs.* R_e points belonging to the same central atom in a certain oxidation state were connected by a smooth curve called the R_a *vs.* R_e correlation curve. The use of smooth curves instead of straight lines in Fig. 1 is connected with the fact that the extrapolation of a linear dependence leads here to a nonphysical result: $R_a = 0$ or $R_e = 0$. The minimum value of $R_e^{min} > 0$ is obtained in square-planar complexes (by $R_a \rightarrow \infty$) and analogically, the minimum value of $R_a^{min} > 0$ occurs in linear MF_2

Table 1. Metal—fluorine distances in $[MF_6]^{4-}$ polyhedra

d^n	Compound	Experimental			Selected		Ref.
		R_L	R_M	R_S	R_a	R_e	
d^4	CrF_2	2.43	2.01	1.98	2.43	1.99	[7]
	$KCrF_3$	2.32	2.00	1.95	2.32	1.97	[8, 9]
		2.14	2.14	2.00	2.00	2.14	[10]
	Cr_2F_5	2.572	2.010	1.955			[11]
d^5	MnF_2	2.14	2.11	2.11	2.14	2.11	[12, 13]
		2.13	2.13	2.10	2.10	2.13	[14, 15]
	$CsMnF_3$	2.12	2.12	2.12	2.12	2.12	[16]
	$LiMnGaF_6$	2.185	2.146	2.062	2.06	2.17	[17]
d^6	Ba_2FeF_6	2.08	2.08	2.08	2.08	2.08	[18]
	FeF_2	2.10	2.10	2.03	2.03	2.10	[13]
		2.12	2.12	1.99	1.99	2.12	[14, 15]
d^7	Ba_2CoF_6	2.13	2.05	2.05	2.13	2.05	[18]
	$CsCoF_3$	2.06	2.06	2.06	2.06	2.06	[19]
	$TlCoF_3$	2.06	2.06	2.06	2.06	2.06	[20]
	Rb_2CoF_4	2.06	2.06	2.06	2.06	2.06	[20]
	Tl_2CoF_4	2.05	2.05	2.05	2.05	2.05	[20]
	$RbCoF_3$	2.05	2.05	2.05	2.05	2.05	[20]
	CoF_2	2.05	2.04	2.04	2.05	2.04	[13]
		2.04	2.04	2.03	2.03	2.04	[14]
	K_2CoF_4	2.03	2.03	2.03	2.03	2.03	[20]
	$KCoF_3$	2.03	2.03	2.03	2.03	2.03	[20]
d^8	NiF_2	2.04	1.98	1.98	2.04	1.98	[13]
		2.01	2.01	1.98	1.98	2.01	[14, 15]
	$CsNiF_3$	2.024	2.024	2.024	2.02	2.02	[19]
	$RbNiF_3$	2.009	2.009	2.009	2.01	2.01	[19]
	Ba_2NiF_6	2.03	2.03	1.97	1.97	2.03	[18]
	K_2NiF_4	2.00	2.00	1.97	1.97	2.00	[21]
d^9	Na_2CuF_4	2.367	1.917	1.901	2.37	1.91	[22]
	Ba_2CuF_6	2.325	1.935	1.85	2.33	1.89	[24, 25]
		2.320	1.867	1.862	2.32	1.86	[23]
		2.08	2.08	1.85			[18]
	K_2CuF_4	2.28	1.95	1.86	2.28	1.90	[26, 9]
		2.237	1.945	1.905	2.24	1.92	[27]
		2.220	1.922	1.919	2.22	1.92	[27]
		2.08	2.08	1.95			[28]
	CuF_2	2.27	1.93	1.93	2.27	1.93	[29]
	$NaCuF_3$	2.26	1.97	1.88	2.26	1.92	[30]
	$KCuF_3$	2.258	1.962	1.888	2.26	1.92	[31]
		2.25	1.96	1.89	2.25	1.92	[32, 33]
		2.07	2.07	1.96			[34]
	CuF_2 (g)			1.72			[35]
d^{10}	ZnF_2	2.04	2.03	2.03	2.04	2.03	[13]
		2.04	2.04	2.01	2.01	2.04	[14, 15]
	Ba_2ZnF_6	2.05	2.05	1.96	1.96	2.05	[18]

Table 2

Metal—fluorine distances in $[MF_6]^{3-}$ polyhedra

d^n	Compound	Experimental			Selected		Ref.
		R_L	R_M	R_S	R_a	R_e	
d^1	Cs_2KTiF_6	2.01	2.01	2.01			[36]
	Rb_2KTiF_6	2.01	2.01	2.01			[36]
	Rb_2NaTiF_6	2.00	2.00	2.00			[36]
	TiF_3	1.97	1.97	1.97			[37]
d^2	VF_3	1.94	1.94	1.94			[38]
d^3	Rb_2CrF_5	1.990	1.882	1.852	1.99	1.87	[39]
	K_2NaCrF_6	1.93	1.93	1.93	1.93	1.93	[40]
	$CsCrF_4$	1.929	1.895	1.895	1.93	1.90	[41]
	$NaCrF_4$	1.926	1.902	1.890	1.93	1.90	[41]
	$BaLiCrF_6$	1.921	1.897	1.890	1.92	1.89	[42]
	CrF_3	1.90	1.90	1.90	1.90	1.90	[43, 7]
	Cr_2F_5	1.904	1.894	1.877	1.88	1.90	[11]
d^4	$MnCrF_5$	1.913	1.900	1.870	1.87	1.91	[54]
	Na_2MnF_5	2.12	1.85	1.84	2.12	1.84	[44, 9]
	MnF_3	2.09	1.91	1.79	2.09	1.85	[45]
	$(NH_4)_2MnF_5$	2.091	1.842	1.838			[55]
		2.101	1.853	1.853	2.10	1.85	[55]
	Cs_2KMnF_6	2.07	1.92	1.92	2.07	1.92	[40]
	K_2NaMnF_6	2.06	1.86	1.86	2.06	1.86	[46]
	$[Cr(NH_3)_6]\,[MnF_6]$	1.922	1.922	1.922	1.92	1.92	[47]
	$CsMnF_4$	2.009	2.009	1.810	1.81	2.01	[48, 9]
d^5	$[Cr(NH_3)_6]\,[FeF_6]$	1.931	1.931	1.931	1.93	1.93	[47]
	Cs_2TlFeF_6	1.93	1.93	1.93	1.93	1.93	[49]
	FeF_3	1.92	1.92	1.92	1.92	1.92	[38]
	Cs_2NaFeF_6	1.918	1.918	1.918	1.92	1.92	[49]
		1.913	1.913	1.913	1.91	1.91	[49]
	K_2NaFeF_6	1.910	1.910	1.910	1.91	1.91	[50, 40]
	Cs_2KFeF_6	1.91	1.91	1.91	1.91	1.91	[49]
	$Rb_2KF_eF_6$	1.91	1.91	1.91	1.91	1.91	[49]
	Rb_2NaFeF_6	1.90	1.90	1.90	1.90	1.90	[49]
	$CsFeF_4$	1.962	1.962	1.861	1.86	1.96	[51]
d^6	CoF_3	1.89	1.89	1.89	1.89	1.89	[38]
	Rb_2NaCoF_6	1.89	1.89	1.89	1.89	1.89	[52]
	Rb_2KCoF_6	1.89	1.89	1.89	1.89	1.89	[52]
	Cs_2KCoF_6	1.89	1.89	1.89	1.89	1.89	[52]
d^7	Cs_2KNiF_6	1.91	1.79	1.79			[9]
	K_2NaNiF_6	1.89	1.89	1.89	1.89	1.89	[53]
	Rb_2NaNiF_6	1.88	1.88	1.88	1.88	1.88	[53]
	Rb_2KNiF_6	1.88	1.88	1.88	1.88	1.88	[53]
	Cs_2KNiF_6	1.88	1.88	1.88	1.88	1.88	[53]
d^8	K_2NaCuF_6	1.82	1.82	1.82	1.82	1.82	[40]

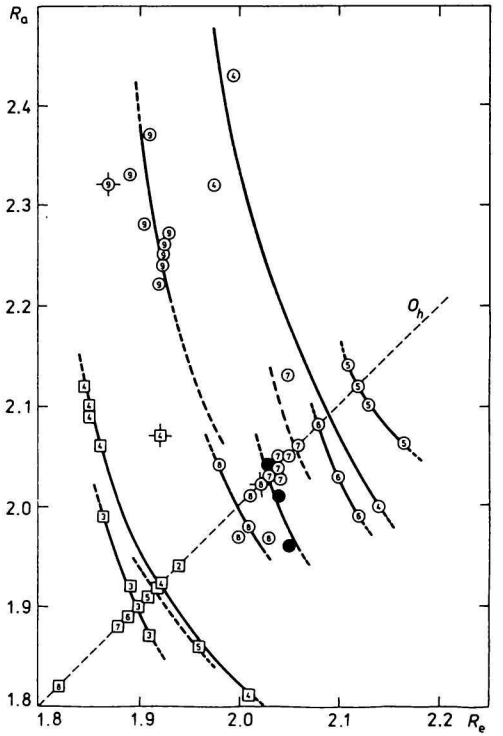

Fig. 1. The R_a *vs.* R_e correlations in hexafluoro complexes.
ⓝ is the d^n system of M(II); ● is the d^{10} system of Zn(II); ⊡ is the d^n system of M(III).
Full lines — the R_a *vs.* R_e correlations; dashed lines — expected dependences or extrapolations; thin dashed line — regular octahedrons ($R_a = R_e$).
Points marked as -⊕- or -⊡- were excluded from statistical analysis. The metal—ligand distances R_a and R_e are in units of 10^{-10} m.

system (by $R_e \rightarrow \infty$). Since the linear form of R_a *vs.* R_e dependences is to be ruled out, the curves in Fig. 1 have only the illustrative meaning. Despite of the low number of experimental points, some statistical characteristics were calculated (Table 3) and they lead to a conclusion that the above-mentioned R_a *vs.* R_e correlation between the metal—ligand distances unambiguously does exist.

On the basis of Fig. 1 the following conclusions may be drawn.

i) The R_a *vs.* R_e correlation curves exhibit a similar course, so that in $[MF_6]^{3-}$ and $[MF_6]^{4-}$ systems there must exist a common intrinsic disposition to undergo tetragonal distortions along the R_a *vs.* R_e dependence.

Table 3

Correlation coefficients, ϱ, in R_a *vs.* R_e dependences using N experimental structures of hexafluoro complexes

M	N	ϱ
Cr(II)	4	0.88
Mn(II)	4	0.99
Fe(II)	3	0.99
Ni(II)	5	0.75
Cu(II)	9	0.67
Zn(II)	3	0.98
Cr(III)	6	0.47
Mn(III)	7	0.93

ii) The cationic part of the crystal affects, however, this general trend: structures with great Cs^+ or Ba^{2+} cations tend to deviate from the above regularity. Therefore, some of these complexes were excluded from the statistical analysis presented in Table 3.

iii) The metal—ligand distances in $[MF_6]^{3-}$ systems are considerably shorter when compared with those in $[MF_6]^{4-}$ systems.

iv) The high-spin complexes of $^5[Cr^{II}]$, $^5[Mn^{III}]$, and $^2[Cu^{II}]$ display the greatest deviation from an octahedral configuration. Their common feature lies in the fact that these systems have in a hypothetical octahedral configuration the doubly degenerate electronic ground state E_g (Table 4). According to the Jahn—Teller theorem [56] the adiabatic potential surface (the total energy dependent on nuclear coordinates) has no minimum in this geometric configuration. As an effect of the $E_g - e_g$ vibronic interaction (the electronic state E_g does interact with the e_g type of normal vibrations) the system is tetragonally or rhombically distorted and consequently the degeneracy is removed. This "mechanism" was accepted in many papers (*e.g.* [2, 9]) in order to explain the distortions of coordination polyhedra, especially in Cu(II) stereochemistry. Also the other systems are able to undergo this "mechanism", *viz.* the low-spin $^2[Co^{II}]$, $^2[Ni^{III}]$, $^1[Ni^{II}]$, and $^1[Cu^{III}]$ complexes which all have the doubly degenerate electronic state E_g in their octahedral configuration. Since fluorine ligands produce a weak ligand field, the high-spin complexes are preferentially stabilized and these mentioned systems are not known within fluoro complexes. Notice that some "Jahn—Teller active" systems can exhibit at room temperature a regular octahedral configuration. This is the case of $[Cr(NH_3)_6]$ $[MnF_6]$, where a dynamic Jahn—Teller effect takes place. That means a rapid interconversion between the distorted structures leading to their averaging, and the $[MnF_6]^{3-}$ polyhedron seems to be a regular octahedron under the conditions of X-ray experiments [47].

Table 4

Characteristics of the high-spin octahedral complexes

d^n	Electron configuration		State	Examples [a]	
	t_{2g}	e_g			
d^1	1	0	$^2T_{2g}$		$^2[Ti^{III}]$
d^2	2	0	$^3T_{2g}$		$^3[V^{III}]$
d^3	3	0	$^4A_{1g}$		$^4[Cr^{III}]$
d^4	3	1	^5E_g	$^5[Cr^{II}]$	$^5[Mn^{III}]$
d^5	3	2	$^6A_{1g}$	$^6[Mn^{II}]$	$^6[Fe^{III}]$
d^6	4	2	$^5T_{2g}$	$^5[Fe^{II}]$	$^5[Co^{III}]$
d^7	5	2	$^4T_{2g}$	$^4[Co^{II}]$	$^4[Ni^{III}]$
d^8	6	2	$^3A_{1g}$	$^3[Ni^{II}]$	$^3[Cu^{III}]$
d^9	6	3	^2E_g	$^2[Cu^{II}]$	
d^{10}	6	4	$^1A_{1g}$	$^1[Zn^{II}]$	

a) The used notation $^4[Cr^{III}]$ means, for example, a complex of Cr(III) with the spin multiplicity equal to four (three unpaired electrons).

v) The R_a *vs.* R_e dependence is exhibited also by systems having a nondegenerate electronic state A_{1g}, namely by $^4[Cr^{III}]$, $^6[Fe^{III}]$, $^6[Mn^{II}]$, $^3[Ni^{II}]$, and $^1[Zn^{II}]$ complexes. Here, in explaining the above-mentioned observations, the Jahn—Teller (vibronic) type of "mechanism" is to be ruled out, of course.

vi) The systems having in their hypothetical octahedral configuration a triply degenerate electronic state T_{2g}, namely $^5[Fe^{II}]$, $^4[Co^{II}]$, and $^4[Ni^{III}]$ complexes, exhibit distortions of approximately the same order as for the A_{1g} state.

Finally, it may be summarized that not only Cu(II) complexes exhibit the R_a *vs.* R_e correlations between the metal—ligand distances. It was demonstrated in the present communication that these dependences are more general and they practically cover the complete first transition metal row. Even though the Jahn—Teller effect, namely the E_g—e_g vibronic interaction, plays a role in the distortions of octahedral complexes, also some other factors must exist here. It was shown that one important factor is represented by the general shape of adiabatic potential surface which exhibits a valley along the R_a *vs.* R_e correlation curve [6, 57—60]. Recently quantum chemical calculations were used in our laboratory for mapping the shape of adiabatic potential surfaces of $[MF_6]^{4-}$ and $[MF_6]^{3-}$ ions. The quantitative characterization of shapes of these adiabatic potential surfaces is in progress.

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