Molecular orbital study of tetragonal distortions in hexahalo complexes
I. Nondegenerate states

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Some problems of stereochemistry of nine first-row transition metal hexahalo complexes in the A_{1g} electronic state are studied on the basis of quantum chemical calculations using the CNDO method. The optimum geometries and the interaction displacement coordinates represent characteristics of free octahedra, namely their degree of compression and their ability to undergo tetragonal distortions called here the plasticity. The opposite characteristic — the rigidity is raised side by side with the compression of the ideal octahedron in dependence on the increasing proton number of the central atom, its oxidation number, and the decreasing proton number of the halogene ligand.

На основании квантово-химических расчетов с использованием метода CNDO были изучены некоторые проблемы стереохимии девяти гексагалоген комплексов переходных элементов первого ряда в электронном состоянии A_{1g}. Оптимальная геометрия и интеракционные координаты отклонения представляют собой характеристики свободных октаэдров, а именно степень их сжатия и способность подвергаться тетрагональному искажению, которое здесь называется пластичностью. Обратная характеристика — жесткость повышается одновременно с сжатием идеального октаэдра, в зависимости от возрастающего протонного числа центрального атома, его степени окисления и понижающегося протонного числа галогенного лиганда.

Recently it was reported [1] that the metal—ligand distances in hexafluoro complexes of $[MF_6]^{4-}$ and $[MF_6]^{3-}$ type exhibit certain correlations along a smooth curve in the variation of axial, R_a, and equatorial, R_e, metal—ligand distances for coordination numbers 4 + 2, 6, and 2 + 4. A central atom effect (not only the proton number influence but also that of oxidation and spin states of the central atom) was well documented in these correlations which are interesting in modern stereochemistry of coordination compounds. Therefore, a detailed quantum chemical investigation of the electronic properties of some hexahalo complexes and their stereochemical consequences was performed for the following classes of the electronic states:

(i) the nondegenerate state A_{1g};

(ii) the degenerate states (doubly — E_g or triply degenerate — T_{2g}) which will be the subject of subsequent publications.

Within the d^4—d^9 systems only those of high-spin d^5 (spin multiplicity $m = 6$), low-spin d^6 ($m = 1$), and high-spin d^8 ($m = 3$) have a nondegenerate electronic state $^mA_{1g}$ in their octahedral surrounding. Therefore the systems of the present study are covered by $^6[MnF_6]^{4-}$, $^6[FeF_6]^{3-}$, $^1[FeF_6]^{4-}$, $^1[CoX_6]^{3-}$, and $^3[NiX_6]^{4-}$ complexes where X means the halogene ligands (X = F, Cl, Br).

The approach presented below is based on the general theory of the mutual consequences among internal coordinates $\{R_n\}$ describing the geometry of a coordination polyhedron through the total energy function $E_T = E_T(\ldots, R_n, \ldots)$. This is the known adiabatic potential surface (APS). However, some limitations of the used approach must be mentioned here.

(i) Starting from the octahedral geometry of the $[MX_6]^q$ complex only the tetragonal distortions will be considered, so that four equatorial metal—ligand distances, R_e, as well as two axial distances, R_a, are to be equivalent thus forming a tetragonal bipyramid (D_{4h} symmetry).

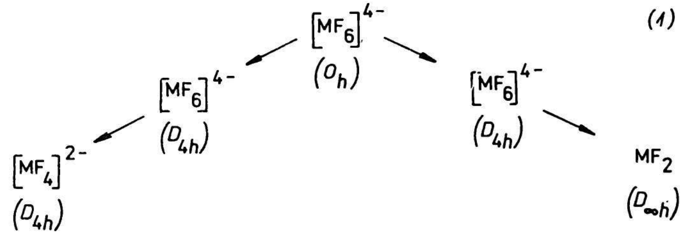
(ii) In extreme distortions such as $R_a \rightarrow \infty$ a square-planar arrangement around the central atom is approached — $[MX_4]^q$ complex, whereas for $R_e \rightarrow \infty$ the MX_2 system becomes linear.

As a consequence of these restrictions the number of internal degrees of freedom is significantly reduced from 15 only to 2, so that APS is to be considered a simple function of the $E_T = E_T(R_a, R_e)$ type.

Adiabatic potential surface

The shape of APS for the systems under study was mapped using the CNDO/2 version [2—4] of semiempirical all-valence MO LCAO SCF calculations. The valence basis set used covers $3d$, $4s$, and $4p$ atomic orbitals of the central atom as well as the valence s and p orbitals of ligands (totally 33 AO's for $[MX_6]^q$ complexes). The parameters used in the calculations correspond to the *Gouterman* AO's [3, 5]. The self-consistent-field procedure converges rapidly: the electronic energy is calculated after 12—14 iterations on 9 digits (threshold of 10^{-4} eV), without a level-shifting or damping procedure.

The total energy E_T was calculated for individual geometries given by a pair of $\{R_a, R_e\}$ values. First, the geometry was varied until the equilibrium octahedral configuration was found ($R_a = R_e = R^0$) so that an expansion or a compression of the octahedron led to an increase of the total energy. Then both the parameters, R_a and R_e, were independently varied around the equilibrium configuration in order to obtain a more detailed map of E_T values. Analogically, the optimum geometries of square planar $[MX_4]^{2-}$ and linear MX_2 systems were found. Finally, starting from the optimum octahedral configuration, one geometric parameter, say R_a, was stretched while the second distance (R_e) was varied until a local energy minimum was obtained. In this way a reaction path was found as follows (Scheme 1).



(1)

Scheme 1

Equilibrium geometry

The equilibrium geometry of free hexahalo complexes of the $[MX_6]^q$ type is exhibited in the octahedral configuration if their electronic state is A_{1g} (Table 1). With increasing proton number of the central atom (M = Mn^{II}, Fe^{II}, Ni^{II} or M = Fe^{III}, Co^{III}) the coordination polyhedron becomes compressed. Simultaneously, the complexes of M^{III} exhibit somewhat shorter metal—ligand distances R^0

Table 1

Calculated characteristics of octahedral $[MX_6]^q$ complexes in the A_{1g} electronic state[a]

d^n	Complex	R^0	HFC			IDC	
			k_{aa}	k_{ae}	k_{ee}	$(d_e)_a$	$(d_a)_e$
d^5	$^6[MnF_6]^{4-}$	2.227	5.65	1.59	12.91	0.123	0.281
	$^6[FeF_6]^{3-}$	2.085	8.47	1.89	18.84	0.100	0.223
d^6	$^1[FeF_6]^{4-}$	2.149	6.71	1.63	15.04	0.108	0.242
	$^1[CoF_6]^{3-}$	1.955	11.28	2.33	24.89	0.094	0.207
	$^1[CoCl_6]^{3-}$	2.289	8.92	2.30	20.14	0.114	0.258
	$^1[CoBr_6]^{3-}$	2.459	10.28	3.19	23.75	0.134	0.310
d^8	$^3[NiF_6]^{4-}$	1.989	10.68	2.56	23.92	0.107	0.240
	$^3[NiCl_6]^{4-}$	2.311	8.30	2.80	19.40	0.144	0.337
	$^3[NiBr_6]^{4-}$	2.482	9.28	3.54	22.11	0.160	0.381

a) The metal—ligand distances R^0 in 10^{-10} m, the harmonic force constants (HFC) in N cm^{-1}; IDC — interaction displacement coordinates.

when compared with those of M^{II}. The compression increases in the order of ligands X = Br, Cl, F.

From the five hexafluoro complexes under study only three are in the ground electronic state, namely the $^6[MnF_6]^{4-}$, $^6[FeF_6]^{3-}$, and $^3[NiF_6]^{4-}$ complexes. Owing to the weak ligand field of the fluorines, the high-spin hexafluoro complexes are preferentially stabilized. Therefore the low-spin $^1[FeF_6]^{4-}$ and $^1[CoF_6]^{3-}$ complexes correspond to certain excited states in which no experimental structural data are available up to now. Some trends in calculated equilibrium geometries were examined by handling with results of X-ray experiments (Table 2). Passing from

Table 2

Experimental metal—ligand distances in octahedral hexafluoro complexes in A_{1g} electronic state

Compound	$R_{M-F}/10^{-10}$ m	Ref.
$CsMnF_3$	2.12	[6]
$CsNiF_3$	2.02	[7]
$RbNiF_3$	2.01	[7]
Cs_2TlFeF_6	1.93	[8]
Cs_2NaFeF_6	1.918	[8]
	1.913	[8]
K_2NaFeF_6	1.91	[9, 10]
Cs_2KFeF_6	1.91	[8]
Rb_2KFeF_6	1.91	[8]
Rb_2NaFeF_6	1.90	[8]

Table 3

Calculated metal—halogene distances, R_{M-X}, and the stretching harmonic force constants, k_e, in square-planar $[MX_4]^{2-}$ ions^a

$[MX_4]^{2-}$	Spin multiplicity	X = F		X = Cl		X = Br	
		R_{M-F}	k_e	R_{M-Cl}	k_e	R_{M-Br}	k_e
$[MnX_4]^{2-}$	2	2.07	19.1	2.36	17.0	2.48	21.7
	6	2.10	18.4	2.38	18.0	2.50	19.3
$[FeX_4]^{2-}$	1	2.03	22.5	2.31	20.2	2.45	22.3
	5	2.06	21.6	2.33	21.1	2.46	22.9
$[CoX_4]^{2-}$	2	1.94	29.2	2.24	27.2	2.39	30.7
	4	1.97	27.4	2.26	28.1	2.41	26.6
$[NiX_4]^{2-}$	1	1.86	33.1	2.18	31.5	2.35	30.5
	3	1.89	36.1	2.19	32.3	2.36	31.1
$[CuX_4]^{2-}$	2	1.87	36.5	2.17	32.7	2.34	37.5

a) The metal—halogene distances in 10^{-10} m, the force constants in N cm^{-1}.

$CsMnF_3$ to $CsNiF_3$ a compression of the $[MF_6]^{4-}$ octahedron was registered. The same situation is found passing from M^{II} complexes to those of Fe^{III}. The smaller cations in the crystal, the stronger their lattice potential influencing the $[MF_6]^q$ octahedron owing to which the coordination polyhedron of the complex is compressed. This finding is shown on the structures listed in Table 2.

According to Scheme 1, the lowest value of R_e^{min} corresponds to the limit case of $R_a \rightarrow \infty$, *i.e.* to the square-planar $[MX_4]^{2-}$ complexes. On the other hand, the lower limit of R_a^{min} is obtained for $R_e \rightarrow \infty$, *i.e.* in linear MX_2 molecules. The equilibrium geometries of these systems are listed in Tables 3 and 4. Their rigidity can be measured using the stretching harmonic force constants. It has been found that the last quantity increases in the amount simultaneously with the compression of the coordination polyhedron due to the increasing proton number of the central atom.

Minimum energy coordinates

A map of numerical values of E_T around the energy minimum was transformed to an analytical form of APS. Starting from the Taylor power expansion in the point of the energy minimum, the harmonic approximation can be obtained

$$E_T(R_a, R_e) = A + BR_e + CR_a + DR_e^2 + ER_a^2 + FR_aR_e \qquad (1)$$

In order to obtain six constants (A—F) at least six numerical values of E_T must be known. More values can, of course, be used and the best fitting is obtained applying the least-square method. Then it holds for the harmonic force constants: $k_{aa} = (\partial^2 E_T/\partial R_a^2) = 2E$ and analogically $k_{ee} = 2D$ and $k_{ae} = F$. The equilibrium geometric parameters are $R_a^0 = (BF - 2DC)/(4DE - F^2)$ and $R_e^0 = (CF - 2BE)/ /(4DE - F^2)$. The latter relations follow from the solution of two linear equations with two variables resulting from the conditions of the energy minimum, *i.e.* $(\partial E_T/\partial R_a) = (\partial E_T/\partial R_e) = 0$. The force constant matrix

$$\mathbf{K} = \begin{pmatrix} k_{aa} & k_{ae} \\ k_{ae} & k_{ee} \end{pmatrix} \qquad (2)$$

contains information about properties of the APS around the energy minimum but a more chemical interpretation can be obtained if only the below presented procedure is accepted.

By inversion of the force constant matrix ($\mathrm{C} = \mathrm{K}^{-1}$) primary, c_{ii}, and interaction, c_{ij}, compliants are calculated. They define the interaction displacement coordinates (IDC)

$$(d_j)_i = c_{ij}/c_{ii} \qquad (3)$$

Table 4

Metal—halogene distances, R_{M-X}, and the stretching harmonic force constants, k_e, in linear MX_2 molecules[a,b]

MX_2	Spin multiplicity	X = F			X = Cl			X = Br		
		R_{M-F}		k_e	R_{M-Cl}		k_e	R_{M-Br}		k_e
		exp	calc	calc	exp	calc	calc	exp	calc	calc
MnX_2	2	(1.67)	1.96	11.9	2.20	2.21	12.1		2.31	13.5
	4		1.97	12.3		2.22	11.7		2.31	13.9
FeX_2	1		1.93	13.9	2.17	2.17	13.7	(2.24)	2.27	14.9
	3		1.93	13.9		2.17	13.7		2.27	15.2
CoX_2	2	(1.72)	1.84	18.5	2.12	2.11	16.8	(2.32)	2.22	18.6
	4		1.86	17.8		2.11	16.9		2.22	18.9
NiX_2	1		1.77	22.2	2.06	2.05	20.5	2.21	2.18	23.2
	3		1.79	21.2		2.05	20.5		2.18	23.2
CuX_2	2	(1.72)	1.77	23.5	(2.09)	2.03	22.6	(2.24)	2.16	24.3

a) The metal—halogene distance in 10^{-10} m, the force constants in N cm^{-1}.

b) The experimental data according to Ref. [11—13]. Data in parenthesis are estimated.

and finally, the minimum energy coordinates (MEC) are found [14—17]

$$\mathcal{R}_i = R_i + \sum_{j \neq i} (d_j)_i R_j \tag{4}$$

This means that $\mathcal{R}_i$ describes in the internal coordinate space how the remaining coordinates ($j \neq i$) are changed by a fixed distortion of the selected coordinate, say R_i. Thus MEC represents a harmonic approximation to the minimum energy path, which is expressed through a linear function around the energy minimum.

In fact, in the two-dimensional space $\{R_a, R_e\}$ the simplified expressions hold

$$\mathcal{R}_a = R_a + (d_e)_a R_e = R_a - (k_{ae}/k_{ee}) R_e \tag{5}$$

$$\mathcal{R}_e = R_e + (d_a)_e R_a = R_e - (k_{ae}/k_{aa}) R_a \tag{6}$$

and their meaning is illustrated in Fig. 1. The calculated IDC are listed in Table 1 together with the harmonic force constants and the equilibrium geometric parameters. The value of $(d_e)_a = 0.107$, for as an example the $^3[NiF_6]^{4-}$ complex, means that the distance R_e is compressed by 10.7% of the length by stretching the R_a, in order that the complex should relax to a local energy minimum. Analogically, the value of $(d_a)_e = 0.240$ for the same complex indicates that R_a is compressed by 24.0% of the amount by stretching the coordinate R_e. From the point of view of the above interpretation, MEC's can, in the harmonic approximation, be accepted as quantitative criteria for the plasticity (or rigidity) of coordination polyhedra.

Analyzing the data listed in Table 1, the following conclusions can be drawn:

(i) in the series of ligands X = F, Cl, Br the rigidity of coordination polyhedra decreases so that $[MBr_6]^q$ complexes exhibit a greater plasticity when compared with $[MCl_6]^q$ and $[MF_6]^q$ analogues;

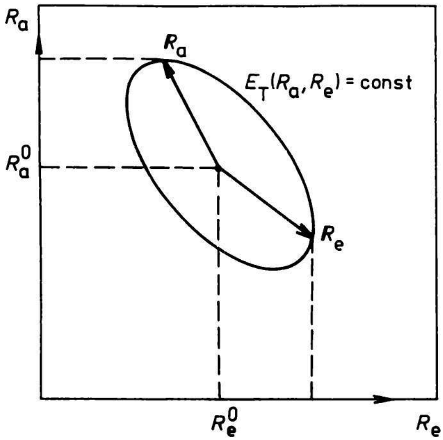


Fig. 1. Meaning of the minimum energy coordinates.

(ii) complexes having their central atom in the higher oxidation state (M^{III} or $q = -3$) exhibit a somewhat greater rigidity with respect to those of M^{II} ($q = -4$);

(iii) the plasticity of the coordination polyhedra decreases with increasing proton number of the central atom ($M = Mn^{II}$, Fe^{II}, Ni^{II} or $M = Fe^{III}$, Co^{III}).

R_a *versus* R_e *dependences*

Experimental data analysis [1] unambiguously shows that in the variation of metal—ligand distances of $^3[NiF_6]^{4-}$ systems the R_a *vs.* R_e dependence holds. In analogical $^2[CuF_6]^{4-}$ systems this phenomenon was explained on the basis of the general form of APS [18]. It was found that APS exhibits a valley passing from octahedral configuration and approaching the dissociation limits ($[CuF_4]^{2-}$ and CuF_2). This is well fulfilled also for the $^3[NiF_6]^{4-}$ complex. The valley on the two-dimensional APS was found in the following way.

Starting from the octahedral $^3[NiF_6]^{4-}$ complex, the coordinate R_a was systematically displaced by a certain step, say $\Delta R_a = 3$ pm. Then the remaining coordinate R_e was varied until the function $E_T(R_a^c = \text{const}; R_e)$ relaxed to a local energy minimum where $(\partial E_T/\partial R_e)_{R_a^c} = 0$ was valid. By the fixed R_a^c the coordinate R_e^0 was optimum. The obtained local minima were connected with a smooth curve and thus the first part of the valley was found. Individual pairs of $\{R_a^c, R_e^0\}$ values define in the coordinate sub-space the function $f(R_a, R_e) = 0$ which is the R_a *vs.* R_e correlation curve. The procedure was repeated for fixed displacements of R_e by a step of ΔR_e. Then the distance R_a was varied until the function $E_T(R_e^c = \text{const}; R_a)$ relaxed to the local energy minimum, where $(\partial E_T/\partial R_a)_{R_e^c} = 0$ was valid. Within $\{R_a^0, R_e^c\}$ points the coordinate R_a^0 was optimum by the fixed R_e^c so that the second part of R_a *vs.* R_e correlation curve $f(R_a, R_e) = 0$ was found.

The calculated R_a *vs* R_e correlation curve is plotted in Fig. 2 between $[NiF_4]^{2-}$ and NiF_2 limit cases. Also the experimental points resulting from the X-ray diffraction analysis of some hexafluoro nickelates are included in Fig. 2 and the remarkable agreement is registered. Thus it has been shown that in octahedral complexes an intrinsic disposition does exist owing to which the complexes can undergo tetragonal distortions along the R_a *vs.* R_e dependence. The distorted structure (a tetragonal bipyramid) can be stabilized in the presence of an external perturbation. In the role of the external perturbation a lattice potential of the cationic part of the crystal can operate [19, 20] and influences of pressure [20] and temperature [21] also can manifest themselves.

Conclusion

Several publications are known in literature [3, 22—24] where the optimum geometries of transition metal halo complexes are reported on the basis of

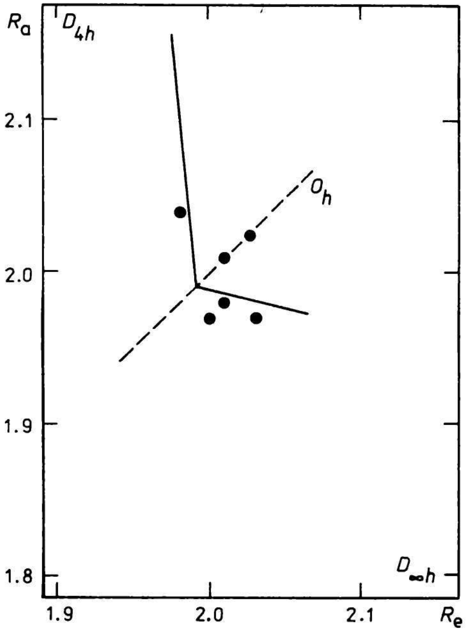


Fig. 2. Calculated R_a *vs.* R_e correlation curve for the $^3[NiF_6]^{4-}$ complex. ● Experimental structures taken from Ref. [1].

semiempirical or *ab initio* calculations. The scope of the present communication does not lie in the reproduction of these data. Recently it was emphasized [1, 18, 20, 21, 25, 26] that the tetragonal distortions of ideal octahedra often occur in the solid state. Two factors are important for the study of this phenomenon. The former is represented by finding a valley on the two-dimensional adiabatic potential surface. In the presence of an external perturbation the ideal octahedral geometry is removed and the complex can relax to another geometrical configuration along the valley. The latter factor is connected with the possibility quantitatively to describe the plasticity and/or rigidity of the octahedron with respect to the tetragonal distortions. This disposition is suitably described using the minimum energy coordinate approach. The calculated optimum geometries as well as the interaction displacement coordinates lead to the principal result: the greater compression of the octahedron, the greater its rigidity, or in other words, the less the expansion (a symmetric stretching) of the octahedron, the less its plasticity (the ability to undergo tetragonal distortions). The compression and the rigidity raise in the amount (*i.e.* the expansion and the plasticity decrease) with increasing proton number of the central atom and its oxidation number and with decreasing proton number of the halogene ligand.

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