

Axial versus equatorial metal—ligand distances in transition metal compounds

II. Hexanitro complexes

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Hexanitro complexes of Co^{II} , Ni^{II} , and Cu^{II} represent systems under investigation. They exhibit phase transitions depending on temperature. The central atom—ligand distances in these square-bipyramidal complexes correlate in the way that with increasing axial distance, R_a , the value of equatorial central atom—ligand distance, R_e , decreases and *vice versa*. Thus the so-called R_a vs. R_e dependence is registered within the individual compounds as a consequence of changes in the amount of the total energy.

Изучались гексанитрокомплексы Co^{II} , Ni^{II} и Cu^{II} . Они оказывают фазовые переходы в зависимости от температуры. Расстояния центральный атом—лиганд в этих квадратно-бипирамидальных комплексах коррелируют таким образом, что с возрастающим аксиальным расстоянием, R_a , величина экваториального расстояния центральный атом—лиганд, R_e , понижается и наоборот. Этим способом регистрирована так называемая зависимость R_a от R_e в рамках отдельного соединения в следствии изменения в содержании полной энергии.

A detailed analysis of experimental structure data leads to the observation that in some transition metal compounds there exists a well-defined R_a vs. R_e dependence by variation of the axial, R_a , and equatorial, R_e , central atom—ligand distances. This dependence manifests itself in the way that with increasing R_a the distance R_e decreases and *vice versa*. This finding was registered in systems showing an elongated or compressed form of a square bipyramid (the coordination number 4 + 2, 6, and 2 + 4) [1—5].

Originally, the R_a vs. R_e dependences were found for Cu^{II} complexes with a common chromophore, say CuO_6 , CuN_6 , or CuN_4O_2 [1, 2], but differing in their ligand sphere. These dependences were registered also for some Ni^{II} and Mn^{III} complexes [3]. An elongated form of the tetragonal bipyramid is typical for

coordination polyhedra of Cu^{II} complexes. Therefore, the original notation R_l (long) and R_s (short) was not in discrepancy with the knowledge in earlier works [1, 2] concerning the R_a vs. R_e dependences. Since in the last few years an experimental proof of the compressed form of the tetragonal bipyramid was unambiguously evidenced also for some Cu^{II} complexes, the R_a and R_e notation seems to be more suitable and it has been accepted also in recent papers dealing with the R_a vs. R_e dependences [4, 5].

A second level in evolution of this research was opened for $[\text{MF}_6]^{4-}$ and $[\text{MF}_6]^{3-}$ systems [4, 5] differing from each other in the cationic part of the crystal. Here the central atom in M^{II} and M^{III} oxidation states varies throughout the first transition metal row ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) whereas the ligand sphere retains the same quality. A detailed discussion of the central atom effect in these systems of hexafluoro complexes was the subject of the previous paper of this series [5]. The scope of the present communication covers a next stage in the research of R_a vs. R_e dependences. Complexes with homogeneous ligand sphere of the ML_6 type were taken into consideration for which varying temperature led to phase transitions. They are particularly represented by hexanitro complexes.

Results and discussion

The compounds under study are characterized by the following formula: $\text{A}_2\text{A}^{\text{I}}\text{M}^{\text{II}}(\text{NO}_2)_6$, metals being $\text{A}^{\text{I}} = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$; $\text{A}^{\text{II}} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$; $\text{M}^{\text{II}} = \text{Co}, \text{Ni}, \text{Cu}$. These compounds exhibit well defined $[\text{M}^{\text{II}}(\text{NO}_2)_6]^{4-}$ units. Since NO_2^- ligands produce a strong ligand field, the low-spin Co^{II} complexes are preferentially stabilized with the spin multiplicity of $m = 2$ (Table 1). Therefore, the electronic ground state of the low-spin Co^{II} and Cu^{II} hexanitro complexes is 2E_g [6] whereas that of Ni^{II} hexanitro complexes is ${}^3A_{1g}$. The degenerate electron state E_g does interact with e_g modes of normal vibrations. This leads to the distortion of the hypothetical octahedral configuration along the e_g vibrational modes (tetragonal or ortho-rhombic distortion); as an effect of this E_g — e_g vibronic interaction the degeneracy is removed as it has been predicted by the Jahn—Teller theorem.

Table 1
Characteristics of some hexanitro complexes

Configuration			Electronic state	Example
d^n	t_{2g}	e_g		
7	6	1	2E_g	$[\text{Co}(\text{NO}_2)_6]^{4-}$
8	6	2	${}^3A_{1g}$	$[\text{Ni}(\text{NO}_2)_6]^{4-}$
9	6	3	2E_g	$[\text{Cu}(\text{NO}_2)_6]^{4-}$

Three geometric parameters describe systems with *ortho*-rhombic symmetry: the long central atom—ligand distance, R_L , the medium, R_M , and the short one, R_S . Two of them are often nearly equal and they define an equatorial plane of the complex. After averaging, if necessary, the mean equatorial central atom—ligand distance, R_e , is obtained. The remaining parameter completes a tetragonal bipyramid (of the elongated or compressed form) and it was marked as R_a (axial central atom—ligand distance).

Several compounds under investigation exhibit phase transitions with decreasing temperature. Their structures are known for certain phases: α , β , β' , and γ . The available X-ray and neutron diffraction data were analyzed and the above-mentioned distances — the experimental (R_L , R_M , R_S) as well as the selected (R_a , R_e) values, are listed in Table 2. The values of R_a were plotted vs. R_e distances (Fig. 1) and the points belonging to the individual compounds were connected by smooth curves.

Two possibilities may be taken into consideration for the shape of an R_a vs. R_e dependence. The first is represented by a straight line. Its extrapolation, however, yields an unreasonable result: either $R_e=0$ or $R_a=0$ is obtained. Actually, the

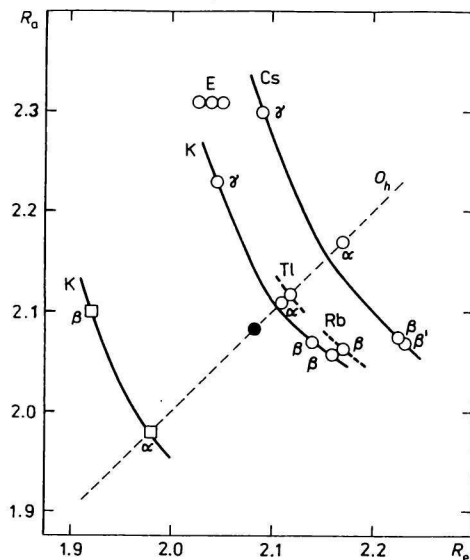


Fig. 1. The R_a vs. R_e dependence in $A_2A^{II}M(NO_2)_6$ complexes.

\square $K_2PbCo(NO_2)_6$; \bullet $K_2A^{II}Ni(NO_2)_6$ for $A^{II} = Sr, Ba, Pb$; \circ $K_2ECu(NO_2)_6$ for $E = Ca, Sr, Ba$ or $A^I PbCu(NO_2)_6$ for $A^I = K, Rb, Tl, Cs$.

Full lines — the R_a vs. R_e dependences; dashed lines — expected course; thin dashed line — regular octahedrons ($R_a = R_e$).

The central atom—ligand distances R_a and R_e are in units of 10^{-10} m.

Table 2. The central atom—nitrogen distances in $[M(\text{NO}_2)_6]^{4-}$ polyhedra^a

d^n	Compound	Phase		Experimental			Selected		Method ^b	Ref.
		Type	T/K	R_L	R_M	R_S	R_a	R_c		
d^7	$\text{K}_2\text{BaCo}(\text{NO}_2)_6$	α	room	1.98(2)	1.98(2)	1.98(2)	1.98	1.98	XS	[7]
		β	233	2.10(2)	1.94(6)	1.90(2)	2.10	1.92	XS	[8]
d^8	$\text{K}_2\text{SrNi}(\text{NO}_2)_6$		295	2.078(1)	2.078(1)	2.078(1)	2.08	2.08	XS	[9]
			295	2.080(2)	2.080(2)	2.080(2)	2.08	2.08	XS	[10]
	$\text{K}_2\text{PbNi}(\text{NO}_2)_6$		295	2.080(2)	2.080(2)	2.080(2)	2.08	2.08	XS	[11]
			room	2.13	2.13	2.13			XP	[12, 13]
	$\text{Cs}_2\text{SrNi}(\text{NO}_2)_6$		room	2.13	2.13	2.13			XP	[12, 13]
			295	2.313(1)	2.052(1)	2.050(1)	2.31	2.05	XS	[14]
d^9	$\text{K}_2\text{SrCu}(\text{NO}_2)_6$		295	2.310(2)	2.041(2)	2.029(2)	2.31	2.03	XS	[9]
			295	2.311(2)	2.048(2)	2.038(2)	2.31	2.04	XS	[15]
	$\text{K}_2\text{BaCu}(\text{NO}_2)_6$	α	room	2.114(5)	2.114(5)	2.114(5)	2.11	2.11	NS	[16]
		α	room	2.111(4)	2.111(4)	2.111(4)	2.11	2.11	XS	[17]
		α	295	2.118(2)	2.118(2)	2.118(2)	2.12	2.12	XS	[11]
		β	276	2.116(13)	2.153(14)	2.058(9)	2.06	2.16	XS	[18]
		β	193	2.151(16)	2.133(31)	2.071(14)	2.07	2.14	XS	[18]
		γ	160	2.230(19)	2.050(10)	2.046	2.23	2.05	XS	[19, 13]
	$\text{Rb}_2\text{PbCu}(\text{NO}_2)_6$	β	295	2.176(5)	2.166(5)	2.063(4)	2.06	2.17	XS	[20, 21]
		β	295	2.179(5)	2.169(5)	2.063(4)	2.06	2.17	XS	[21]
	$\text{Cs}_2\text{PbCu}(\text{NO}_2)_6$	α	420	2.174(7)	2.174(7)	2.174(7)	2.17	2.17	NS	[22]
		β	323	2.227(8)	2.221(7)	2.074(6)	2.08	2.22	NS	[23]
		β'	293	2.232(7)	2.227(8)	2.071(6)	2.07	2.23	NS	[24]
		γ	160	2.300(7)	2.115(7)	2.073(6)	2.30	2.09	NP	[25]
$\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$		295	2.118(6)	2.118(6)	2.118(6)	2.12	2.12	XS	[26]	

a) Distances in units of 10^{-10} m.

b) XS: single crystal X-ray diffraction, NS: single crystal neutron diffraction;
XP: powder X-ray diffraction, NP: powder neutron diffraction.

minimum value of $R_c^{\min} > 0$ is obtained for square-planar complexes (for $R_a \rightarrow \infty$) and analogically, the minimum value of $R_a^{\min} > 0$ is obtained for linear arrangement of the MN_2 chromophore (for $R_c \rightarrow \infty$). These limit cases must be respected in the correct extrapolation of the R_a vs. R_c dependence (Fig. 1). Therefore only a smooth curve appears to be an acceptable form of the R_a vs. R_c dependence despite of a low number of experimental data (two points for $K_2PbCo(NO_2)_6$, three phases for $K_2PbCu(NO_2)_6$, and four structures for $Cs_2PbCu(NO_2)_6$). Since in the given case a statistical approach is rather problematic, a high correlation coefficient of the order correlation was obtained: $\rho = 0.99$ for both, $K_2PbCu(NO_2)_6$ and $Cs_2PbCu(NO_2)_6$ compounds.

The conclusions based on Fig. 1 follow:

i) The obtained R_a vs. R_c dependences for three different compounds show a similar course. This finding resembles the data found for hexafluoro complexes [5].

ii) The cationic part of the crystal affects the position of the R_a vs. R_c correlation curve. In the series of $A^I = Cs, Rb, K$ in $A_2^I PbCu(NO_2)_6$ compounds with increasing lattice energy a compression of the coordination polyhedron (a shortening of all central atom—ligand distances) is expected like for hexafluoro complexes [27].

iii) In a compound, say $K_2PbCu(NO_2)_6$ or $Cs_2PbCu(NO_2)_6$, a transition from elongated to the compressed form of the tetragonal bipyramid was observed (γ to β transition) by increasing temperature. The high-temperature α phase, however, exhibits a regular octahedral structure under the conditions of X-ray or neutron diffraction measurements. This is the case when the dynamic Jahn—Teller effect takes place [13]. Here a rapid interconversion between three equivalent distorted structures makes the observed structure as it would be a regular octahedron. An individual polyhedron of the α phase is probably more distorted when compared with the β phase. Therefore, the observed (averaged) α phase lies in Fig. 1 somewhat outside the R_a vs. R_c correlation curve.

The main result of this communication represents a finding according to which the R_a vs. R_c dependence between the central atom—ligand distances can be exhibited also within the same compound. Its individual phases (α , β , γ) differ from each other only in the amount of the total energy E_T . Therefore, in square-bipyramidal complexes a common intrinsic disposition must exist owing to which the variation of the central atom—ligand distances follows the R_a vs. R_c dependence. This disposition is based on energetic criteria. The corresponding functional dependence of the $E_T = f(R_a, R_c)$ form is the known adiabatic potential surface (APS). Recent quantum chemical calculations certify the suggestion that a valley on the APS does exist along the R_a vs. R_c correlation curve [4, 28—30]. Raising the total energy of the system, e.g. by simple heating, the complex can relax to another geometric configuration through a defined reaction path. The minimum energy path is well approximated by the so-called minimum energy

coordinates if the harmonic approximation is considered [31, 32]. Thus the above-mentioned R_a vs. R_c dependences are to be explained in terms of this theoretical language [33].

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