Axial *versus* equatorial metal—ligand distances in transition metal compounds

III. Hexaaqua and hexachloro complexes

R. BOČA

Department of Inorganic Chemistry, Slovak Technical University,
CS-812 37 Bratislava

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By analyzing experimental structure data of hexaaqua and hexachloro complexes it was found that the tetragonal bipyramid is a more frequent form of the coordination polyhedron in comparison with the octahedral configuration. Moreover, the axial and equatorial metal—ligand distances exhibit, also in these complexes, a mutual dependence of the smooth curve type which manifests itself so that with increasing axial bond length the equatorial distance is shortened and *vice versa*. Individual factors operative in such dependences are discussed in more detail, namely the central atom effect and the host lattice effect.

При анализе экспериментальных структурных данных гексаакво и гексахлоро комплексов было отмечено, что тетрагональная бипирамида является более частым видом координационного полиэдра, чем октаэдр. Более того, аксиальные и экваториальные расстояния металл—лиганд находятся в этих комплексах во взаимной зависимости типа плавной кривой, отражающей тот факт, что с увеличением длины аксиальных связей сокращается экваториальное расстояние и наоборот. Отдельные факторы, влияющие на эту зависимость обсуждаются более подробно, а именно эффект центрального атома и эффект решетки.

A dependence of the smooth curve type which represents the correlation between axial, R_a, and equatorial, R_e, metal—ligand distances in hexacoordinated complexes is known since 1976 [1]. Such a knowledge was successively generalized beginning with the Cu^{II} complexes with certain chromophores [1, 2], through the Ni^{II} complexes [3, 4], towards the other central atoms, M, of the first transition metal row (M = Cr, Mn, Fe, Co, Ni, Cu, and Zn) [5—8]. Recently it was found [7] that various oxidation states (M^{II} and M^{III}) and spin states (with the spin multiplicity of $m = 1, 2, 3, 4, 5$, and 6) have no principal influence on the general shape of the correlation curve R_a *vs.* R_e for hexafluoro complexes. On the other hand, the central atom effect appears to be significant when looking on the degree of the coordination polyhedra tetragonality. The effect of temperature [8] and the effect of external pressure [9] on the degree of the tetragonality were also registered. The evidence that the dependences R_a *vs.* R_e are valid for various electronic states (degenerate — E_g, T_{1g} or T_{2g}, and nondegenerate — A_{1g} or A_{2g}) [5—7] makes the explanation of such a behaviour to be more complicated. The case of the nondegenerate electronic state indicates that not only the Jahn—Teller effect does operate in tetragonal distortions of coordination polyhedra.

It was emphasized in the recent paper [10] that these observations can be rationalized in terms of an equatorial-axial influence. That means a collective, integral influence of the equatorial ligand plane on properties of ligands situated in axial positions, *via* the central atom. On the basis of experimental data it was deduced [7, 8] that a certain intrinsic disposition does exist in hexacoordinated complexes, according to which the complex undergoes stereochemical changes along the dependence R_a *vs.* R_e; this disposition being connected with energetic conditions. A quantum-chemical mapping of the adiabatic potential surfaces for free complexes of ${}^m[MX_6]^q$ type shows [5, 6, 10, 11] that the total energy function $E_T = f(R_a, R_e)$ exhibits a valley; its course being identical with the correlation curve R_a *vs.* R_e. This valley represents a minimum energy path when the octahedral geometry is removed towards the dissociation limit cases — $[MX_4]^q$ or MX_2.

According to the CNDO type calculations [10], the isolated Jahn—Teller active systems (having the degenerate electronic ground-state E_g, T_{1g} or T_{2g} in the octahedral geometry) exhibit tetragonal distortions of the order of 10^{-13}—10^{-12} m, *i.e.* outside the experimental range in the solid state: 0.1—0.4 (10^{-10} m). Thus, the solid state effects, probably, play an important role in removing the octahedral (nearly octahedral) geometry of the free complex. Here an additional lattice potential, V_L, is to be added to the free-particle adiabatic potential E_T. Since V_L depends on the crystal packing as well as on the quality of individual ions, the octahedral geometry is removed in dependence on the chemical constitution of the compound; the most probable equilibrium geometry in the solid state lies along the correlation curve R_a *vs.* R_e.

However, the above explanation is rather rough. Several questions require a more detailed analysis of experimental data. For example, the hexafluoro complexes, studied in Part I [7], often exhibit strong interactions between individual polyhedra (here the one-, two- or three-dimensional bridging takes place). Such a situation is eliminated in the hexaaqua complexes. These complexes represent a subject under present study where the central atom effect on the correlations R_a *vs.* R_e has been investigated. Moreover, the host lattice effect on the correlations mentioned has been cleared up in the series of hexachloro complexes.

Results and discussion

The tetragonal distortions of MX_6 polyhedra are often accompanied with a slight *ortho*-rhombic component. Therefore, the geometry of MX_6 systems with a centre of symmetry is usually described by three parameters: the long central atom—ligand distance, R_L, the medium, R_M, and the short, R_S, distance. These parameters are listed in Table 1 for the hexaaqua complexes of some transition metals. Two identical (nearly equal) distances define the equatorial plane of a complex and their mean value was marked as R_e. The remaining parameter, R_a,

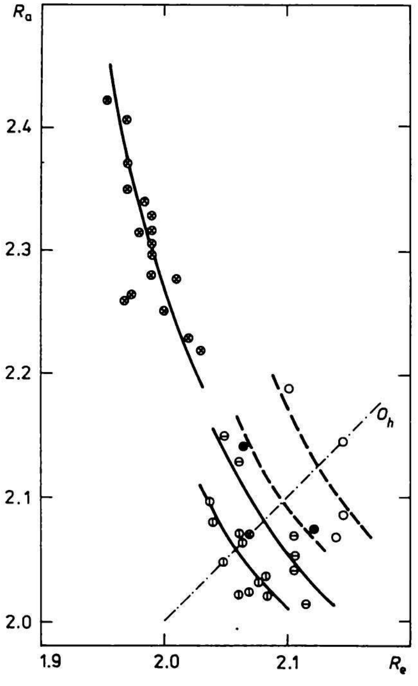

Fig. 1. R_a vs. R_e dependences in hexaaqua complexes.
○ d^6, ⊖ d^7, ⦶ d^8, ⊗ d^9, ● d^{10} system of $[M(H_2O)_6]^{2+}$ for M = Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}. Dashed line — expected dependence. Distances R_a and R_e are in units of 10^{-10} m.

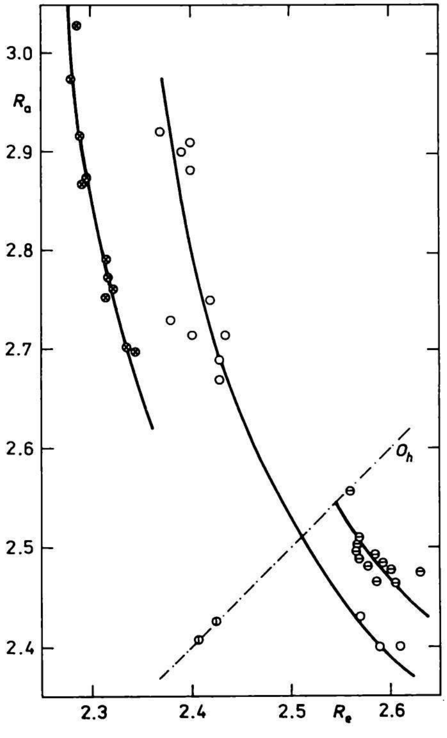

Fig. 2. R_a vs. R_e dependences in hexachloro complexes.
○ d^4, ⊖ d^5, ⦶ d^8, ⊗ d^9 system of $[MCl_6]^{4-}$ for M = Cr^{II}, Mn^{II}, Ni^{II}, and Cu^{II}. Distances R_a and R_e are in units of 10^{-10} m.

Table 1

Central atom—oxygen distances (10^{-10} m) in $[M(OH_2)_6]^{2+}$ polyhedra

d^n	Compound	Note	Experimental			Selected		Ref.
			R_l	R_M	R_S	R_a	R_e	
0	$Mg(H_2O)_6S_2O_3$		2.118	2.046	2.042	2.118	2.044	[12]
			2.115	2.068	2.068	2.115	2.068	[13]
	$Mg(H_2O)_6[MgC_6H_5O_7(H_2O)]_2 \cdot 2H_2O$		2.081	2.080	2.061	2.061	2.080	[14]
3	$(NH_4)_2V(H_2O)_6(SO_4)_2$		2.16	2.16	2.12	2.12	2.16	[15]
5	$(NH_4)_2Mn(H_2O)_6(SO_4)_2$		2.200	2.193	2.150	2.150	2.196	[16]
6	$FeSO_4 \cdot 7H_2O$	*a*	2.188	2.109	2.096	2.188	2.102	[17]
		b	2.144	2.136	2.068	2.068	2.140	[17]
	$Fe(H_2O)_6SiF_6$		2.146	2.146	2.146	2.146	2.146	[18]
	$(NH_4)_2Fe(H_2O)_6(SO_4)_2$		2.156	2.136	2.086	2.086	2.146	[15]
7	$Co(H_2O)_6[Co(C_9H_7NO_3)_2]_2 \cdot 2H_2O$		2.129	2.073	2.049	2.129	2.061	[19]
	$(NH_4)_2Co(H_2O)_6(SO_4)_2$		2.107	2.106	2.070	2.070	2.106	[15]
	$(NH_4)_2Co(H_2O)_6(BeF_4)_2$		2.111	2.104	2.053	2.053	2.107	[20]
	$Co(H_2O)_6(NO_3)_2 \cdot 2C_6H_{12}N_4 \cdot 4H_2O$		2.115	2.098	2.040	2.040	2.106	[21]
	$Co(H_2O)_6(C_8H_5O_4)_2$	*a*	2.128	2.105	2.014	2.014	2.116	[22]
		b	2.150	2.054	2.047	2.150	2.050	[22]
8	$Ni(H_2O)_6S_2O_3$		2.097	2.043	2.043	2.097	2.043	[23]
	$Ni(H_2O)_6SeO_4$		2.08	2.05	2.04	2.08	2.045	[24]
	$[(NH_2)_3C]_2Ni(H_2O)_6(SO_4)_2$		2.070	2.065	2.062	2.070	2.063	[25]
	$Ni(H_2O)_6I_2$		2.064	2.064	2.064	2.064	2.064	[26]
	$Ni(H_2O)_6SiF_6$		2.047	2.047	2.047	2.047	2.047	[27]
	$(NH_4)_2Ni(H_2O)_6(SO_4)_2$		2.085	2.083	2.036	2.036	2.084	[28]
	$Ni(H_2O)_6(NO_3)_2$		2.080	2.076	2.033	2.033	2.078	[29]
	$Ni(D_2O)_6SO_4$		2.10	2.07	2.02	2.02	2.085	[30]
	$NiK_4(P_3O_9)_2 \cdot 7H_2O$		2.082	2.056	2.023	2.023	2.069	[31]
	$(NH_4)_2Ni(H_2O)_6(CrO_4)_2$		2.073	2.054	2.022	2.022	2.063	[32]

Table 1 (Continued)

d^n	Compound	Note	Experimental			Selected		Ref.
			R_L	R_M	R_S	R_a	R_e	
9	$Cu(H_2O)_6(CH_3\cdot C_6H_4\cdot SO_3)_2$		2.423	1.954	1.953	2.423	1.953	[33]
	$Cu_2(ZrF_8)\cdot 12H_2O$	⌀	2.407	2.011	1.939	2.407	1.975	[34]
	$Cu(H_2O)_6SiF_6$	*a*	2.367	1.970	1.970	2.367	1.970	[35]
		b	2.074	2.074	2.074	2.074	2.074	[35]
	$Cu_3(ZrF_7)_2\cdot 16H_2O$		2.355	1.983	1.954	2.355	1.968	[36]
	$K_2Cu(H_2O)_6(Zr_2F_{12})$		2.327	2.024	1.967	2.327	1.995	[37]
	$(NH_4)_2Cu(H_2O)_6(CuSO_3)_4$	*a*	2.339	2.006	1.965	2.339	1.985	[38]
		b	2.329	2.005	1.980	2.329	1.992	[38]
	$Tl_2Cu(H_2O)_6(SO_4)_2$		2.317	2.017	1.957	2.317	1.987	[39]
	$Cs_2Cu(H_2O)_6(SO_4)_2$		2.315	2.004	1.966	2.315	1.985	[40]
	$Rb_2Cu(H_2O)_6(SO_4)_2$	77 K	2.317	2.000	1.978	2.317	1.989	[41]
		R	2.307	2.031	1.957	2.307	1.994	[42]
	$K_2Cu(H_2O)_6(SeO_4)_2$		2.297	2.044	1.937	2.297	1.990	[43]
	$K_2Cu(H_2O)_6(SO_4)_2$		2.278	2.069	1.943	2.278	2.006	[44]
	$Cu(H_2O)_6(C_6H_5SO_3)_2$	*a*	2.264	1.986	1.961	2.264	1.973	[33]
		b	2.259	1.979	1.958	2.259	1.968	[33]
	$(NH_4)_2Cu(H_2O)_6(SO_4)_2$	145 K	2.278	2.012	1.970	2.278	1.991	[45]
		215 K	2.250	2.041	1.967	2.250	2.004	[45]
		R	2.233	2.080	1.968	2.233	2.024	[46]
		R	2.19	2.06	2.04			[47]
		R	2.219	2.095	1.961			[48]
	$Cu(H_2O)_6(C_{10}H_{15}OSO_3)_2$	⌀	2.12	2.11	1.97			[33]
10	$Zn(H_2O)_6(CH_3\cdot C_6H_4\cdot SO_3)_2$		2.14	2.08	2.05	2.14	2.065	[49]
	$(NH_4)_2Zn(H_2O)_6(SO_4)_2$		2.129	2.117	2.075	2.075	2.123	[50]
	$(NH_4)_2Cd(H_2O)_6(SO_4)_2$		2.298	2.297	2.241	2.241	2.297	[51]

R — room temperature; *a*, *b* — different coordination polyhedra; ⌀ — averaged values for noncentrosymmetric coordination polyhedra.

in the axial (out of the plane) direction completes a square-bipyramidal form of the coordination polyhedron. Some experimental data presented in Table 1 were deleted by the next consideration because their little reliability was shown or because there exist later reinvestigations. The selected values of R_a were plotted vs. the corresponding distances R_e and thus a smooth curve type dependence between them was obtained (Fig. 1). A more detailed analysis of Fig. 1 leads to the following conclusions.

i) A statistical processing of the set of $\{R_a, R_e\}$ data is allowed for hexaaqua complexes of Cu^{II}, Ni^{II}, Co^{II}, and Fe^{II} (there are 19, 10, 6, and 4 relevant structural determinations). The calculated correlation coefficients as well as their significance levels (Table 2) display an evidence that a statistical correlation does exist between the values of R_a and R_e.

ii) The mean central atom—ligand distances increase in directions of darts within the series of $\mathrm{Fe^{II}} \leftarrow \mathrm{Co^{II}} \leftarrow \mathrm{Ni^{II}} \rightarrow \mathrm{Cu^{II}} \rightarrow \mathrm{Zn^{II}}$. A similar trend was found previously for the hexafluoro complexes [7].

iii) The highest degree of tetragonal distortions (R_a—R_e up to 0.47×10^{-10} m, the tetragonality parameter $T = R_e/R_a \approx 0.8$) is registered in complexes having a doubly degenerate electronic ground-state ^2E_g in the octahedral geometry, *i.e.* in the hexaaqua complexes of $^2[\mathrm{Cu^{II}}]$.

iv) The tetragonal distortions occur also in complexes with a nondegenerate electronic state A_{1g} or A_{2g}, namely in hexaaqua complexes of $^4[\mathrm{V^{II}}]$, $^6[\mathrm{Mn^{II}}]$, $^3[\mathrm{Ni^{II}}]$, and $^1[\mathrm{Zn^{II}}]$. Here the high-spin states are preferred as a consequence of the weak ligand field produced by the aqua-ligands.

v) The tetragonal distortions are exhibited also in hexaaqua complexes of $^5[\mathrm{Fe^{II}}]$ and $^4[\mathrm{Co^{II}}]$ having the triply degenerate electronic state $^5T_{2g}$ and $^4T_{1g}$, respectively. The degree of distortions, however, is of the same order as for the nondegenerate states.

It may be concluded that the main features of the dependences R_a vs. R_e retain unchanged when comparing the hexafluoro complexes and the hexaaqua complexes. Therefore, the tetragonal distortions in complexes $[\mathrm{MX_6}]$ cannot be explained by means of a simple bridging of ligands X (this is eliminated in the latter case).

A similar analysis of the structural data was performed for the hexachloro complexes (Table 3, Fig. 2) and the following conclusions can be drawn.

i) Relevant structural data for compounds containing the $[\mathrm{MCl_6}]^{4-}$ polyhedra, M = Cr^{II}, Mn^{II}, and Cu^{II}, yield significantly high correlation coefficients for the dependence R_a vs. R_e (Table 2).

ii) The complexes having the doubly degenerate electronic ground-state E_g, namely the hexachloro complexes of $^5[\mathrm{Cr^{II}}]$ and $^2[\mathrm{Cu^{II}}]$, exhibit a great degree of tetragonal distortion: R_a—R_e up to 0.55 and 0.77 (10^{-10} m), respectively.

iii) The remaining high-spin hexachloro complexes of $^6[\mathrm{Mn^{II}}]$ exhibit tetragonal distortions within a significantly lower extent (the $^6A_{1g}$ electronic state).

Table 2

Statistics of the structural data analysis for $[M^{II}X_6]^{n}$ complexes

M	State	X = H_2O					X = Cl				
		N	$\bar{R}_{M-X}$	T	$\lvert\varrho\rvert$	α	N	$\bar{R}_{M-X}$	T	$\lvert\varrho\rvert$	α
Mg^{II}	$^1A_{1g}$	3	2.08	0.97—1.01			—				
V^{II}	$^4A_{2g}$	1	2.15	1.02			1	2.48	1.0		
Cr^{II}	^5E_g	—					12	2.53	0.81—1.09	0.94	0.001
Mn^{II}	$^6A_{1g}$	1	2.18	1.02			13	2.56	1.0 —1.06	0.62	0.05
Fe^{II}	$^5T_{2g}$	4	2.13	0.96—1.03	0.73	0.3	—				
Co^{II}	$^4T_{1g}$	6	2.09	0.95—1.05	0.97	0.001	—				
Ni^{II}	$^3A_{2g}$	10	2.06	0.97—1.03	0.72	0.02	2	2.42	1.0		
Cu^{II}	^2E_g	19	2.09	0.81—1.00	0.84	0.001	12	2.49	0.75—0.86	0.88	0.001
Zn^{II}	$^1A_{1g}$	2	2.10	0.97—1.02			—				
(Mn^{II}, Cr^{II})		—					9	2.52	0.88—1.06	0.99	0.001

N — number of structures; $\bar{R}_{M-X}$ — mean central atom—ligand distance; $T = R_e/R_a$ — tetragonality parameter; ϱ — correlation coefficient of the R_a vs. R_e dependence; α — significance level, i.e. the probability that $\{|t| = |\varrho|\sqrt{(N-2)/(1-\varrho^2)} \geq t_\alpha\}$ is equal to α.

Table 3

Central atom—chlorine distances (10^{-10} m) in $[MCl_6]^{4-}$ polyhedra

d^n	Compound	Note	Experimental R_L	R_M	R_S	Selected R_a	R_e	Ref.
3	$CsVCl_3$		2.478	2.478	2.478	2.478	2.478	[52]
4	$CrCl_2$		2.91	2.40	2.40	2.91	2.40	[53]
			2.90	2.39	2.39	2.90	2.39	[53]
			2.92	2.37	2.37	2.92	2.37	[53]
			2.88	2.40	2.40	2.88	2.40	[53]
	$CsCrCl_3$	60 K, *a*	2.67	2.43	2.43			[54]
		b	2.55	2.55	2.36			[54]
		γ, 60 K, ⌀ *a*	2.730	2.405	2.365	2.730	2.385	[55]
		⌀ *b*	2.715	2.437	2.437	2.715	2.437	[55]
	$RbCrCl_3$	γ, 100 K, ⌀ *a*	2.750	2.445	2.390	2.750	2.417	[56]
		⌀ *b*	2.715	2.402	2.402	2.715	2.402	[56]
		β, 295 K, *a*	2.69	2.43	2.43	2.69	2.43	[54]
		b	2.59	2.59	2.40	2.40	2.59	[54]
	Rb_2CrCl_4	77 K	2.700	2.379	2.357			[57]
		R	2.57	2.57	2.43	2.43	2.57	[58]
	Cs_2CrCl_4		2.61	2.61	2.40	2.40	2.61	[59]
5	Na_2MnCl_4		2.603	2.603	2.463	2.463	2.603	[60]
	Rb_2MnCl_4		2.53	2.53	2.50			[61]
	$(CH_3NH_3)_2MnCl_4$	γ, 188 K	2.578	2.556	2.499	2.499	2.567	[62]
			2.579	2.556	2.489	2.489	2.567	[63]
		β, 293 K	2.57	2.57	2.51	2.51	2.57	[64]
		α, 404 K	2.56	2.56	2.50			[64]
			2.569	2.569	2.491	2.491	2.569	[65]
	$(C_2H_5NH_3)_2MnCl_4$	γ, 126 K	2.585	2.572	2.481	2.481	2.578	[66]
		β, 295 K	2.591	2.591	2.466	2.466	2.591	[67]
		β, 294 K	2.593	2.593	2.482	2.482	2.593	[68]

Table 3 (Continued)

d^n	Compound	Note	Experimental			Selected		Ref.
			R_L	R_M	R_S	R_a	R_e	
	$(C_3H_7NH_3)_2MnCl_4$	δ, 180 K	2.601	2.601	2.478	2.478	2.601	[69]
		295 K	2.629	2.629	2.475	2.475	2.629	[70]
	$(C_4H_9NH_3)_2MnCl_4$	294 K	2.588	2.588	2.468	2.468	2.588	[71]
	$[NH_3(CH_2)_3NH_3]MnCl_4$	295 K	2.584	2.584	2.491	2.491	2.584	[72]
	$N(CH_3)_4MnCl_3$		2.560	2.560	2.560	2.560	2.560	[73]
8	$CsNiCl_3$		2.43	2.43	2.43			[74]
	$NiCl_2$		2.426	2.426	2.426	2.426	2.426	[75]
	$(C_9H_{14}N)NiCl_3$	⌀	2.426	2.418	2.410			[76]
	$(CH_3)_4NNiCl_3$		2.408	2.408	2.408	2.408	2.408	[77]
	$CH_3NH_3NiCl_3$		2.405	2.351	2.351			[78]
9	NH_4CuCl_3	⌀	3.060	2.297	2.284	3.060	2.291	[79]
		⌀	3.09	2.29	2.285			[80]
	$KCuCl_3$	⌀	3.027	2.294	2.281	3.027	2.288	[80]
	$(C_2H_5NH_3)_2CuCl_4$		2.975	2.285	2.277	2.975	2.281	[81]
	$(C_6H_5NH_3)_2CuCl_4$		2.918	2.301	2.280	2.918	2.291	[82]
	$[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$		2.872	2.311	2.282	2.872	2.296	[83]
	$Rb_3Cu_2Cl_7$	⌀	2.870	2.353	2.234	2.870	2.293	[55]
	$(NH_4)_2CuCl_4$		2.793	2.332	2.300	2.793	2.316	[84]
	$CsCuCl_3$	β, R	2.776	2.355	2.281	2.776	2.318	[85]
		β, 400 K	2.762	2.354	2.292	2.762	2.323	[55]
	$RbCuCl_3$	γ, 4 K, ⌀ *a*	2.755	2.35	2.28	2.755	2.315	[55]
		⌀ *b*	2.70	2.345	2.345	2.70	2.345	[55]
		β, 295 K	2.706	2.369	2.307	2.706	2.338	[55]

α, β, γ, δ — various phases; R — room temperature; *a*, *b* — different coordination polyhedra; ⌀ — averaged values for noncentrosymmetric coordination polyhedra.

By the temperature changes some systematic trends have been registered: with increasing temperature the tetragonality parameter usually decreases. This finding is based on the data known:

i) for $(NH_4)_2Cu(H_2O)_6(SO_4)_2$ (where $T_{295} = 0.91$, $T_{215} = 0.89$, $T_{145} = 0.87$) and $Rb_2Cu(H_2O)_6(SO_4)_2$ ($T_{295} = 0.864$, $T_{77} = 0.858$) as recently reported elsewhere [45];

ii) for $RbCrCl_3$ (where $T_{295} = 1.08$ and 0.90, $T_{100} = 0.88$), Rb_2CrCl_4 ($T_{295} = 1.06$, $T_{77} = 0.88$), $(CH_3NH_3)_2MnCl_4$ ($T_{404} = 1.031$, $T_{293} = 1.024$, $T_{188} = 1.031$ or 1.027), $(C_2H_5NH_3)_2MnCl_4$ ($T_{295} = 1.051$, $T_{294} = 1.045$, $T_{126} = 1.039$), $(C_3H_7NH_3)_2MnCl_4$ ($T_{295} = 1.062$, $T_{180} = 1.050$), $CsCuCl_3$ ($T_{400} = 0.841$, $T_{295} = 0.835$), and $RbCuCl_3$ ($T_{295} = 0.864$, $T_4 = 0.868$ or 0.840) as pointed out here.

This conclusion is in agreement with the data for $K_2PbCu(NO_2)_6$ (where $T_{276} = 1.05$, $T_{193} = 1.03$, $T_{100} = 0.92$) and $Cs_2PbCu(NO_2)_6$ ($T_{323} = 1.07$, $T_{293} = 1.07$, $T_{100} = 0.91$) which have been reviewed, for instance, in Ref. [8]. An exception from this rule is represented by the high-temperature α phase in hexanitro complexes of Cu^{II} and Co^{II} (due to the dynamic Jahn—Teller effect a regular octahedron is registered under the conditions of X-ray or neutron diffraction measurements) and the high-temperature α phases in some hexachloro complexes of Cu^{II} and Cr^{II} (these often exhibit the D_{3d} or C_{3v} symmetry of the chromophore $MCl'_3Cl''_3$). The latter case is, however, out of the range of the R_a vs. R_e description.

A detailed neutron diffraction study [86] has been recently reported for the mixed crystal of $Rb_2Cr_{1-x}Mn_xCl_4$, $0 < x < 1$. It was found that with increasing value of x the tetragonal distortion of $[(Mn, Cr)Cl_6]^{4-}$ polyhedra decreases. At the same

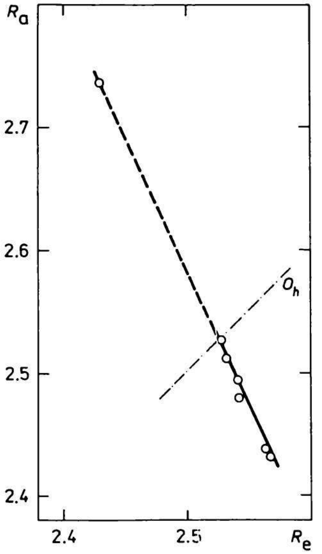

Fig. 3. R_a vs. R_e dependence in the mixed crystal of $Rb_2Cr_{1-x}Mn_xCl_4$ for $0 < x < 1$. Experimental data according to Ref. [86]. Distances R_a and R_e are in units of 10^{-10} m.

time the angular overlap method calculations indicated that the individual e_g-active polyhedra of $[CrCl_6]^{4-}$ are more distorted in comparison with e_g-inactive polyhedra of $[MnCl_6]^{4-}$. The values of R_a and R_e for $Rb_2Cr_{1-x}Mn_xCl_4$ correlate along a smooth curve (Fig. 3) being nearly linear within the range of $x \in (0, 1)$. This knowledge leads to the finding of a new factor — the host lattice effect, which is operative in the dependences R_a *vs.* R_e. It must be mentioned in this connection that the host lattice effect can manifest itself also in a discontinuous change in the degree of tetragonality. As an example, the mixed crystal of $Ba_2Zn_{1-x}Cu_xF_6$ may be mentioned [87], where for $x > 0.6$ the cooperative Jahn—Teller effect prevails.

Finally, significant tetragonal distortions were found also in hexafluoro complexes of Sn^{IV} [88, 89], hexaaqua complexes of Mg^{II} and Cd^{II}, and in hexachloro complexes of Ti^{IV} [90], Cd^{II} [91, 92], and Sn^{IV} [93] (the d^0 and d^{10} electronic systems). It indicates that such distortions and R_a *vs.* R_e dependences occur not only for transition metal complexes but they are, probably, of a more general nature. Several factors are operative in these dependences and according to the present knowledge they may be summarized as follows:

i) the central atom effect (*i.e.* the proton number, oxidation and spin state influence) which determines either the nondegenerate electronic states A_{1g} or A_{2g} (these are e_g-inactive by means of the vibronic coupling) or degenerate (e_g-active) states E_g, T_{1g} or T_{2g};

ii) the thermodynamic state characteristics such as temperature or pressure;

iii) the host lattice effect which produces either the continuous or discontinuous changes in the degree of the tetragonality.

References

1. Gažo, J., Bersuker, I. B., Garaj, J., Kabešová, M., Kohout, J., Langfelderová, H., Melnik, M., Serátor, M., and Valach, F., *Coord. Chem. Rev. 19,* 253 (1976).
2. Macášková, Ľ. and Gažo, J., *Koord. Khim. 4,* 1314 (1978).
3. Jóna, E., Valach, F., Gažo, J., Fendrich, E., and Šramko, T., *Proceedings of the 8th Conference on Coordination Chemistry,* p. 143. Bratislava—Smolenice, 1980.
4. Jóna, E., *Thesis.* Slovak Technical University, Bratislava, 1980.
5. Boča, R., Pelikán, P., and Gažo, J., *Proceedings of the 8th Conference on Coordination Chemistry,* p. 37. Bratislava—Smolenice, 1980.
6. Boča, R. and Pelikán, P., *Inorg. Chem. 20,* 1618 (1981).
7. Boča, R., *Chem. Zvesti 35,* 769 (1981).
8. Boča, R., *Chem. Zvesti 35,* 779 (1981).
9. Zemskov, S. V. and Gabuda, S. P., *Zh. Strukt. Khim. 17,* 904 (1976).
10. Gažo, J., Boča, R., Jóna, E., Kabešová, M., Macášková, Ľ., Pelikán, P., Šima, J., and Valach, F., *Coord. Chem. Rev. 43,* 87 (1982).
11. Boča, R. and Pelikán, P., *Chem. Zvesti 36,* 35 (1982).

12. Baggio, S., Amzel, L. M., and Becka, L. N., *Acta Crystallogr. B25,* 2650 (1969).
13. Nardelli, M., Fava, G., and Giraldi, G., *Acta Crystallogr. 15,* 227 (1962).
14. Johnson, C. K., *Acta Crystallogr. 18,* 1004 (1965).
15. Montgomery, H., Chastain, R. V., Natt, J. J., Witkowska, A. M., and Lingafelter, E. C., *Acta Crystallogr. 22,* 775 (1967).
16. Montgomery, H., Chastain, R. V., and Lingafelter, E. C., *Acta Crystallogr. 20,* 731 (1966).
17. Baur, W. H., *Acta Crystallogr. 17,* 1167 (1964).
18. Hamilton, W. C., *Acta Crystallogr. 15,* 353 (1962).
19. Nassimbeni, L. R., Percy, G. C., and Rodgers, A. L., *Acta Crystallogr. B32,* 1252 (1976).
20. Vicat, J., Trangui, D., and Aléonard, S., *Acta Crystallogr. B33,* 1180 (1977).
21. Viossat, B., Khodadad, P., and Rodier, N., *Bull. Soc. Chim. Fr. 1981 I,* 69.
22. Adividjaja, G. and Rossmanith, E., *Acta Crystallogr. B34,* 3079 (1978).
23. Elerman, Y., Aydin Uraz, A., and Armagan, N., *Acta Crystallogr. B34,* 3330 (1978).
24. Fues, H., *Z. Anorg. Allg. Chem. 379,* 204 (1970).
25. Morimoto, C., cited in Ref. [32].
26. Lonër, M., Grandjean, D., and Weigel, D., *J. Solid State Chem. 7,* 222 (1973).
27. Ray, S., Zalkin, A., and Templeton, D., *Acta Crystallogr. B29,* 2741 (1973).
28. Montgomery, H. and Lingafelter, E. C., *Acta Crystallogr. 17,* 1478 (1964).
29. Bigoli, F., Braibanti, A., and Tiripicchio, A., *Acta Crystallogr. B27,* 1427 (1971).
30. O'Connor, B. H. and Dale, D. H., *Acta Crystallogr. 21,* 707 (1966).
31. Seethanen, F., Tordjman, I., and Averbuch-Pouchot, M. F., *Acta Crystallogr. B34,* 2387 (1978).
32. Montgomery, H., *Acta Crystallogr. B35,* 155 (1979).
33. Coudwell, C., Prout, K., Robey, D., Taylor, R., and Rossotti, F. J. C., *Acta Crystallogr. B34,* 14 (1978).
34. Fischer, J., Elchinger, R., and Weiss, R., *Acta Crystallogr. B29,* 1967 (1973).
35. Ray, S., Zalkin, A., and Templeton, D. H., *Acta Crystallogr. B29,* 2748 (1973).
36. Fischer, J. and Weiss, R., *Acta Crystallogr. B29,* 1963 (1973).
37. Fischer, J. and Weiss, R., *Acta Crystallogr. B29,* 1958 (1973).
38. Nyberg, B., *Acta Crystallogr. B34,* 1418 (1978).
39. Schields, K. G., van der Zee, J. J., and Kennard, C. H. L., *Cryst. Struct. Commun. 1,* 371 (1972).
40. Schields, K. G. and Kennard, C. H. L., *Cryst. Struct. Commun. 1,* 189 (1972).
41. Smith, G., Moore, F. H., and Kennard, C. H. L., *Cryst. Struct. Commun. 4,* 407 (1975).
42. Van der Zee, J. J., Schields, K. G., Graham, A. J., and Kennard, C. H. L., *Cryst. Struct. Commun. 1,* 367 (1972).
43. Whitnall, J., Kennard, C. H. L., Nimmo, J. K., and Moore, F. H., *Cryst. Struct. Commun. 4,* 709 (1975).
44. Robinson, D. J. and Kennard, C. H. L., *Cryst. Struct. Commun 1,* 185 (1972).
45. Hathaway, B., Duggan, M., Murphy, A., Mullane, J., Power, C., Walsh, A., and Walsh, B., *Coord. Chem. Rev. 36,* 267 (1981).
46. Brown, G. M. and Chidambaram, R., *Acta Crystallogr. B25,* 676 (1969).
47. Webb, M. W., Kay, H. F., and Grimes, N. W., *Acta Crystallogr. 18,* 740 (1965).
48. Montgomery, M. and Lingafelter, E. C., *Acta Crystallogr. 20,* 659 (1966).
49. Hargreaves. A., *Acta Crystallogr. 10,* 191 (1957).
50. Montgomery, H. and Lingafelter, E. C., *Acta Crystallogr. 17,* 1295 (1964).
51. Montgomery, H. and Lingafelter, E. C., *Acta Crystallogr. 20,* 728 (1966).
52. Niel, M., Cros, C., Vlasse, M., Pouchard, M., and Hagenmuller, P., *Mater. Res. Bull. 11,* 827 (1976).
53. Tracy, J. W., Gregory, N. W., Lingafelter, E. C., Dunitz, J. D., Mez, H. C., Rundle, R. E., Scheringer, Ch., Yakel, H. L., Jr., and Wilkinson, M. K., *Acta Crystallogr. 14,* 927 (1961).

54. Crama, W. J., Maaskant, W. J. A., and Verschoor, G. C., *Acta Crystallogr. B34*, 1973 (1978).
55. Crama, W. J., *Thesis*. Leiden, 1980.
56. Crama, W. J., Bakker, M., Verschoor, G. C., and Maaskant, W. J. A., *Acta Crystallogr. B35*, 1875 (1979).
57. Day, P., Hutchings, M. T., Janke, E., and Walker, P. J., *J. Chem. Soc., Chem. Commun. 1979*, 711.
58. Fair, M. J., Gregson, A. K., Day, P., and Hutchings, M. T., *Physica* (Utrecht) *B86—88*, 657 (1977).
59. Hutchings, M. T., Gregson, A. K., Day, P., and Leech, D. H., *Solid State Commun. 15*, 313 (1974).
60. Goodyear, J., Ali, S. A. D., and Steigmann, G. A., *Acta Crystallogr. B27*, 1672 (1971).
61. Goodyear, J., Ali, E. M., and Steigmann, G. A., *Acta Crystallogr. B33*, 2932 (1977).
62. Heger, G., Mullen, D., and Knorr, K., *Phys. Status Solidi* (a) *35*, 627 (1976).
63. Mikhail, I., *Acta Crystallogr. B33*, 1317 (1977).
64. Heger, G., Mullen, D., and Knorr, K., *Phys. Status Solidi* (a) *31*, 455 (1975).
65. Mikhail, I., *Acta Crystallogr. B33*, 1321 (1977).
66. Depmeier, W., *Acta Crystallogr. B33*, 3713 (1977).
67. Depmeier, W., *Acta Crystallogr. B32*, 303 (1976).
68. Depmeier, W. and Heger, G., *Acta Crystallogr. B34*, 1698 (1978).
69. Depmeier, W., and Mason, S., *Acta Crystallogr. B34*, 920 (1978).
70. Peterson, E. R. and Willett, R. D., *J. Chem. Phys. 56*, 1879 (1972).
71. Depmeier, W. and Chapuis, G., *Acta Crystallogr. B35*, 1081 (1979).
72. Willett, R. D. and Reidel, E. F., *Chem. Phys. 8*, 112 (1975).
73. Morosin, B. and Graeber, E. J., *Acta Crystallogr. 23*, 766 (1967).
74. Tischenko, G. N., *Tr. Kristallogr. Akad. Nauk SSSR 11*, 93 (1955).
75. Ferrari, A., Braibanti, A., and Bigliardi, G., *Acta Crystallogr. 16*, 846 (1963).
76. Harlow, R. L. and Simonsen, S. H., *Acta Crystallogr. B33*, 3234 (1977).
77. Stucky, G. D., *Acta Crystallogr. B24*, 330 (1968).
78. Willett, R. D., *J. Chem. Phys. 45*, 3737 (1966).
79. O'Bannon, G. and Willett, R. D., *Inorg. Chim. Acta 53*, L 131 (1981).
80. Willett, R. D., Dwiggins, C., Jr., Kruh, R. F., and Rundle, R. E., *J. Chem. Phys. 38*, 2429 (1963).
81. Steadman, J. P. and Willett, R. D., *Inorg. Chim. Acta 4*, 367 (1970).
82. Larsen, K. P., *Acta Chem. Scand. A28*, 194 (1974).
83. Greenhough, T. J. and Ladd, F. C., *Acta Crystallogr. B33*, 1266 (1977).
84. Willett, R. D., *J. Chem. Phys. 41*, 2243 (1964).
85. Schlueter, A. W., Jacobson, R. A., and Rundle, R. E., *Inorg. Chem. 5*, 277 (1966).
86. Münninghoff, G., Treutmann, W., Hellner, E., Heger, G., and Reinen, D., *J. Solid State Chem. 34*, 289 (1980).
87. Friebel, C., Propach, V., and Reinen, D., *Z. Naturforsch. 31b*, 1574 (1976).
88. Hoppe, R. and Dähne, W., *Naturwissenschaften 49*, 254 (1962).
89. Hebecker, Ch., von Schnering, H. G., and Hoppe, R., *Naturwissenschaften 53*, 154 (1966).
90. Hey, E. and Müller, U., *Z. Naturforsch. 36b*, 135 (1981).
91. Chapuis, G., *Acta Crystallogr. B34*, 1506 (1978).
92. Willett, R. D., *Acta Crystallogr. B33*, 1641 (1977).
93. Boysen, H. and Hewat, A. W., *Acta Crystallogr. B34*, 1412 (1978).

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