

CORRELATION CURVES FOR EQUATORIAL-AXIAL INTERACTIONS

ROMAN BOČA

Department of Inorganic Chemistry, Slovak Technical University, SK-812 38 Bratislava, Slovakia

(Received 16 February 1994; accepted 12 July 1994)

Abstract—Metal–ligand distances for hexacoordinate complexes show a mutual interrelation manifested in the fact that with increasing axial distances the equatorial ones decrease and vice versa. These R_a vs R_e dependences have been registered for certain chromophores and also for hexafluoro, hexachloro, hexanitro and hexaaqua complexes. Based on the anharmonic shape of the adiabatic potential surface, a theoretical analysis yields the form of the R_a vs R_e dependence which, in the most simple form, is a hyperbolic function.

Accumulation and comparison of a large number of structural data for structural units of AB_n type by various groups led to the following findings.

(i) In linear fragments of $B-A-B'$ type, the lengthening of one bond (say $A-B$) is accompanied by shortening of the second bond ($A-B'$) so that the R_{A-B} vs $R_{A-B'}$ dependence follows a smooth descending line. Such behaviour has been reported¹ for the systems $I-I-I$, $Cl-Sb-Cl$, $S-S-S$, $Mo-O-Mo$, $X-Cd-Y$ and $O-H-O$.

(ii) In tetracoordinate fragments of $B'AB_3$ type, correlations of $R_{A-B'}$ vs $\angle B'AB$ and R_{A-B} vs $\angle B'AB$ have been registered,² the former along a descending line and the latter along an ascending one. OSO_3 , OPO_3 , XSO_3 , $XSnCl_3$ and $ClAlCl_3$ fragments serve as examples of this behaviour.

(iii) In square-bipyramidal complexes having $\{CuO_6\}$, $\{CuN_6\}$, $\{NiO_6\}$ and $\{NiN_6\}$ chromophores, an R_a ($2x$) vs R_e ($4x$) correlation holds according to a descending line.³⁻⁹

(iv) Analogous correlations have been reported for cobalt(III), nickel(II) and zinc(II) complexes of the $trans-[M(L_N)_4X_2]$ type, $(L_N)_4$ being a nitrogen donor macrocyclic ligand.^{10,11}

(v) In uranyl complexes of $[UO_2L_n]$ type ($n = 4, 5$ and 6) the mean axial, $U-O$, distances correlate with the mean equatorial, $U-L$, distances.^{12,13}

(vi) Similar correlations also occur in complexes

with homogeneous ligand spheres, namely in those having $[MF_6]^{3-}$, $[MF_6]^{4-}$, $[MCl_6]^{4-}$, $[M(NO_2)_6]^{4-}$ and $[M(H_2O)_6]^{2+}$ units, where M covers the whole first transition metal row but also magnesium, zinc and cadmium as central atoms.¹⁴⁻¹⁸

(vii) In Group IV and V halides, having collinear homoligand L_a-M-L_b *trans* bond pairs, the interrelation of the conjugated bond lengths is expressed by an empirically chosen functional form of $R_a - R_0 = K/(R_e - R_0)^c$, with the parameter c ranging from 0.47 to 1.57.¹⁹

(viii) In Werner clathrates of $[Ni(4-MePy)_4(NCS)_2] \cdot nG$ type, a guest-to-host influence has been registered; it manifests itself in a systematic correlation of R_a vs R_e type.^{20,21}

(ix) The concept of equatorial-axial interactions, originally reported for hexacoordinate complexes, has been extended to be operative also for pentacoordinate complexes having $\{NiN_5\}$ and $\{NiN_4X\}$ chromophores. Again, an R_a vs R_e correlation holds true.²²

The above correlations can be rationalized in terms of the structural path concept.²³ Our understanding of this concept is that the units of AB_n or AB_nC_m type (with a single central atom A and peripheral atoms B and C) have an internal disposition to prefer a definite type of distortion; this disposition is encoded in the shape of the adiabatic potential surface (APS).

THEORY

Starting from an equilibrium geometry of the free AB_n system, a variation (stretching) of one bond generates a relaxation of the remaining bonds. This variation may originate, for example, in setting the system into the environment of the solid state so that the perturbation of one A—B bond may be caused by a counterion or other particles Z composing the crystal: $Z \cdots B-A-B$.

A relaxed coordinate R_j^c will be proportional to the displacement R_p , e.g.

$$R_j^c = D_{jp}R_p + D_{jpp}R_p^2 + \cdots \quad (1)$$

The adiabatic potential may be written in the form of a Taylor expansion:

$$E = E^0 + \sum_i F_i R_i + (1/2) \sum_i \sum_j F_{ij} R_i R_j + (1/6) \sum_i \sum_j \sum_k F_{ijk} R_i R_j R_k + \cdots, \quad (2)$$

where the individual orders mean a gradient (vanishing in the equilibrium), harmonic and cubic-anharmonic contributions. Restricting ourselves to the linear proportionality (first term) in eq. (1) and the harmonic approximations of eq. (2) the evaluation of D_{jp} is straight forward:^{24,25}

$$D_{jp} = C_{jp}/C_{pp}, \quad (3)$$

where C_{jp} are the matrix elements of the compliance matrix $C = F^{-1}$, which is the inverse of the harmonic constant matrix F . The above interaction displacement coordinates D_{jp} represent a degree of relaxation and thus they may be accepted as quantitative criteria of the coordination sphere plasticity.

For a particular case of a tetragonal distortion of $[ML_6]$ type complexes, two axial (R_a) and four equatorial (R_e) metal–ligand distances describe the geometry of the system. Then the APS may be considered in the following functional form:

$$E = E_0 + F_a R_a + F_e R_e + (1/2) F_{aa} R_a^2 + (1/2) F_{ee} R_e^2 + F_{ae} R_a R_e. \quad (4)$$

The condition for the local energy minima (minimum energy path) is

$$(\partial E / \partial R_a)_{R_e} = F_a + F_{aa} R_a + F_{ae} R_e = 0 \quad (5)$$

and thus

$$R_a = -(F_a/F_{aa}) - (F_{ae}/F_{aa}) R_e = A + D_{ae} R_e. \quad (6)$$

This is a linear equation: as far as R_e is stretched the R_a parameter relaxes proportionally and the

proportionality constant is simply the interaction displacement coordinate D_{ae} .

Analogously, for a fixed distortion of R_a we get

$$R_e = -(F_e/F_{ee}) - (F_{ae}/F_{ee}) R_a = B + D_{ea} R_a \quad (7)$$

or

$$R_a = -(F_e/F_{ae}) - (F_{ee}/F_{ae}) R_e = C + D_{ea}^{-1} R_e. \quad (8)$$

Now it is evident that within the harmonic approximation the R_a vs R_e dependence is represented by a pair of descending straight lines, eqs (6) and (8), with differing slopes, given by interaction displacement coordinates.¹⁸

In large displacements, however, unphysical predictions are obtained: either $R_a \leq 0$ for large displacements of R_e or $R_e \leq 0$ in the opposite case. This artifact of the harmonic approximation disappears when more complex forms of the APS are considered. For example:

$$E = E_0 + F_a R_a + F_e R_e + (1/2) F_{aa} R_a^2 + (1/2) F_{ee} R_e^2 + F_{ae} R_a R_e + (1/6) F_{aaa} R_a^3 + (3/6) F_{aae} R_a^2 R_e + (3/6) F_{aee} R_a R_e^2 + (1/6) F_{eee} R_e^3 \quad (9)$$

yields the condition

$$(\partial E / \partial R_a)_{R_e} = F_a + F_{aa} R_a + F_{ae} R_e + (1/2) F_{aaa} R_a^2 + F_{aae} R_a R_e + (1/2) F_{aee} R_e^2 = 0. \quad (10)$$

By neglecting the quadratic dependence of R_a (or $F_{aaa} = 0$) we get

$$R_a = -(F_a + F_{ae} R_e + 1/2 F_{aee} R_e^2) / (F_{aa} + F_{aae} R_e). \quad (11)$$

The omission of higher order terms in R_a is possible because we are dealing with small displacements from the equilibrium. The last expression is a generalization of eq. (6), which is obtained in the limit of $F_{aee} = F_{aae} = 0$. This expression shows that the R_a vs R_e dependence, for fixed displacements of R_e , is given by the ratio of two polynomials.

Another expression of eq. (11) is possible:

$$R_a = (K_1 + K_2 R_e + K_3 R_e^2) / (K_4 + R_e), \quad (12)$$

where $K_1 = -F_a/F_{aae}$, $K_2 = -F_{ae}/F_{aae}$, $K_3 = -F_{aee}/2F_{aae}$ and $K_4 = F_{aa}/F_{aae}$. Here, only K_1 and K_4 are expected to have relevant values as they contain the diagonal force constants (F_a , F_{aa}) in the numerator. The constants K_2 and K_3 containing the off-diagonal force constants (F_{ae} , F_{aee}) in the numerator will have much lower values. Thus, an approximation of

$$R_a = K_1 / (K_4 + R_e) \quad (13)$$

may be fulfilled satisfactorily. This is simply the equation of a shifted hyperbola. Then K_4 is expected to be negative ($-K_4 = -F_{aa}/F_{aac} = R_{e0}$) and it has the meaning of the lowest possible value of R_c :

$$R_a = K_1/(R_c - R_{e0}). \tag{14}$$

This function can be expanded using the relationship for

$$C/(A-B) = \frac{C}{A} \left(1 - \frac{B}{A} - \frac{B^2}{A^2} - \dots \right) \tag{15}$$

when $A > B$ holds true. Hence we arrive at the expression

$$R_a = \frac{K_1}{R_c - R_{e0}} = \frac{K_1}{R_c} - \frac{K_1 R_{e0}}{R_c^2} - \dots, \tag{16}$$

which can be satisfactorily terminated after the second term. The last form is suitable for an application of bilinear regression of the type

$$R_a = a(1/R_c) + b(1/R_c)^2. \tag{17}$$

Alternatively, we can rewrite eq. (14) in the form

$$R_c = R_{e0} + K_1(1/R_a), \tag{18}$$

which is a linear function of $(1/R_a)$.

Analogously, the second basic equation is obtained for fixed displacements of R_a :

$$R_e = -(F_e + F_{ae}R_a + 1/2F_{caa}R_a^2)/(F_{ee} + F_{eea}R_a) \tag{19}$$

and, eventually,

$$R_c = L_1/(R_a - R_{a0}) \tag{20}$$

or after simple reordering

$$R_a = L_1/R_c + R_{a0}, \tag{21}$$

with $R_{a0} = -L_4 = -F_{ce}/F_{cea} > 0$ adopting the meaning of the lowest possible value of R_a .

It may be concluded that the R_a vs R_e dependence deviating from linear behaviour may be expressed either by a pair of polynomial functions (11) and (19) or, more simply, by a pair of hyperbolae (13) and (20) or equivalently by eqs (14) and (21). A simple modelling of this situation is presented in Fig. 1.

A generalization of eq. (11) is still possible when using the biquadratic form of the APS:

$$\begin{aligned} E = & E_0 + F_a R_a + F_e R_e + (1/2)F_{aa} R_a^2 \\ & + (1/2)F_{ee} R_e^2 + F_{ae} R_a R_e + (1/6)F_{aaa} R_a^3 \\ & + (3/6)F_{aee} R_a^2 R_e + (3/6)F_{eee} R_e^2 R_a \\ & + (1/6)F_{eee} R_e^3 + (1/24)F_{aaaa} R_a^4 \end{aligned}$$

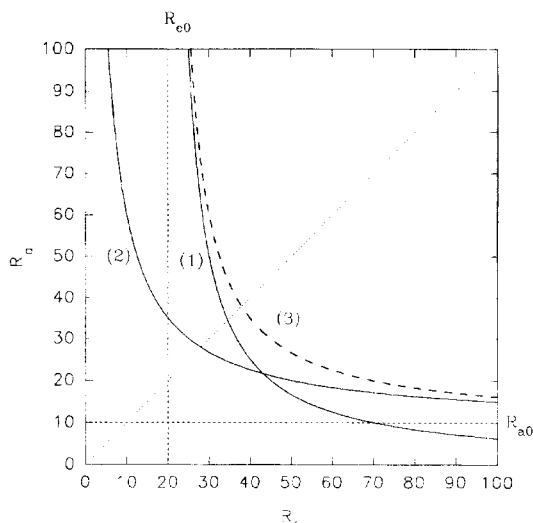


Fig. 1. Correlation curves for equatorial-axial interactions: (1) $R_a = K_1/(R_c - R_{e0})$; (2) $R_a = L_1/R_c + R_{a0}$; (3) $R_a = C/(R_c - R_{e0}) + R_{a0}$.

$$\begin{aligned} & + (1/6)F_{aae} R_a^3 R_e + (1/4)F_{aace} R_a^2 R_e^2 \\ & + (1/6)F_{acee} R_a R_e^3 + (1/24)F_{eeee} R_e^4. \end{aligned} \tag{22}$$

Using the condition of

$$(\partial E / \partial R_a)_{R_e} = 0 \tag{23}$$

and considering only the linear terms in R_a (or $F_{aaa} = F_{aaaa} = F_{aaae} = 0$), we obtain

$$R_a = - \frac{F_a + F_{ae} R_e + 1/2 F_{aee} R_e^2 + 1/6 F_{aeee} R_e^3}{F_{aa} + F_{aae} R_e + 1/2 F_{aaee} R_e^2}. \tag{24}$$

Strictly speaking, the above equations hold true for a free particle (complex) of the ML_n type. We derived that the disposition to follow a certain type of distortion with minimum energy requirements, i.e. the minimum energy path, is encoded in the values of the force constants. When passing to the solid state we expect that an additional environmental potential V acts on the coordination polyhedron. This influence can be viewed as a perturbation which, in terms of the Rayleigh-Schrödinger perturbation theory, yields the following first-order result:

$$E^{(1)} = \langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle + \langle \Phi_0 | \hat{V} | \Phi_0 \rangle. \tag{25}$$

Here, the first term describes the zero-order (unperturbed) contribution $E^{(0)}$, corresponding to the APS of the free system, whereas the second term accounts for the perturbation \hat{V} . Thus, the adiabatic potential surface of the free system is modified by a non-spherical (tensor) solid-state potential which

Table 1. Calculated parameters of the R_a vs R_c correlation curves

System	Non-linear fit ^a				Linear fit ^b	
	n	C (10^{-24} m ²)	R_{e0} (pm)	R_{a0} (pm)	a (pm)	b
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	35	19,207	115.3		764.0	-2.68
$[\text{Cu}(\text{NO}_2)_6]^{4-}$	6	19,535	119.1		737.4	-2.49
$[\text{CuF}_6]^{4-}$	9	23,931	86.3		653.9	-2.22
$[\text{CuCl}_6]^{4-}$	12	23,027	150.3		1030.7	-3.22
$[\text{CrCl}_6]^{4-}$	9	26,143	147.0		1001.7	-3.00
	12	4539	201.9	161.6	790.7	-2.12

^a According to the equation $R_a = C/(R_c - R_{e0}) + R_{a0}$.

^b According to the equation $R_a = a + bR_c$.

results in the shift of the minimum of $E^{(1)}$ relative to that of $E^{(0)}$. Our expectation is that the new minima follow a valley of $E^{(0)}$ which is determined by the minimum energy path. Thus, eqs (14) and (21) can be used as correlation curves expressing a mutual relationship between R_a and R_c parameters for solid-state ML_6 complexes.

EXAMPLES

The equations derived above have been tested numerically to fit the structural data collected for $[\text{ML}_6]$ type compounds.¹⁴⁻¹⁶ A set of R_a and R_c values has been collected from literature data for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, $[\text{CuF}_6]^{4-}$, $[\text{CuCl}_6]^{4-}$, $[\text{Cu}(\text{NO}_2)_6]^{4-}$ and $[\text{CrCl}_6]^{4-}$ polyhedra-containing compounds. All these systems exhibit strong Jahn-Teller distortions to elongated tetragonal bipyramids (with a small rhombic component which has been averaged). Table 1 presents the calculated parameters

of the R_a vs R_c correlation curves in the linear as well as the hyperbolic approximation.

In Fig. 2, an R_a vs R_c dependence is shown for the $[\text{CrCl}_6]^{4-}$ chromophore. It is seen that the linear approximation is quite satisfactorily fulfilled within the range of experimental data. Non-linear regression, however, yields a curve which passes through the experimental data (12 points) more closely.

Figure 3 presents R_a vs R_c correlations for various $\{\text{Cu}^{\text{II}}\text{L}_6\}$ chromophores. It can be concluded that the above correlations are very similar; the major difference is seen in the limiting value of R_{e0} , whereas the constant C (equal to K_1) alters only slightly. Interestingly, the R_{e0} values correlate with the covalent radii of the donor atoms. Thus, R_{e0} reflects the quality of the ligand or its donor atom, whereas the curvature C is characteristic of the cen-

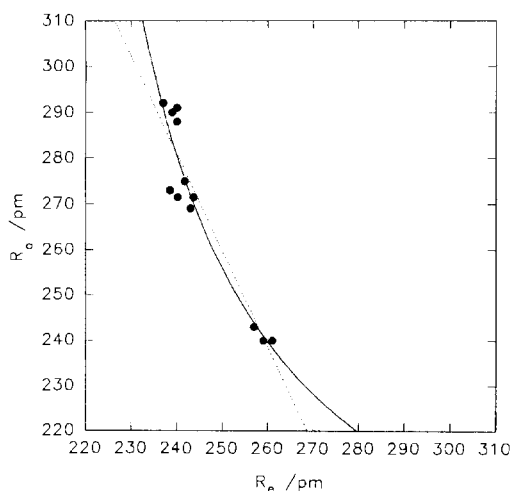


Fig. 2. An R_a vs R_c dependence for the $[\text{CrCl}_6]^{4-}$ chromophore. Solid, non-linear regression: $R_a = C/(R_c - R_{e0}) + R_{a0}$; dashed, linear regression: $R_a = a + bR_c$.

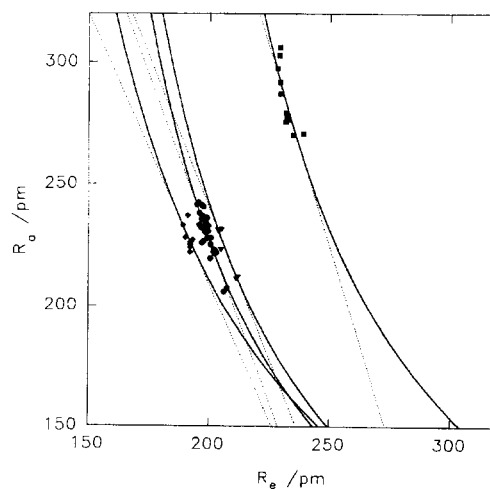


Fig. 3. R_a vs R_c dependences for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complexes (circles), $[\text{Cu}(\text{NO}_2)_6]^{4-}$ complexes (triangles), $[\text{CuF}_6]^{4-}$ chromophore (diamonds) and $[\text{CuCl}_6]^{4-}$ chromophores (squares). Solid, non-linear regression: $R_a = K_1/(R_c - R_{e0})$; dashed, linear regression.

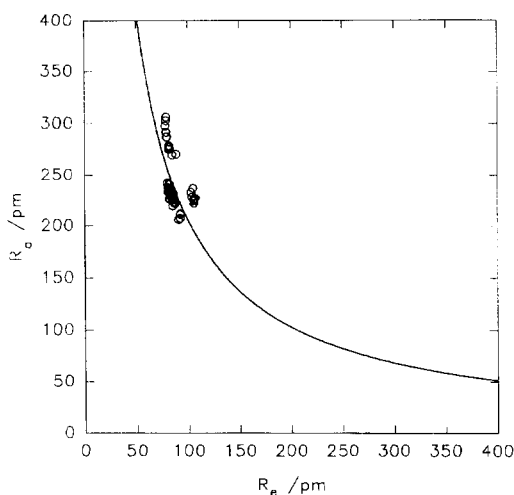


Fig. 4. An overall R_a vs R_e^{corr} dependence for copper complexes: $R_a = K/R_e^{\text{corr}}$.

tral atom. In order to verify the latter statement, the corrected values $R_e^{\text{corr}} = R_e - R_{e0}$ have been generated; they were used in an overall correlation of the $R_a = K_1/R_e^{\text{corr}}$ type for all $\{\text{Cu}^{\text{II}}\text{L}_6\}$ chromophores. The results are shown in Fig. 4 and they confirm that the constant K_1 may be considered as a characteristic parameter of the central atom: it measures the central atom plasticity—a tendency to undergo tetragonal distortions of its coordination polyhedra.

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