Comments on the Interligand Repulsion Model for Explaining the Molecular Structures of Tris-Chelate Complexes

GEORGE ST. NIKOLOV and NATASHA S. TRENDAFILOVA

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria

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*It is shown that when applying the interligand repulsion model (IRM) to tris-bidentate complexes, M(*bidentate*)$_3$, the repulsion between the bonding atoms of each bidentate ligand cannot always be disregarded, as suggested in the initial version of this model. The* intra*ligand repulsion is essential in determining the geometries of complexes such as dithiolates. Correlations between structure parameters help to reveal the ligand stereorigidity and the effect of the metal ion size on the geometry of the complexes.*

Introduction

It is now generally acknowledged that repulsion between the non-bonded atoms (*inter*ligand repulsion) in coordination compounds plays an essential role in determining the geometry or the molecular structure of these compounds [1–3]. The chelate compounds take a special position amongst this class of compounds, for which steric requirements imposed by the chelate ring formation may dominate the factors influencing the molecular structures [4].

A general assumption of the Interligand Repulsion Model (IRM) when applied to complexes of bidentate ligands, M(*bidentate*)$_n$, is that the ligands are considered as stereochemically rigid [1]. Consequently, the repulsion between the bonding atoms in each ligand is neglected as being part of the ligand energy, and only repulsions between bonding atoms of different ligands are taken into account [1].

We shall show here that for the M(*bidentate*)$_3$ complexes: (i) this assumption is not always justified; (ii) the bidentate ligands could be classified with respect to their stereochemical behaviour on the basis of whether this assumption holds or not; (iii) correlations between structure parameters and with the size of the metal ion could be useful in revealing the changes occurring with the ligand upon coordination.

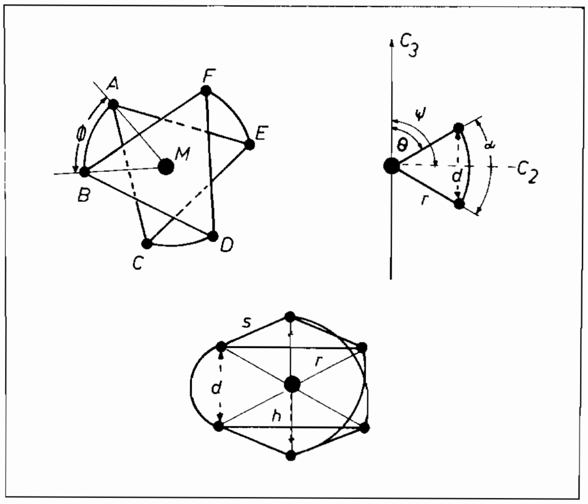

Fig. 1. Geometry of a M(*bidentate*)$_3$ complex of D_3 symmetry. In eqns. (5)–(9): A = 5, B = 3, C = 6, D = 1, E = 4, F = 2.

Theory

With the exception of six tris (dithiolato) complexes and three tris (*acac*) complexes that are close to the D_{3h} (trigonal prismatic) limit, all structurally established tris chelates have D_3 or near D_3 symmetry [3,4]. This is illustrated in Fig. 1.

In terms of the Repulsion Energy Model, the quantity to be minimized is [1]

$$U = \sum_{i<j} a_n d_{ij}^{-n} = a_n X r^{-n} \qquad (1)$$

or

$$X = \sum_{i<j} d_{ij}^{-n}/r^{-n} = f(\theta_j, \phi_j) \qquad (2)$$

where U is the repulsion energy between the ligands atoms located on a sphere of radius r, r is the distance between the metal ion and the ligand bonding atoms, d_{ij} is the distance between the i-th and j-th ligand atoms, n is the exponent in the repulsion law, X is the repulsion energy coefficient, and θ, ϕ are the polar angles of the ligand bonding atoms. The summation is carried over all ligand bonding atoms.

Usually the problem of minimizing U is replaced by minimizing X from eqn. (2), for in such a case the proportionality constant a_n is cancelled.

With the constraint imposed by the D_3 symmetry (Fig. 1), the distances between the ligand bonding atoms may be expressed in terms of two (out of four) angles defining either the structure of the complex (θ, ϕ or ψ) or that of the bonded ligand (α). These are: α the bite angle, ϕ the trigonal twist angle, which by definition [3] is the projection of α onto the plane which is normal to the C_3 axis, ψ the pitch angle subtended by the plane of the chelate ring and the C_3 axis, and finally θ the polar angle subtended by the M–L bonds and the C_3 axis. If r is kept constant (the ligand atoms are considered as points moving on a sphere of radius r), only two angles are needed to describe fully the geometry of the complex, the other two angles being redundant. They are related by [3]:

$$\cos(\alpha/2) = \sin\theta \cdot \cos(\phi/2) \tag{3}$$

$$\sin(\alpha/2) = \cos\theta/\cos\psi \tag{4}$$

While the choice between θ, ϕ and ψ is arbitrary, α should be used as an important feature of the coordinated ligand. The plots of $U = f(\theta, \alpha)$, $U = f(\phi, \alpha)$ and $U = f(\psi, \alpha)$ have revealed that the variation of U is the greatest for ϕ and for this reason we shall use further the set (ϕ, α).

It follows from the imposed symmetry constraint that the three ligands have equal α's, and ϕ should describe the rotation of the upper triangle with respect to the fixed lower triangle (see Fig. 1). In such a case simple trigonometry gives:

$$d_{12}^2 = d_{13}^2 = d_{23}^2 = d_{45}^2 = d_{46}^2 = d_{56}^2 = $$

$$= 3\cos^2(\alpha/2)/\cos^2(\phi/2) \tag{5}$$

$$d_{14}^2 = d_{25}^2 = d_{36}^2 =$$

$$= 4 - 2[1 + \cos(\phi + 0)]\cos^2(\alpha/2)/\cos^2(\phi/2) \tag{6}$$

$$d_{15}^2 = d_{26}^2 = d_{34}^2 =$$

$$= 4 - 2[1 + \cos(\phi + 120)]\cos^2(\alpha/2)/\cos^2(\phi/2) \tag{7}$$

$$d_{16}^2 = d_{24}^2 = d_{35}^2 =$$

$$= 4 - 2[1 + \cos(\phi + 240)]\cos^2(\alpha/2)/\cos^2(\phi/2) \tag{8}$$

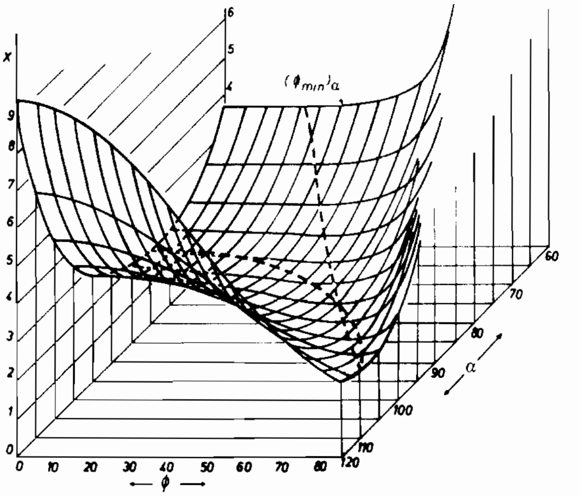

Fig. 2. Dependence of the repulsion energy coefficient X on the bite (α) and trigonal twist (ϕ) angles of M(*bidentate*)$_3$. The dashed lines depict the paths of the minima of the parametric equations $X = f(\phi)_\alpha$ and $X = f(\alpha)_\phi$, denoted as $(\phi_{min})_\alpha$ and $(\alpha_{min})_\phi$, respectively. The absolute minimum is at the cross point at $\phi = 60°$ and $\alpha = 90°$, *i.e.* for a pseudo-octahedral structure. *Intra*ligand repulsions are included.

Thus from (2) setting r = 1, we obtain

$$X = 6/d_{12}^n + 3(1/d_{14}^n + 1/d_{15}^n + 1/d_{16}^n) \tag{9}$$

Hence from (5)–(9) it follows that X is a function of only two variables and its critical points (extrema) are given by the conditions:

$$\left(\frac{\partial X}{\partial \alpha}\right)_\phi = 0 \quad \text{and} \quad \left(\frac{\partial X}{\partial \phi}\right)_\alpha = 0 \tag{10}$$

It should be noted at this stage that eqns. (5)–(8) have been written in a form suitable for computer programming. Kepert [1] and Fackler *et al.* [2] have preferred the use of the *normalized bite distance b* and with the initial assumption of constant *intra*-ligand repulsion, they have minimized $X = f(\phi)$ at constant *b* *i.e.* $X(\phi)_b$. The quantity *b* is defined [1,3] by

$$b = \overline{LL}/\overline{ML} = 2\sin(\alpha/2) \tag{11}$$

for symmetrically bonded ligands. $\overline{LL}$ is the distance between the bonding atoms of the bidentate ligand and $\overline{ML}$ = r, as defined above. A general expression for $X = f(\phi)_b$ had been obtained previously [2].

The use of *b* instead of α when studying X in our opinion blurs features of the tris-chelate complexes, since *b* is a ratio of two quantities which may or may not vary independently.

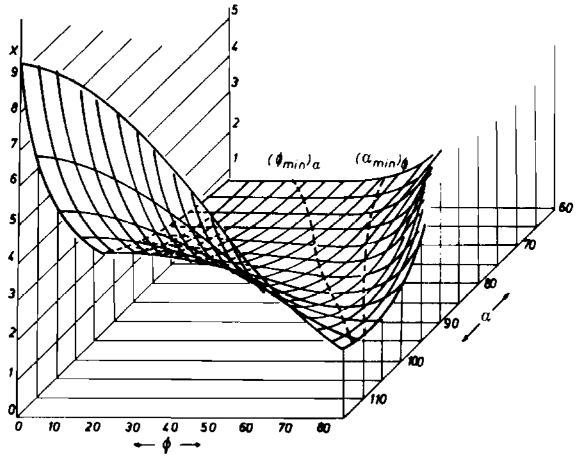

Fig. 3. Dependence of the repulsion energy coefficient X on the bite angle (α) and the trigonal twist angle (ϕ) of M-(*bidentate*)$_3$. *Intra*ligand repulsions are neglected.

Applications

1. Effect of the Neglect of Intraligand Repulsion and the Choice of Empirical Potential

When (5)–(10) are used consistently the answer is trivial: X is minimum* at $\alpha = 90°$ and $\phi = 60°$ (see Fig. 2). This implies that when the ligand bonding atoms are allowed to move freely, the minimum of repulsion energy is for the O_h arrangement [5].

For chelate complexes, however, the ligand atoms cannot move freely and we shall pursue this problem further. It has been stated: "each bonded bidentate ligand is sufficiently rigid that interaction between its donor atoms can be considered constant and this interaction is therefore omitted when summing over all other donor atoms repulsions" [1].

To check the general validity of this assumption, we have calculated $X(\phi, \alpha)$ (see Fig. 2). The same calculations were repeated omitting however the term d_{14} (*intra*ligand repulsion) in eqn. (9) (see Fig. 3). The two Figures also show the paths of the minima of the parametric equations $X = f(\phi)_\alpha$ and $X = f(\alpha)_\phi$, denoted as $(\phi_{\min})_\alpha$ and $(\alpha_{\min})_\phi$, respectively.

It is readily seen from Fig. 2 that the absolute minimum (the cross point of the two paths) occurs at the angles for the octahedron. The absolute minimum in Fig. 3, however, is outside the studied range ($\alpha = 110°$, $\phi = 85°$ for n = 6 and 12) and therefore it is of no practical interest.

When comparing the two Figures it is seen that the neglect of *intra*ligand repulsion depresses the potential energy sheet at the lower α values; further, while $(\phi_{\min})_\alpha$ is the same in *both* cases, $(\alpha_{\min})_\phi$ differs widely.

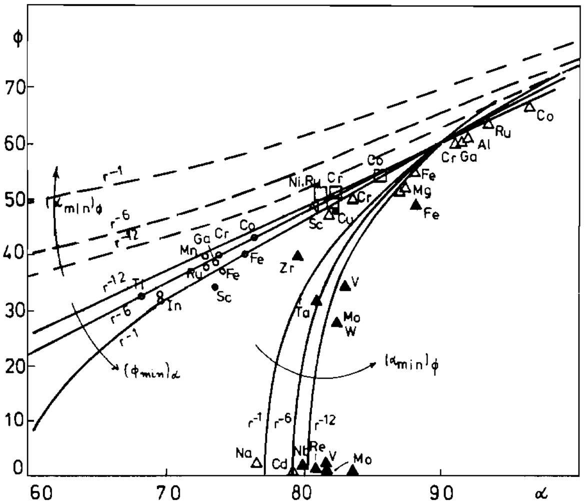

Fig. 4. The minima of the parametric equations $X = f(\phi)_\alpha$ and $X = f(\alpha)_\phi$, denoted as $(\phi_{\min})_\alpha$ and $(\alpha_{\min})_\phi$, respectively. The experimental data are from refs. [1–3]. ○ *dtc*, △ *acac*, ● *trop*, □ *en*, ▲ *dto*. Solid lines have been obtained with *intra*ligand repulsions included, dashed lines with *intra*ligand repulsions neglected; those for $(\phi_{\min})_\alpha$ in both cases coincide.

In both cases $(\phi_{\min})_\alpha$ is a shallow valley while $(\alpha_{\min})_\phi$ is deep if *intra*ligand repulsions are included (Fig. 2) and becomes shallower with the neglect of this repulsion (Fig. 3).

To check which of the two cases under consideration describes the available experimental data [1–3], we have plotted the $(\phi_{\min})_\alpha$ and $(\alpha_{\min})_\phi$ curves. For comparison we also include computational results with n = 1 (as in [2]), n = 6 (as in [1]) and n = 12 (the repulsive part of the Lennard-Jones potential [1, 6]). One of the $(\phi_{\min})_\alpha$ curves (n = 6) is similar to that in Fig. 6, ref. [1], where ϕ *vs.* b (= 2sinα/(2)) was minimized, considering b to be parameter instead of variable, *e.g.* $X(\phi)_b$.

The important result from Fig. 4 is that for all points close to $(\phi_{\min})_\alpha$ it is immaterial whether the *intra*ligand repulsions are included or not in the REM calculations; both curves are coincident. However, the $(\alpha_{\min})_\phi$ curve with neglected *intra*ligand repulsions is widely off the experimental points. Thus, for the complexes whose data fall on the $(\alpha_{\min})_\phi$ line (class B in Fackler's notation [2]), the *intra*ligand repulsions must be an important part of the overall energy change and cannot be neglected. It follows further that for these complexes ϕ is a parameter and not a variable.

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*Equation (10) gives the critical points. To find the absolute minimum the second derivatives have to be considered.

TABLE I. The Coefficients of Linear Regression $y = a + b' x$, Obtained by Least-Square Procedure. r_M Are Ionic Radii (Å) [9].

Type of complex[a]	Linear regression[b] $y = a + b' x$	Δy	No[c]	Corr. coeff.
M(*dtc*)$_3$	$1/b = 0.33 \pm 0.06 + (0.21 \pm 0.03)R(ML)$	0.005	10	0.986
M(*acac*)$_3$	$1/b = -0.09 \pm 0.16 + (0.41 \pm 0.10)R(ML)$	0.009	10	0.937
M(*trop*)$_3$	$1/b = 0.09 \pm 0.22 + (0.35 \pm 0.11)R(ML)$	0.006	4	0.978
M(*en*)$_3$	$1/b = 0.07 \pm 0.13 + (0.32 \pm 0.06)R(ML)$	0.006	4	0.942
M(*dto*)$_3$	$1/b = 0.05 \pm 0.17 + (0.30 \pm 0.07)R(ML)$	0.004	6	0.970
M(*dtc*)$_3$	$R(ML) = 1.78 \pm 0.16 + (0.96 \pm 0.12)r_M$	0.02	7	0.978
M(*acac*)$_3$	$R(ML) = 1.39 \pm 0.06 + (0.93 \pm 0.10)r_M$	0.01	10	0.988
M(*trop*)$_3$	$R(ML) = 1.34 \pm 0.06 + (1.04 \pm 0.09)r_M$	0.01	4	0.993
M(*en*)$_3$	$R(ML) = 1.42 \pm 0.06 + (0.99 \pm 0.09)r_M$	0.01	4	0.993
M(*dtc*)$_3$	$1/b = 0.70 \pm 0.12 + (0.21 \pm 0.04)r_M$	0.006	8	0.992
M(*acac*)$_3$	$1/b = 0.48 \pm 0.17 + (0.37 \pm 0.11)r_M$	0.010	7	0.920
M(*trop*)$_3$	$1/b = 0.56 \pm 0.17 + (0.36 \pm 0.11)r_M$	0.008	4	0.956
M(*en*)$_3$	$1/b = 0.59 \pm 0.14 + (0.30 \pm 0.06)r_M$	0.008	4	0.915

[a] *dtc* = N,N-dialkyldithiocarbamate, *acac* = acetylacetonate, *trop* = tropolonate, *en* = ethylenediamine, *dto* = dithiolate. [b] *b* and R(ML) taken from refs. [1–3], r_M from ref. [9]. The three regressions were treated independently. [c] Points used in the calculations. Experimental points at variance with the regression line by more than twice the s_y value were rejected in the final fit. Error limits $\pm\, s \cdot t/\sqrt{N}$, where s is the standard deviation of the slope or the intercept and t is the Student t factor.

2. *Classes of Tris-Chelate Complexes as Discerned from the Location on the α–ϕ Curves*

It is seen from Fig. 4 that the experimental points for the *dtc* complexes fall on the $(\phi_{min})_\alpha$ lines (α parametric as in the bis-*dtc*-complexes [7]), while those for the dithiolate complexes fall on the $(\alpha_{min})_\phi$ line ($n = 12$) (*intra*ligand repulsions included, ϕ parametric).

The points for the diamino(*en, tren, pen*) and acetylacetonato (*acac*) complexes, with few exceptions (considered in detail by Kepert [1]) are close to the absolute minimum, pointing out that for these complexes the ligand bonding atoms are not much hindered in assuming position around M by the presence of a chelate ring.

The above distinction is the same as that found by Fackler *et al.* [2] for group A (*dtc, acac, en* etc.) and group B (dithiolates) compounds (see Figs. 4 and 6 in [2]). Interligand donor atom bonding was thought [2] to be the reason for the formation of a separate group (B) by the dithiolate complexes. Such a bonding would be governed to a very large extent by the ϕ value giving the slanted 'stacking' of the ligands about the central atom. It follows from our discussion that *intra*ligand repulsion is also important for these complexes.

Almost constant *b* (1.31 ± 0.03) and α (82 ± 2°) have been observed for the dithiolate complexes, while ϕ = 0–50° and θ = 49–53° [1–3]. The constant *b* (or α) values are difficult to explain. In a series of complexes where M differs and L is the same, the size of M must affect $\overline{ML}$. To have *b* constant this must be accompanied by a corresponding variation of $\overline{LL}$ (*intra*ligand). Inspection of the available data, however, shows that *both* $\overline{ML}$ and $\overline{SS}$ are approximately constant for a large variety of M, thus ruling out the possibility of parallel $\overline{ML}$ and $\overline{LL}$ increase or decrease. It is thus obvious that the *dto* ligands are capable of accomodating M as if its size is of no importance.

3. *Correlations with Structure Parameters*

Some important features of the tris-bidentate complexes can be high lighted through correlations between structure parameters and with the size of the metal ion.

Consider eqn. (11). The inverse is

$$1/b = \overline{ML}/\overline{LL} \tag{12}$$

Writing

$$\overline{ML} = r_M + r_L + c \tag{13}$$

whence

$$1/b = r_M/\overline{LL} + (r_L + c)/\overline{LL} \tag{14}$$

TABLE II. Experimental [1–3] and Calculated *Intra*ligand Separation.

Series	*dtc*	*acac*	*trop*	*dto*	*en*
Experimental	2.87(6)	2.77(10)	2.52(2)	3.13(7)	2.77(4)
Calculated	4.8 ± 0.6	2.4 ± 0.4	2.9 ± 0.7	3.3 ± 0.6	3.1 ± 0.5

Here r_M and r_L are the atomic or ionic radii of M and L and c is a correction to the sum of radii, accounting for the ionicity or the covalency of the bond, respectively.

Equation (13) was written in analogy with the well known Schomaker-Stevenson relation [8] and it is expected to be a rough approximation. The bond lengths $\overline{ML}$ reflect the oxidation and spin states of M. For this reason, the use of ionic radii in (13) offers certain advantages over the use of atomic or orbital radii which are independent of the oxidation and spin states [9]. Table I lists the linear regression coefficients.

It follows from eqn. (12) that a straight line 1/b *vs.* R(ML) should be obtained if $\overline{LL}$ is constant or its variation is statistically insignificant for the entire series under consideration. Furthermore, the intercept should be zero. Table I shows that these requirements are met by all series with the exception of the *dtc*'s. The $\overline{LL}$ values calculated from the slope coefficients are compared with the experimental ones in Table II.

It is seen that with the exception of the *dtc* complexes, the experimental and calculated $\overline{LL}$ values are in fair agreement. This is not the case with the *dtc* complexes where variations of $\overline{LL}$ with $\overline{ML}$ was statistically proved to be significant: $\overline{SS} = 1.72 \pm 0.21 + (0.48 \pm 0.09)\ \overline{ML}$, r = 0.949. Hence the *intra*ligand separation $\overline{SS}$ in the *dtc* complexes changes upon coordination so as to accomodate the central ion, thus giving rise to a non-zero intercept and lower slope of the 1/b *vs.* R(ML) curve. $\overline{LL}$ and $\overline{ML}$ were proved statistically to be independent of each other for the other complexes.

The second correlation R(ML) *vs.* r_M checks the validity of eqn. (13). The multipliers of r_M should be unit. Table I shows that this is the case. The intercepts follow the ligand's bonding atom covalency series ($S > N \gtrsim O$) [10].

The third correlation was obtained by treating 1/b *vs.* r_M. It can be obtained also as a sum of eqns. (12) and (13), and in fact adding (12) and (13) the third correlation is obtained within the error limits. The slope parameters of the first and third correlations should be the same. It is gratifying to see that this is approximately so. Since the two correlation equations were obtained by treating independently 1/b *vs.* R(ML) and 1/b *vs.* r_M, the arguments being R(ML) and r_M, respectively this finding lends support to the assumptions implicit in eqn. (14).

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