I) is nearly 0.9 V more negative than reduction of complexes I–IV.[10] However, the uniqueness of the $Rh^{II}Rh^{I}$ formation in $Rh_2(PhC(NPh)_2)_4$[14] must remain unexplained in the absence of clear characterizations for reaction 3.

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Registry No. I, 101652-69-1; I^+, 84810-83-3; I^-, 101652-70-4; II, 101652-66-8; II^+, 101348-72-5; II^-, 101652-71-5; III, 101652-67-9; III^+, 101652-65-7; III^-, 101652-72-6; IV, 101652-68-0; IV^+, 101348-74-7; IV^-, 101652-73-7; $Rh_2(O_2CCH_3)_4$, 15956-28-2; $Rh_2(O_2CCH_3)_4^-$, 94342-85-5; $Rh_2(PhC(NPh)_2)_4$, 99148-26-2; $Rh_2(PhC(NPh)_2)_4^-$, 99148-28-4.

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Interligand Repulsion Energy and the Twisting of Hexadentate Chelating Ligands

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The simple repulsion energy model, which has quite successfully explained the observed twist angles of tris-bidentate complexes, has been applied to 24 complexes of six hexadentate ligands having C_3 symmetry. The mean difference between observed and calculated twist angles is between 2 and 3°.

Kepert[1,2] and Avdeef and Fackler[3] have demonstrated that the twist angle[1,4] (ϕ) of tris-bidentate complexes can be predicted given the ratio of the chelate bite distance to the metal–ligand atom distance (bite/r). The ligand atoms are represented by point charges, and ϕ is found such that the total computed repulsion energy among the charges is a minimum. (The metal–ligand atom distance and the chelate bite distance are assumed to be fixed as the complex is twisted.) The computed ϕ corresponding to this "repulsion" minimum is usually within a few degrees of the ϕ observed in the complexes.[1,3,5-8] In the cases of several complexes where ϕ(found) is more than 2° different from ϕ(calcd), steric interactions among ligands have been postulated as the cause of the deviation.[9-12] In addition to the six-coordinate tris-bidentate complexes, the minimum repulsion energy model has been applied to four-, five-, seven-, eight-, nine-, ten- and twelve-coordinate complexes.[13-17]

It was of interest to us to further test the efficacy of the repulsion model by applying it to chelates containing hexadentate ligands. One such set of complexes, briefly discussed elsewhere[18], contains $EDTA^{4-}$ and similar ligands. The following discussion is addressed to chelates of C_3 symmetry where the ligands have the general topology illustrated in Figure 1. Although such ligands give rise to complexes closely related to the tris-bidentate chelates, there are two differences of interest here: for these "C_3" chelates two bite distances (not one) must be considered, and two metal–ligand atom distances may be characteristic of a complex instead of one. The two bites are BITE, which is the L1–L4 distance (assumed to be equal to L2–L5 and L3–L6), and TOP, which is the L1–L2 distance (equal to L2–L3 and L1–L3). The metal–ligand distances are M–L1 (equal to M–L2 and M–L3) and M–L4 (equal to M–L5 and M–L6).

In the tris-bidentate chelates the repulsions to be minimized (see Figure 2) are the six pairs L1–L2 and equivalents, the three pairs L1–L5 and equivalents, and the three pairs L1–L6 and equivalents, whereas in the "C_3" chelates the repulsions to be minimized are the three pairs L4–L5 and equivalents, the three pairs L1–L5 and equivalents, and the three pairs L1–L6 and equivalents (Figure 3).

Figures 3 and 4 show the spherical polar coordinate system used to describe the "C_3" chelates. Each point represents a ligand atom i having coordinates r_i, θ_i, and ϕ_i, where r_i is the metal–ligand distance, θ_i is the azimuthal angle (from the polar axis, Figure 4) and ϕ_i is the third coordinate (Figure 3). Assuming C_3 symmetry, the M–L1, M–L2, and M–L3 distances are r_1 and the M–L4, M–L5, and M–L6 distances are r_4. Similarly, θ_1 is the azimuthal angle for L1, L2, and L3, and θ_4 is the azimuthal angle for L4, L5, and L6.

Given r_1, r_4, BITE, and TOP, the value of θ_1 is unambiguously determined from eq 1, and the problem then is to find the sets

$$\theta_1 = \sin^{-1} [(\mathrm{TOP})/(3^{1/2} r_1)] \qquad (1)$$

of specific values of θ_4 and ϕ attainable with the given values for r_1, r_4, BITE, TOP, and θ_1 and then to find that set corresponding to the minimum total Coulombic repulsion energy.

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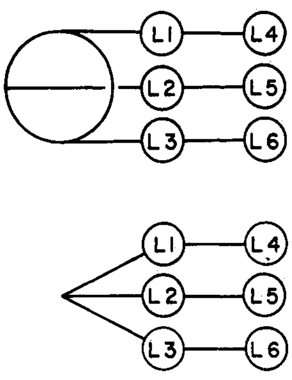

Figure 1. Topology of "C_3" ligands.

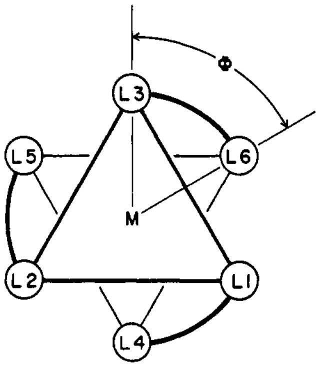

Figure 2. Tris-bidentate complex.

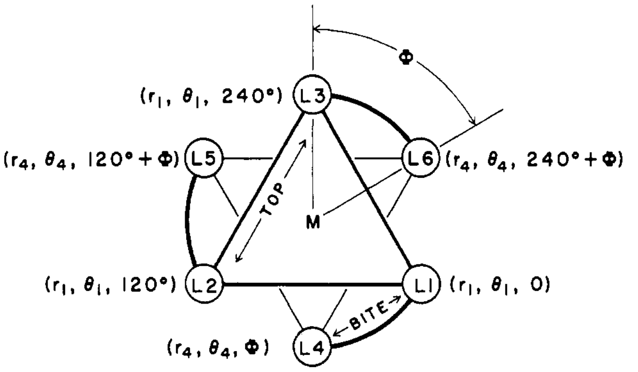

Figure 3. Ligand atom coordinates in the "C_3" ligand.

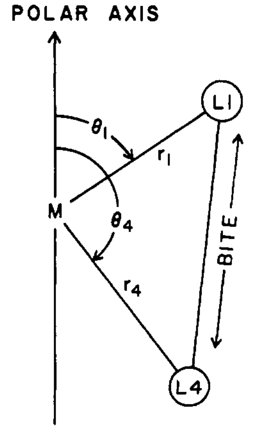

Figure 4. View normal to C_3 axis.

Given, then, r_1, r_4, BITE, TOP, and θ_1, for each assumed value of ϕ a single value of θ_4 is possible, giving a complete set of coordinates for the six ligand atoms, from which the repulsion energy can be calculated. An iterative procedure leads to the value of ϕ (and of θ_4) corresponding to the minimum repulsion energy.

Table I. Twist Angles (deg) for C_3 Complexes of Hexadentate Ligands

				calcd by repn model			
complex[a]	anion	ref	exptl	$r_1 \neq r_4$	$r_1 = r_4$	TOP free	D^{-6}
$Mn(py_3tren)^{2+}$	BF_4^-	29	43.0	47.3	43.4	35.3	44.9
$Fe(py_3tren)^{2+}$	BF_4^-	29	54.0	51.4	50.7	48.0	51.0
$Co(py_3tren)^{2+}$	BF_4^-	29	48.7	50.7	47.3	40.4	48.5
$Ni(py_3tren)^{2+}$	BF_4^-	29	49.1	48.5	48.1	44.4	48.2
$Ni(py_3tren)^{2+}$	PF_6^-	29	50.9	48.5	47.8	43.8	48.0
$Cu(py_3tren)^{2+}$	BF_4^-	29	47.7	49.5	48.5	43.2	48.5
$Zn(py_3tren)^{2+}$	BF_4^-	29	45.9	48.7	45.6	40.6	47.1
$Fe(py_3tach)^{2+}$	ClO_4^-	30	42.1	44.0	42.5	48.0	45.4
$Co(py_3tach)^{2+}$	ClO_4^-	31	5.4	19.3	14.0	39.3	28.0
$Ni(py_3tach)^{2+}$[b]	ClO_4^-	28	32.2	35.1	34.5	43.9	39.1
$Ni(py_3tach)^{2+}$[b]	ClO_4^-	28	32.9	34.3	32.0	43.8	37.8
$Ni(py_3tach)^{2+}$[c]	ClO_4^-	30	31.5	34.9	33.0	43.5	38.4
$Zn(py_3tach)^{2+}$	ClO_4^-	31	5.4	17.9	12.0	38.2	27.0
$Mn(py_3tame)^{2+}$	ClO_4^-	32	21.9	0.0	0.0	37.7	23.8
$Fe(py_3tame)^{2+}$	ClO_4^-	28	43.4	42.1	39.6	47.8	43.7
$Co(py_3tame)^{2+}$	ClO_4^-	32	28.0	26.1	24.0	41.2	32.7
$Ni(py_3tame)^{2+}$	ClO_4^-	32	36.3	33.4	32.4	43.9	37.8
$Zn(py_3tame)^{2+}$	ClO_4^-	28	27.8	21.7	21.4	40.7	30.9
$Mn(pro_3tren)$		33	50.8	48.3	50.7	44.7	49.0
$Fe(pro_3tren)$		34	54.6	53.3	54.6	47.8	52.9
$Cr(Clsal_3tren)$		35	62.2	62.5	65.9	56.6	62.1
$Mn(Clsal_3tren)$		35	62.6	62.9	66.5	56.9	62.5
$Fe(Clsal_3tren)$		36	60.2	59.8	64.7	54.3	60.0
$Co(sal_3tach)$		37	60.5	62.7	63.5	61.0	62.6

[a] See Figure 1 of ref 27 for key to ligands: pro_3tren is $(pyrrole)_3tren$; $Clsal_3tren$ is $(5\text{-Cl-salicylidene})_3tren$. [b] Two independent complexes in the unit cell. [c] Second polymorph.

To calculate θ_4 from ϕ, we have found the following to be the most convenient:

$$x = -((\mathrm{BITE})^2 - r_1{}^2 - r_4{}^2)/2r_1r_4$$

$$y = \sin\theta_1 \cos\phi$$

$$z = \cos\theta_1$$

$$\cos\theta_4 = xz \pm (x^2z^2 - (z^2 + y^2)(x^2 - y^2))^{1/2}/(z^2 + y^2)$$

θ_4 must be >90° with

$$\mathrm{RE} = \frac{3}{D(4-5)} + \frac{3}{D(1-5)} + \frac{3}{D(1-6)}$$

We have found 18 structure reports of complexes of three different neutral "C_3" chelating agents with bivalent metal ions and six complexes of three different negatively charged "C_3" chelating agents with trivalent metal ions. Column 5 of Table I gives the results of this calculation for each of the 24 cases.

Other computations were performed with a view to identifying key parameters or assumptions in the calculations. Some of these results are presented in columns 6–8. Results in column 6 arise when the observed value for TOP from the crystal structure is retained, but an average value, r_{av}, for r_1 and r_4 is employed ($r_1 = r_4 = r_{av}$). For column 7, TOP was allowed to vary, so that the complexes were treated as tris-bidentate and the 1/(L1–L2), 1/(L1–L3), and 1/(L2–L3) terms were included in the $1/D$ summation. Column 8 differs from column 5 only in that a summation of $1/D^6$ was minimized instead of $1/D$, to allow the comparison suggested by Kepert.[1]

A careful examination of Table I leads to a number of interesting observations. A comparison of columns 4 and 5 shows fairly good agreement between observed and calculated ϕ values, except for three cases. These three cases, all with discrepancies greater than 10°, are the three for which the calculated ϕ is less than 20°. The next largest discrepancy, 6.1°, occurs for the case for which the calculated ϕ is 21.7°. Plots of calculated repulsion energy against ϕ are quite similar to the corresponding plots shown by Kepert,[1] and suggest that for cases with small values of BITE/r and TOP/r, which give very small (<20°) calculated values of ϕ, the repulsion energy minimum is extremely shallow, so that other factors, such as crystal-packing forces or strain energy of the chelating agent, may cause the observed ϕ to differ markedly from the value calculated from the repulsion model. Setting $r_1 = r_4 = r_{av}$ lowers the calculated ϕ in all of the bivalent metal cases, which improves the agreement between observed and calculated ϕ for the py$_3$tren and py$_3$tach cases but worsens the agreement for the py$_3$tame cases. Using r_{av} for the trivalent cases increases the calculated ϕ. Allowing TOP to vary causes the calculated ϕ to decrease for the py$_3$tren case and to increase for the py$_3$tach and py$_3$tame cases and causes the mean discrepancy between observed and calculated ϕ to increase by a factor of about 3 for all bivalent cases. For the trivalent cases, freeing TOP causes a large decrease in calculated ϕ for all tren complexes, but very little change for the tach complexes. For the bivalent metal ion cases, using D^{-6} instead of D^{-1} for the repulsion energy calculation causes ϕ to increase for low ϕ values and to decrease for high ϕ values, in such a way that ϕ(from D^{-6}) − ϕ(from D^{-1}) ranges nearly linearly from about 20° for ϕ(from D^{-1}) = 0° to about −3° for ϕ(from D^{-1}) = 52°; however, the average agreement between observed and calculated ϕ values remains essentially the same, as shown for tris-bidentate complexes in general by Kepert.[1,2] For the trivalent cases the differences between the D^{-1} and the D^{-6} calculations are quite small and show no particular pattern.

The overall results seem to justify the notion that the distance, TOP, in these complexes is determined by factors similar to those which determine BITE; i.e., the ϕ values computed with observed values of TOP (columns 5 and 6, Table I) are nearer to the experimental values than are the ϕ values computed without restraining TOP (column 7). Further, the predictive value of the calculated values in column 5 are only slightly weaker than those computed for tris-bidentate acac complexes.[19-26] The use of r_{av} as opposed to $r_1 \neq r_4$ is not as critical a factor as is a fixed TOP.

It now seems feasible to use calculations of the type used in this study to semiquantitatively guide the synthesis of hexadentate chelates intended to have certain ϕ values. Such a guide is presented in Figure 5, where $r_1 = r_4 = 2$ Å. For example, if a ϕ of 30° were sought, an acceptable pair of design parameters for the hexadentate ligand would be BITE = 2.4 Å and TOP = 2.8 Å.

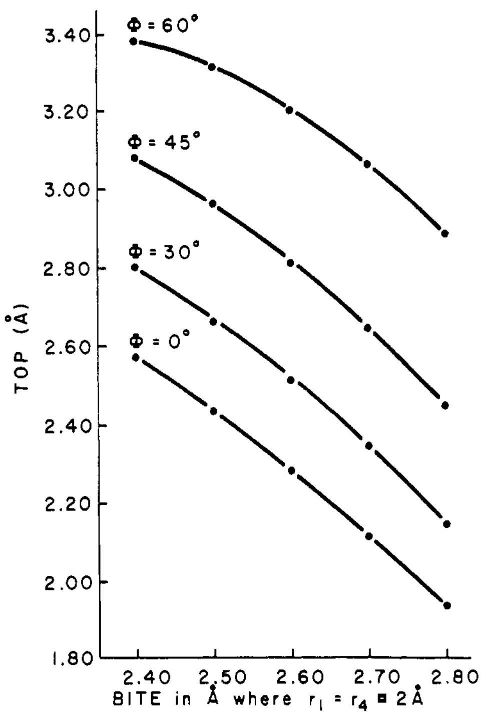

Figure 5. Relation between TOP and BITE for different ϕ values.

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