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The significance of ligand–ligand interactions for transition metal complex geometries

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Abstract

An atom–atom interaction model (AAIM) for determining the stable geometries of ML_λ molecules is discussed and applied to tris-chelate complexes. This case study illustrates the importance of both attractive and repulsive ligand–ligand interactions in determining transition metal complex geometries. The successes and also failures of Kepert's purely repulsive approach can, as a result, be understood.

Introduction

The number of electrons in most transition metal complexes makes routine *ab initio* molecular orbital (MO) calculations impracticable [1]. Various empirical MO methods [2] are currently feasible for molecules containing transition metals. However, the difficulty of determining parameters and then of interpreting the results has meant that inorganic chemists have been slow to adopt them. A completely different type of approach is to ignore the details of the bonding in a molecule and to try to rationalize the observed geometries in terms of atom–atom interactions. Perhaps the simplest successful example of this is the ligand–ligand repulsion model of Kepert [3, 4] in which the geometry of a transition metal complex is assumed to be dominated by the repulsion between ligating atoms. The repulsive potential adopted by Kepert is r^{-n} where n varies from 1 to 12, taking an 'average' value of 6. Another simple approach is the non-bonded radii approach of Bartell [5] and later Glidewell [5] which also ignores the details of the bonding. In their approach the stable geometry is taken to be the one where atom–atom distances are determined by the non-bonded radii of each atom. Molecular mechanics calculations [6] also fall under this general heading since the most stable geometry is determined by minimizing the total energy of the molecule expressed in terms of bond bending, bond stretching and bond torsion force constants, and the interactions between non-bonded atoms. Transferable parameters are used for each of these interactions. The main justification for all of these 'atom–atom interaction' approaches to molecular structure is their notable degree of success in rationalizing observed structures.

We have recently developed a model, the atom–atom interaction model (AAIM) [7], for determining the geometries of ML_λ systems (for M a central atom with the L bonded directly to M) that provides some justification for these atom–atom interaction approaches and is at least a first step toward identifying the limitations of each approach. Furthermore, it can itself be used to determine molecular geometries and has been successfully applied to carbonyl transition metal cluster compounds [8]. In this paper we focus on the consequences of our model for tris-chelate complexes.

The bases of the AAIM are the assumptions (i) that M–L bond strength is independent of the relative orientations of the L, and (ii) that non-bonding electrons do not dominate the energy of a structure. When these assumptions (which have previously been discussed in some detail [7]) hold, isotropic atom–atom interactions determine the most stable geometry of a complex. Thus the anisotropic parts of the twist and bend energies parameters of molecular mechanics are implicitly assumed to be small. This is clearly invalid for molecules such as ethylene, but for systems where it is impossible to characterize the bonding in terms of single, double, etc. bonds it is a good starting point. Atom–atom interactions can be modelled by a 'multipole' type expansion, the most significant terms being (i) a short range repulsion (most simply hard sphere or r^{-12} where

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r is the L–L distance) which is dominant at small atom–atom distances (it reflects the repulsion due to overlapping electron clouds), (ii) an intermediate range attractive dispersion energy whose distance dependence is r^{-6}, and (iii) a longer range repulsive (or sometimes attractive) r^{-1} charge–charge interaction. One then sums the pairwise atom–atom interactions, so the total ligand–ligand interaction energy may be written

$$U(\mathrm{L{-}L}) = \sum_{ij} c_{12} r_{ij}^{-12} - c_6 r_{ij}^{-6} + c_1 r_{ij}^{-1}$$

where the sum is over all interactions.

The parameters c_{12}, c_6, and c_1 can be determined by fitting the form of the potential to experimental data. For those cases where $c_1 = 0$, the ratio c_6/c_{12} is defined by the minimum energy geometry. The magnitude of c_6/c_{12} qualitatively relates to the size of the atoms since it gives the relative importance of the repulsive (c_{12}) and attractive (c_6) interactions. For small atoms with small electron clouds the short range repulsion only switches on for small r, so c_{12} scales down that interaction with respect to the dispersive attraction. Thus, although dispersion type attractions are larger for systems with more electrons and greater polarizability (which generally correlates with larger size), in the close packed region relevant for molecular geometries, the short range repulsion increases faster with increasing atom size. As a result, small atoms have large values of c_6/c_{12}, and large atoms have small values of c_6/c_{12}.

Geometries of tris-chelate complexes

The atom–atom distances between ligating atoms in a complex are usually much smaller than those between other atoms, so the L–L interaction is usually the dominant determiner of the geometry adopted. Tris-chelate complexes make an ideal case study for investigating the AAIM because, following Kepert, their geometry can be parametrized in terms of the twist about the three-fold axis, θ, and the distance between ligating atoms of the chelate, b. $\mathrm{M(LL)_3}$ has four distinct L–L distances: b, the distance across a chelate bite; d_3, the distance between two Ls whose connecting line is perpendicular to the three-fold rotation axis; d_s and d_l, respectively the shorter and the longer of the two distances across the quadrilateral faces between two chelates. Note that $d_s = d_l$ for a trigonal geometry, and for an octahedral geometry $d_s = d_3$ and d_l is the distance between two *trans* L.

Avdeef and Fackler [9] found that intraligand repulsive interactions (i.e. variations in b) had some importance for dithiolene and diselenolene complexes, though the overall picture was not significantly altered by their inclusion. Nikolov and Trendafilova [10] have suggested that intraligand repulsions are important, especially for dithiolate compounds, however, they find it difficult to account for the almost constant experimental values for b in a series of compounds. We therefore follow Kepert [4] and take b to be constant for a given complex and the units to be such that the M–L bond length, $d_{(\mathrm{M-L})}$ is 1. If the 6 Ls are at the vertices of a regular octahedron, then $b = d_3 = d_s = \sqrt{2}$, $d_l = 2$ and $\theta = 30°$; for a trigonal prism $\theta = 0°$ (Fig. 1).

If there were no L–L attractive interactions, the geometry of $\mathrm{M(LL)_3}$ would be that which minimizes the short range repulsion. The solid line in Fig. 2 indicates the twist angle θ, which minimizes an r^{-12} repulsive L–L interaction for different b. Those with $b < \sqrt{2}$, have a geometry twisted from a regular octahedron towards a trigonal prism, and those with $b > \sqrt{2}$ twist further from the trigonal prismatic geometry. The diamonds correspond to experimentally determined complex geometries using the experimental data summarized in ref. 4. Thus Fig. 2 is similar to Fig. 6 of ref. 4 where the same experimental data was compared with an r^{-6} repulsive interaction. There is good qualitative agreement between the experimental points and the solid line. However, a purely repulsive interaction is not sufficient to account for the exact geometry for most complexes and for some it seems to bear no relationship to what is found experimentally. The agreement is best for complexes with large values of b, $b > \sqrt{2}$, which are generally complexes where L is large compared with the M–L distance. In other words, for complexes with large ligands that are close packed, the geometry is determined by a short range repulsion due to overlapping electron clouds.

The situation is both more complicated and more interesting for complexes with ligands that are smaller with respect to their M–L distance, since the effect of attractive forces should be detectable. The short-range repulsive forces are still usually most important, so it is convenient to consider the attractive force as a perturbation which modifies the repulsion determined geometry. A twist in either direction from the repulsion-determined value of θ, θ_{rep}, is likely to stabilize the complex. The direction and amount of twist depends on the values of both b and the size of the ligand.

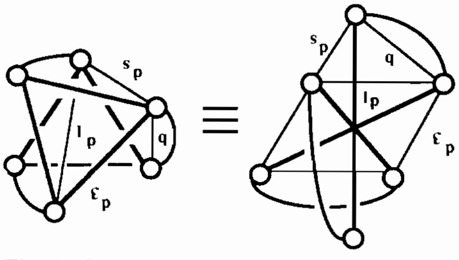

Fig. 1. Geometry of the tris-chelate complexes.

c_6/c_{12} also depends on the size of the ligand, as discussed above. It is therefore convenient to compare different geometries whose energies are minimized for a given c_6/c_{12} and b. Some sample calculation results are given in Table 1.

For $b = 1.1$, the energy difference between untwisted and more twisted (relative to θ_{rep}) geometries is 4–6%, with θ_+ (more twisted) being more stable for small L (maximum c_6/c_{12}) and θ_- (untwisted) for large L. Since for b to take the value of 1.1 the ligands must be small, θ_+ is expected to be the experimental geometry.

For $b = 1.3$ the difference in energy between the θ_+ and θ_- geometries is 1–2%. For maximum c_6/c_{12}, i.e. small L, θ_- is 2% more stable, and for larger L, θ_+ is only just more stable. Thus for intermediate size b, in contrast to small b, one would expect small ligands (large c_6/c_{12}) to favour a geometry closer to a trigonal prism than the repulsion determined geometry, and larger ligands to result in some untwisted and some more twisted geometries relative to the repulsion determined geometry. These conclusions are borne out by the data in Fig. 2. Perhaps the most surprising feature of the geometries adopted by intermediate size ligands is that the favoured untwisted geometry is often a long way from the repulsion determined geometry. Given the small energy differences between twisted and untwisted forms (Table 1) this means that only small differences in energies can result from large differences in geometries. In some cases, therefore, the smaller interactions between the non-ligating atoms in the chelates (which have been explicitly ignored in this treatment) or crystal packing forces in fact determine the molecular geometry that is observed. Since the chelates come closest together in a trigonal prismatic geometry, the non-ligating atoms of the chelates favour the most untwisted geometry.

TABLE 1. Some examples of geometry and energy parameters and the resulting L–L interaction energy[a]

b	θ_{rep}	c_6/c_{12}	θ	$E(\theta)$
1.1	16.5	0.32	0	−0.063
			22	−0.067
		0.34	9.5	−0.068
			22.5	−0.071
1.2	21.3	0.36	0	−0.079
			14	−0.079
			24.5	−0.080
		0.40	17.5	−0.090
			25.2	−0.092
1.3	24.5	0.44	0	−0.117
			23	−0.112
			28.5	−0.115
		0.40	13.5	−0.101
			21.5	−0.101
			27.5	−0.102

[a] b is the chelate bite, θ_{rep} is the twist angle for the case where no L–L attractive interactions are included, c_6/c_{12} is the relative contribution of the attractive and repulsive interactions to the energy, θ is the twist angle, and $E(\theta)$ is the energy for that twist.

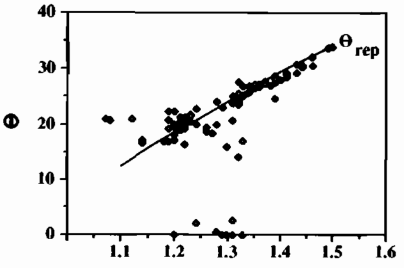

Fig. 2. The solid line indicates the twist angle, θ, which minimizes an r^{-12} repulsive L–L interaction. The diamonds correspond to experimental complex geometries [4].

TABLE 2. Some experimental geometric data [4] and its comparison with the AAIM

Compound	b	θ_{rep} (°)	θ (°)	c_6/c_{12}
A				
$[Fe(S_2C_2(CN)_2)_3]^{2-}$	1.39	29	24.5	0.43
$[V(S_2C_2(CN)_2)_3]^{2-}$	1.33	26	17	0.42
$[Mo(S_2C_2H_2)_3]$	1.33	26	0	0.49
$[Mo(Se_2C_2(CF_3))_3]$	1.33	26	0	0.49
$[Mo(S_2C_2(CN)_2)_3]^{2-}$	1.32	25	14	0.42
$[W(S_2C_2(CN)_2)_3]^{2-}$	1.32	25	14	0.42
$[Mo(S_2C_6H_4)_3]$	1.31	25	0	0.45
$[V(S_2C_2(Ph)_2)_3]$	1.31	25	0	0.45
$[Re(S_2C_2(Ph)_2)_3]$	1.30	24.5	0	0.45
$[Nb(S_2C_6H_4)_3]^-$	1.29	24	0	0.43
B				
$[Zr(S_2C_6H_4)_3]^{2-}$	1.28	24	≈20	0.39
C				
$[Fe(phen)_3](ClO_4)_3 \cdot H_2O$	1.32	25.5	27.8	0.40
$[Fe(phen)_3](SbC_4O_6H_2)$	1.32	25.5	27.6	0.39
$(bipyH)[Fe(bipy)_3](ClO_4)_4$	1.32	25.5	27.6	0.39
$[Cr(en)_3][Ni(CN)_5] \cdot H_2O$	1.32	25.5	25.6	0.0
$[Al(trop)_3]$	1.32	25.5	24.3	0.45
$[Cr(S_2P(OEt)_2)_3]$	1.32	25.5	23.8	0.43
$[Al(O_2C_2S_2Ag(PPh_3)_2)_3]$	1.32	25.5	23.5	0.42

These general conclusions are consistent with most of the experimental data. The geometries of tris-chelate complexes formed from transition metals on the left hand side of the periodic table and ligands $S_2C_2(CN)_2$, $S_2C_2H_2$, $S_2C_2Ph_2$ and $S_2C_6H_4$ have b values of about 1.3, and small L, so we predict an untwisted geometry, relative to θ_{rep}. Relevant data is given in Section A of Table 2. It has been suggested [11] that the approximately constant S–S distance (the M–S distance varies significantly), which is shorter than might be expected, is due to attractive interligand bonding-type interactions between the Ss. However, an actual 'bonding' interaction in not required — an S–S non-bonding attraction (i.e. an attractive interaction between two S atoms too far apart to make a bond) is sufficient to account for the observed geometries. The small variation in c_6/c_{12} should be noted, particularly for a given ligand, reflecting the similar size of L in the different complexes. Inspection of Table VII of ref. 4 shows how little the interligand S–S distance varies for a given ligand and charge on the metal. (Variations in the intraligand distance reflect the changes in size of S). For example, for $S_2C_2(CN)_2$ the intraligand S–S distance is 3.12–3.13 Å, the interligand S–S distance is 3.20 ± 0.01 Å and the M–L distance varies by over 0.1 Å.

$[Zr(S_2C_6H_4)_3]^{2-}$ (Section B, Table 2) has approximately the same energy for θ_+ and θ_- twists, with θ_+ having slightly more stable L–L interactions (by less than 1%). When the θ_+ and θ_- L–L interaction energies are so close, the interactions between other parts of the ligands may determine the geometry adopted. In this case the attractive interaction of the π-systems of the phenyl rings of the ligands favours θ_-.

The seven non-dithiolate complexes of ref. 4 with $b = 1.32$ illustrate the situation for larger (but not large) ligands. $\theta_{rep} = 25.5°$ for these complexes, and the observed geometries are given in Section C of Table 2. The (phen) and (bipy) complexes, as expected, adopt the θ_+ geometry. $[Cr(en)_3][Ni(CN)_5] \cdot H_2O$ adopts a geometry very close to the purely repulsive one with a L–L distance of 3.0 Å. It is interesting to note that the same L–L distance is present in $[Ru(en)_3]^{2+}$ which thus adopts θ_+. The remaining compounds have larger c_6/c_{12} values and they adopt an untwisted geometry as expected.

Finally we consider the complexes with L = oxygen whose data is summarized in ref. 4. [Er(BuCOCHCOBu)$_3$] ($b = 1.2$) is another example where non-ligating atoms play a significant role. The ligands of this complex are bulky and their attractive interactions are optimized in the trigonal prismatic geometry. This is sufficient to overcome the preference of the L–L interactions for the θ_+ geometry of 25° twist. Thus the 'unusual' geometry of this complex is seen to be entirely consistent with a model where attractive interactions of all chelate atoms are accounted for. Further support for this explanation comes from consideration of other $M(OO)_3$ complexes. [Co(acac)$_3$] achieves the maximum possible d_s value of 2.64 Å consistent with its M–O bond length by adopting the repulsion determined geometry ($b = 1.5$, $\theta = \theta_{rep} = 34°$). [Er(BuCOCHCOBu)$_3$], on the other hand, adopts the close packed trigonal prismatic geometry, and thus achieves the minimum possible O–O distance, 3.07 Å, allowed by its M–O bond length. Other O–O distances range from 2.7–3.1 Å.

Conclusions

The aim of this work has been to illustrate the importance of both attractive and repulsive ligand–ligand interactions in determining the geometries adopted by transition metal complexes. The importance of attractive ligand interactions in accounting for the deviations from the geometry that minimizes repulsion have been emphasized and illustrated. This essentially 'isotropic' or 'steric' analysis cannot account for electronic factors such as Jahn–Teller distortions. It does, however, provide a good starting point to then introduce anisotropic electronic influences as a perturbation.

Application of the AAIM to non-bond-breaking rearrangement reactions of metal complexes and in particular to tris-chelates has also proved successful [12]. The main limitations of its quantitative application for both structure and reactivity studies is that one assumes the M–L bonding interactions are constant (or determined by the amount of stretching required to accommodate ligands in different geometries) over the range of variation being considered. Thus, for example, the relative merits of a five coordination or six coordination geometry can only be analyzed in the most general terms. For practical purposes, the AAIM is closely related to molecular mechanics, the main difference being that twist angle force constants and bond angle force constants are not explicitly considered. The omission of bond angle force constants is, in principle, not a problem, since these are accounted for by the L–L non-bonded interactions. The omission of twist parameters is justified simply because when they are included they are small for transition metal systems [13] due to the flexibility of the bonding. In practice, omission of the bond angle parameters is inconvenient if one's interest is limited to determining stable geometries since angle parameters are already available, but is a crucial flexibility of one is interested in reactivity, where restriction to harmonic motion about the ground state geometry is not appropriate. Thus the AAIM has the potential to replace molecular mechanics for the study of reactivity.

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References

1 R. Broer and W. C. Nieuwpoort, *Theor. Chim. Acta, 73* (1988) 403; R. F. Fenske, *Prog. Inorg. Chem., 21* (1976) 179; L. G. Vanquickenborne, M. Hendrickx and I. Hyla-Kryspin, *Inorg. Chem., 28* (1989) 770; M. Hargittai, *Coord. Chem. Rev., 91* (1988) 35; C. Bo and A. Dedieu, *Inorg. Chem., 28* (1989)

304; L. M. Hansen and D. S. Marynich, *J. Phys. Chem., 92* (1988) 4588.

2 F. A. Cotton, X. Feng and Matusz, *Inorg. Chem., 28* (1989) 594; C. Daniel and A. Veilland, *Inorg. Chem., 28* (1989) 1170; M. Gerlochand, R. G. Woolley, *Prog. Inorg. Chem., 31* (1984) 371; A. Bencini, C. Benelli and D. Gatteschi, *Coord. Chem. Rev., 60* (1984) 131; A. Ceulemans, W. Oldenhof, C. Görller-Walrand and L. G. Vanquickenborne, *J. Am. Chem. Soc., 108* (1986) 1155; C. Dauland, C. W. Schlaepfer, *J. Chem. Soc. Dalton Trans.* (1988) 393; L. G. Vanquickenborne and A. Ceulemans, *Coord. Chem. Rev., 48* (1983) 157.

3 D. L. Kepert, *Inorg. Chem., 11* (1972) 1561.

4 D. L. Kepert, *Prog. Inorg. Chem., 23* (1979) 1, and refs. therein.

5 L. S. Bartell, *J. Chem. Phys., 32* (1960) 827; C. Glidewell, *Inorg. Chim. Acta, 12* (1975) 219.

6 D. B. Boyd and K. B. Lipkowitz, *J. Chem. Educ., 59* (1982) 269; G. J. McDougall, R. D. Hancock and J. C. A. Boeyens, *J. Chem. Soc., Dalton Trans.,* (1978) 1438.

7 A. Rodger and B. F. G. Johnson, *Inorg. Chim. Acta, 146* (1988) 37.

8 D. Braga, A. Rodger and B. F. G. Johnson, *Inorg. Chim. Acta, 174* (1990) 185.

9 A. Avdeef and J. P. Fackler, Jr., *Inorg. Chem., 14* (1975) 2002.

10 G. St. Nikolov and N. S. Trendafilova, *Inorg. Chim. Acta, 68* (1983) 29.

11 R. Eisenberg and H. B. Gray, *Inorg. Chem., 6* (1967) 1844; C. G. Pierpont and R. Eisenberg, *J. Chem. Soc. A,* (1971) 285.

12 B. F. G. Johnson and A. Rodger, *Inorg. Chem., 28* (1989) 1003.

13 M. G. Drew, personal communication.