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Communications

Molecular Mechanics and the Jahn–Teller Effect

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Molecular mechanical calculations have successfully been applied to problems in coordination chemistry.[1] A difficulty not found in the molecular mechanical analysis of organic systems is the electronic effects due to the presence of partially filled d-orbitals, i.e. variable coordination geometries, the *trans* effect and Jahn–Teller effects. A great deal of effort has been expended to account for these effects. Two approaches have been used to model the Jahn–Teller effect, fixed dummy atoms and two sets of different metal ligand force constants.[2] Both approaches are only reliable when the structure and the direction of the Jahn–Teller distortion are known. Clearly these methods are of no general use, nor are they of great predictive utility.

We present a new method to calculate the structure of Jahn–Teller-distorted metal centers. The procedure is straightforward, it requires a ligand field spectrum of the complex and a molecular mechanics program. Despite the fact that the method uses a crude approximation of the Jahn–Teller effect it is of great structural utility and can calculate the magnitude and direction of the Jahn–Teller distortion.

As is the case with organic molecules, in inorganic molecular mechanical calculations[1] the strain energy of a molecule is determined on the basis of its bond, angle and torsional deformations, as well as its nonbonded interactions. We have now introduced an additional term to mimic the Jahn–Teller stabilization energy. The addition of this term to the total strain energy of the optimized structures as a function of fixed metal–ligand distances allows us to calculate the bond lengths in Jahn–Teller-distorted complexes, as shown in this communication for hexacoordinate copper(II) complexes. This is a general approach and donor atoms other than nitrogen, metals besides copper(II) and geometries besides distorted octahedra will be investigated in the future.

Copper(II)–N_6 chromophores, where the six nitrogens need not be equivalent, can easily be modeled by this method. The copper(II) complexes were chosen first, as the Jahn–Teller effects in these complexes are large and have been crystallographically observed, and because copper(II) is of both spectroscopic and biological interest. Advantages of this method are that the copper–nitrogen distances of dynamically Jahn–Teller-distorted complexes or of complexes which have not been crystallographically characterized can be obtained, as can the direction of the distortion, i.e. which metal–ligand bonds will be elongated and which will be compressed. Furthermore, the steric and electronic contributions to the tetragonal distortions can be separated and analyzed.

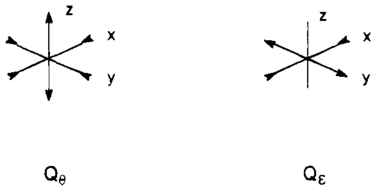

Figure 1. The two components of the ϵ_g Jahn–Teller active mode.

In hexacoordinate copper(II), a d^9 metal ion, Jahn–Teller distortions occur in order to lower the energy of the complex by splitting the unequally occupied e_g orbitals. There are two modes by which this can occur, Q_θ and Q_ϵ, which are shown in Figure 1; these can be related to the individual ligand displacements[3] by

$$Q_\theta = (1/12^{1/2})(\delta x_1 + \delta x_2 + \delta y_3 + \delta y_4 - 2\delta z_5 - 2\delta z_6) \quad (1)$$

and

$$Q_\epsilon = (1/2)(\delta x_1 + \delta x_2 - \delta y_3 - \delta y_4) \quad (2)$$

The total nuclear displacement, Q, can be related to the two components of the degenerate ϵ_g distortion, Q_θ and Q_ϵ.

On the basis of the harmonic first-order model and the equations[4] presented for the Q_θ mode, we can determine the Jahn–Teller stabilization energy (E_{JT} in kJ/mol) for a copper(II) ion as a function of the in-plane displacements ($\delta x = \delta y$)

$$E_{JT} \approx \{(-0.01198)(\delta x)(\Delta')\}/r_0 \quad (3)$$

where Δ' is the energy of the d orbital splitting between the e_g and t_{2g} orbitals in cm^{-1}, if the π-bonding is negligible (for π-donor ligands $\Delta' = 1.36\Delta$) and r_o is the ideal copper(II) nitrogen distance in the absence of the Jahn–Teller effect (r_o = 2.14 (Cu–N(sp^2); r_o = 2.16 (Cu–N(sp^3)).[5] Thus in this

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(5) The following equations given in ref 4

$$V = nm\Delta'/\sqrt{12}r_o \quad (4)$$

$$f = nm\Delta'/12r_o\delta_x \quad (5)$$

$$Q = V/f \quad (6)$$

and

$$m[E(d_{z^2}) - E(d_{x^2-y^2})]/2 = -nmQ\Delta'/\sqrt{12}r_o \quad (7)$$

can be combined and rearranged (eqs 4 and 5 into eq 6, and the resulting expression into eq 7) to give

$$\Delta E = 2/m[-3.464nm\Delta'\delta_x/\sqrt{12}r_o]$$

converting from cm^{-1} to kJ/mol and taking n = 5 and m = 1 for copper(II) , we get (3).

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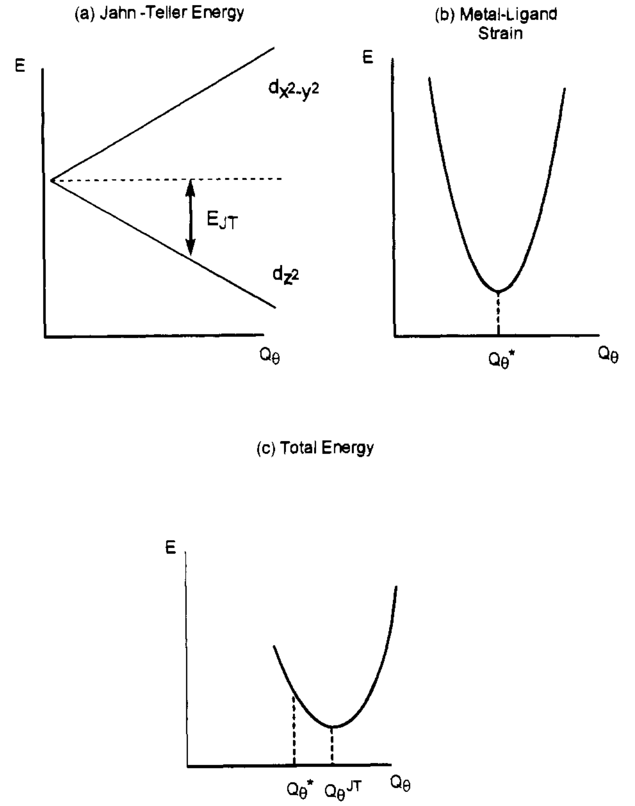

Figure 2. (a) Jahn−Teller stabilization energy as a function of metal−ligand displacements due to the Q_θ distortion, which can be related to the individual ligand displacements by eq 1. (b) Strain energy (MM) as a function of metal−ligand displacements due to the Q_θ distortion, $Q_\theta{}^*$ represents the ideal geometry, in the absence of the Jahn−Teller effect. (c) Sum of the Jahn−Teller stabilization energy (a) and the strain energy (b). $Q_\theta{}^*$ is the ideal geometry, in the absence of the Jahn−Teller effect, and $Q_\theta{}^{JT}$ is that after including the Jahn−Teller effect.

Table 1

compd[a]	cryst in-plane av (Å)	ref	calcd in-plane av (Å)	cryst axial av (Å)	calcd axial av (Å)	Δ[b] (cm^{-1})	ref
$[Cu(tach)_2]^{2+}$	2.07	3	2.07	2.35	2.34	11 350	3
$[Cu(bipy)_3]^{2+}$	2.03	8	2.04	2.34	2.34	11 060	3
$[Cu(phen)_3]^{2+}$	2.04	9	2.04	2.33	2.35	11 400	3
$[Cu(terpy)_2]^{2+}$	2.04	10	2.04	2.29	2.34	11 250	16
$[Cu(en)_3]^{2+}$	2.08	11	2.06	2.34	2.37	11 340	3
$[Cu(9ane3)_2]^{2+}$	2.06	12	2.06	2.32	2.35	12 700	9
$[Cu(pzpy)_2]^{2+}$	2.01	13	2.03	2.39	2.36	12 400	13
$[Cu(tptz)(pca)]^{2+}$	2.03	14	2.06	2.38	2.37	11 160	14
$[Cu(imidazole)_6]^{2+}$	2.03	15	2.01	2.59	2.39	11 000	15

[a] Key: tach = *cis,cis*-1,3,5-triaminocyclohexane; bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline; terpy = 2,2′:6′,2″-terpyridine; en = ethane-1,2-diamine; 9ane3 = 1,4,7-triazacyclononane; pzpy = bis(pyrazol-1-yl)(pyridin-2-yl)methane; tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine; pca = bis(2-pyridylcarbonyl)amide. [b] $\Delta = \Delta E_2 - {}^1/_2\Delta E_1$.

simple model the decrease in energy due to the Jahn−Teller distortion is linearly related to the total nuclear displacement, Figure 2a. However, this decrease in energy is balanced by the increase in strain energy of the molecule due to the associated bond elongation and compression, Figure 2b. Therefore, by finding the minimum total energy of the system, Figure 2c, we can calculate the structure of copper(II) complexes that have undergone a Jahn−Teller induced tetragonal elongation.

The calculations were conducted in the following manner. The copper(II) complexes given in Table 1, were first minimized[6] without involving a Jahn−Teller distortion. The total energy of the system, that is the strain and the Jahn−Teller stabilization energy, was calculated while systematically changing the constrained bond lengths of the in-plane and axial ligands. Due to the nature of the Q_θ distortion, for each in-plane contraction an axial elongation of twice the distance of the in-plane contraction was applied.

The constraints on the metal ligand bonds were set by fixing the internal coordinates with Lagrangian multipliers[17] and using a Urey−Bradley function in place of a L−M−L bending function.[2,7] In Table 1 we compare the in-plane and axial distortions reported on the basis of static crystal structures with those calculated in the manner described above. The complexes reported were chosen from the literature because their crystal structures exhibit statically distorted copper(II) with six coordinating nitrogens and an organic backbone for which molecular mechanical force constants were available. The method worked just as well for ligands with six equivalent donors as found in $[Cu(en)_3]^{2+}$ as for the nonequivalent ligands such as in $[Cu(tptz)(pca)]^{2+}$ (for abbreviations see Table 1). Ligands coordinating by both tertiary and secondary nitrogens were modeled equally well. The direction of the distortion in $[Cu(tptz)(pca)]^{2+}$ was predicted to be within the tptz ligand, and in $[Cu(terpy)_2]^{2+}$, within the same terpy ligand, these are the same distortions observed in the crystal structure. However, the energy difference between the two possible distortions in $[Cu(pzpy)_2]^{2+}$ was not sufficient to predict the direction of the observed distortion, and the axial distortions of $[Cu(imidazole)_6]^{2+}$ were not modeled correctly. These bonds are unusually long and though the copper−ligand distances were the longest calculated for any of the complexes reported here, the predicted distortion was not large enough. Interestingly enough, the in-plane deformations were accurately modeled. We think the reason for these observations are as follows: We have coupled the axial and in-plane distortions, and because the nonbonded repulsions rapidly increase with contraction, this becomes problematic with large axial distortions with their associated large in-plane compressions (for a Cu−N distance of 2.59 Å as found in $[Cu(imidazole)_6]^{2+}$ one expects a in-plane Cu−N distance of 1.91 Å). The Hooke's law type functions that are in the force field used are very accurate at small deformations, but for modeling a large deformation a Morse type potential would be more suitable. The method presented here can also be improved by adding second-order effects to eq 3.

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(6) The MOMEC[7] program was used with parameters described in ref 2. Additional parameters used were $Cu-N_{sp^3}$ (0.250 mdyn/Å; 2.16 Å) $Cu-N_{sp^2}$ (0.250 mdyn/Å; 2.14 Å), $Cu-N_{amide}$ (0.300 mdyn/Å; 2.12 Å).

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