

A Density Functional Approach to the Jahn–Teller Effect of $[\text{Cu}(\text{en})_3]^{2+}$ as a Model for a Macrocyclic Cage Complex of Copper(II)

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Introduction

Hexacoordinated copper(II) chromophores (CuL_6 ; $L = \text{N}, \text{O}, \text{S}, \text{Cl}$, etc.) are very interesting systems for investigating their structural, spectroscopic, and magnetic properties because of their important “plasticity” properties.¹ In the presence of a 6-fold cubic ligand field, the ground state of such Cu^{2+} ions is doubly degenerate and hence, according to the Jahn–Teller theorem,² subject to distortion. The simplest manifestation of the Jahn–Teller effect is the one in which the doubly degenerate electronic state (E) couples linearly to the doubly degenerate vibrational mode (ϵ) resulting in an $E \otimes \epsilon$ Jahn–Teller coupling. Soon after the report of Longuet-Higgins et al.,³ this type of Jahn–Teller effect was studied extensively because it is considered to be relatively simple and nontrivial.^{4–6}

To evaluate some Jahn–Teller parameters, it is necessary to consider the adiabatic potential energy surface (APES) as a function of nuclear coordinates. The theoretical determination of the Jahn–Teller stabilization energy, E_{JT} (i.e., the depth of the minimum of the APES relative to the regular configuration) and the Jahn–Teller radius, R_{JT} , is quite interesting (see Figure 1). Although the APES has no directly observable effects, its parameters are intrinsically correlated to a series of observable properties and hence can be used for further deductions.

The accurate calculation of the electronic structure of transition metal complexes remains a challenging task for quantum chemistry. Although both Hartree–Fock and DFT exploit molecular symmetry, the latter has certain advantages over the former. In the DFT method, correlation is partly taken into account by considering the functional form of the exchange–correlation contribution. Thus, DFT appears to be an excellent approach for optimizing the geometries and computing the state energies of systems containing first-row transition metals.⁷ With

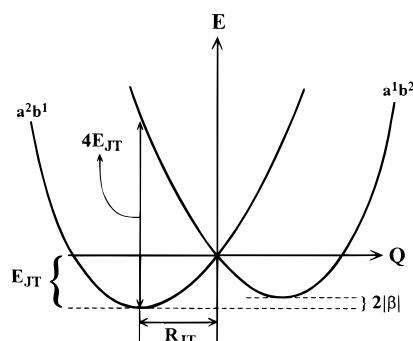


Figure 1. Potential energy surfaces in $E \otimes \epsilon$ Jahn–Teller coupling indicating the Jahn–Teller stabilization energy (E_{JT}), Jahn–Teller radius (R_{JT}), and barrier height ($2|\beta|$).

this in mind, we have followed a simple recipe previously proposed by us⁸ for the calculation of the ground-state Jahn–Teller stabilization energy and the resulting properties of a Jahn–Teller-active molecule, $[\text{Cu}\{(\text{NH}_3)_2\text{sar}\}](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ (where sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane), involving a CuN_6 subunit, with the use of a nonempirical approach like that of DFT. Since the energy of the Jahn–Teller-active ϵ_g vibration has been roughly estimated as $h\nu = 340 \text{ cm}^{-1}$ and the Jahn–Teller stabilization energy $E_{\text{JT}} = 2125 \text{ cm}^{-1}$,⁹ it is quite justifiable to consider that this experimental system represents a case of strong vibronic coupling because $E_{\text{JT}} \gg h\nu$. The polycrystalline EPR results, together with X-ray crystal structure data^{10,11} and single-crystal EPR, optical, and powder magnetic susceptibility results,⁹ have revealed that $[\text{Cu}\{(\text{NH}_3)_2\text{sar}\}](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ suffers from a Jahn–Teller distortion with R_{JT} and E_{JT} values of 0.195 \AA and 2125 cm^{-1} , respectively. In this paper, we consider theoretical calculations performed on the above system for comparison with these experimental findings.

Methodology

Density Functional Calculations. The linear combination of Slater type orbitals (STO) with frozen cores method as implemented in the Amsterdam Density Functional program (ADF version 2.3)^{12–15} was used for the present calculations. For the treatment of exchange–correlation effects, the Vosko–Wilk–Nusair expression¹⁶ was used for the local density approximation (LDA), and the same, augmented by gradient corrections of Becke¹⁷ and Perdew,¹⁸ was applied as a generalized gradient approximation (GGA) functional. Since we are dealing with an open-shell system, spin-unrestricted calculations were also performed to account for the difference in spin polarization between α and β spins. The molecular orbitals for N and C were expressed with an uncontracted triple- ζ STO basis set augmented by a single-polarization function, whereas for Cu a triple- ζ 3d basis was used,

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augmented with a 4p polarization STO. In these calculations the 1s² configuration of N and C and the 1s²2s²2p⁶ configuration of Cu were treated as cores and kept frozen. The initial geometry of [Cu{(NH₃)₂-sar}](NO₃)₄·H₂O was taken from an X-ray diffraction study.¹¹ However, to reduce the complexity of calculation, all pendant groups on the cage were replaced by H atoms. This was expected not to alter the overall symmetry as well as the final energies to any significant amount. Eventually, this molecule was given a [Cu(en)₃]²⁺ structure (en = ethylenediamine).

Calculation of Jahn–Teller Distortion. The complex under investigation has a D₃ symmetry and a ²E electronic ground state with Jahn–Teller-active vibrations of a₁ and e symmetries. Assuming a seven-atom (Cu + 6 N) cluster with quasi-O_h symmetry and neglecting the a₁ modes (since they do not change the symmetry of the molecule) and four out of five e modes (since they involve bending motions and do not have appreciably large vibronic coupling), this problem can be treated as an ideal E⊗e coupling case. Thus, the components Q_ε and Q_θ of the remaining e mode participate in this type of coupling.¹⁹ For a degenerate electronic state (²E, as in the present case), the potential energy surface of the nuclei in the average field of the electrons does not have a minimum at the point of the high-symmetry nuclear configuration.¹⁹ To discover whether this surface possesses any minimum and, if so, where it is located, it is necessary to determine the shape of the adiabatic potential of Cu(en)₃²⁺ in the configuration space of the nuclear displacements Q. We analyze the E⊗e vibronic problem by the method described by Bersuker.¹⁹

Considering linear and quadratic vibronic interactions, the Hamiltonian corresponding to the E⊗e coupling can be written as

$$\begin{aligned} H = [E_0 + \frac{1}{2}K_h(Q_\theta^2 + Q_\epsilon^2)]\sigma_0 + [V_E(Q_\epsilon\sigma_x - Q_\theta\sigma_z)] + \\ W_E[(Q_\theta^2 - Q_\epsilon^2)\sigma_z + 2Q_\theta Q_\epsilon\sigma_x] \end{aligned} \quad (1)$$

where E₀ is the energy corresponding to the uncoupled system, K_h is the force constant in harmonic vibration, V_E and W_E are the linear and quadratic vibronic coupling constants, respectively, σ₀ is a 2 × 2 unit matrix, and σ_x and σ_z are Pauli spin matrices. The components of the electronic wave function of the E_g term are represented by Q_θ and Q_ε and are transformed as (3z² - r²) and (x² - y²), respectively. It may be pointed out that the potential constants, viz. K_h, V_E, and W_E, solely determine the main features of the Jahn–Teller distortion.

At this level of approximation and by substituting Q_θ = R cos φ and Q_ε = R sin φ, we can calculate the barrier height (2|β|) and the Jahn–Teller stabilization energy (E_{JT}) from the relations

$$2|\beta| = \frac{2V_E^2 W_E}{K_h^2 - 4W_E^2} \quad (2)$$

$$E_{JT} = \frac{V_E^2}{2(K_h - 2W_E)} \quad (3)$$

The extreme points (R_n, φ_n) of the APES are given as

$$\begin{aligned} R_n = \frac{V_E}{K_h - (-1)^n(2W_E)} \\ \varphi_n = \frac{n\pi}{3}; \quad n = 0, 1, 2, 3, 4, 5 \end{aligned} \quad (4)$$

If the product V_EW_E > 0, the points n = 0, 2, 4 represent absolute minima whereas the points n = 1, 3, 5 represent saddle points; however, the reverse is true when V_EW_E < 0.

It is clear that the whole APES is determined solely by three parameters, K_h, V_E, and W_E, or alternatively by E_{JT}, 2|β|, and R_T (Jahn–Teller radius) (see also Figure 1). The latter ones can, however, easily

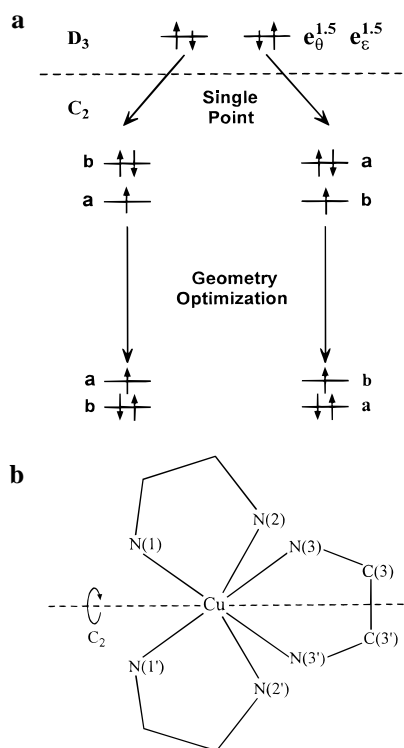


Figure 2. Schematic representations of (a) the calculation recipe and (b) a CuN₆ chromophore.

be obtained from DFT by using the calculation scheme shown in Figure 2a.

Let us consider a molecule with a degenerate state Γ belonging to the point group G₀. Now, among all the subgroups of G₀, let us determine those for which the irreducible representation Γ contains a totally symmetric representation A₁. Among these subgroups, e.g. {S₁, S₂, S₃, ...}, we choose the subgroup with maximal order and denote it as G₁. In G₁, the state Γ will split into Γ₁, Γ₂, ..., etc., some of which might still be degenerate. Now, we perform two types of DF calculations in G₁ symmetry: (i) a single-point calculation imposing G₀ symmetry on the nuclear geometry and G₁ symmetry on the electron density and (ii) a geometry optimization without symmetry constraints imposed on the nuclei. To generate totally symmetric electron densities in G₁, these two steps are repeated for all possible combinations.

The complex under investigation exhibits D₃ (G₀) symmetry, and since it is a d⁹ system, the highest occupied molecular orbital (HOMO) belongs to the irreducible representation e which accommodates the unpaired electron. From the group theoretical character tables one finds G₁ = C₂ for the present system and the HOMO splits into "a" and "b". Thus, there are two distinct ways in which the unpaired electron can be accommodated: (a) a¹b² yielding a density ρ₁ and (b) a²b¹ yielding another density ρ₂. Therefore, we perform four DF calculations corresponding to these occupations, with and without geometry optimization. The total energies obtained in these four calculations are denoted as follows: E(ρ₁, D₃), occupation is a¹b² with imposing D₃ symmetry on the nuclear geometry; E(ρ₁, C₂), occupation is a¹b² with the nuclear geometry of C₂ symmetry; E(ρ₂, D₃), occupation is a²b¹ with imposing D₃ symmetry on the nuclear geometry; E(ρ₂, C₂), occupation is a²b¹ with the nuclear geometry of C₂ symmetry. It is, however, possible to identify the symmetry-adapted nuclear displacements leading from G₀ to G₁. They must be equivalent to those components of the irreducible tensor operators for G₀ which possess full symmetry about the distortion axis in G₁. That is, we must identify the component |Γ_{γa}⟩ of Γ in G₀ which becomes totally symmetric in G₁. This identification can, however, easily be achieved by inspection of the Clebsch–Gordan coefficients for G₀.²⁰ These normal nuclear displacements can be denoted as Q_{γa} and for this particular case Q_{γa} =

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Table 1. Cu–N Bond Distances (Å) As Obtained from the Calculations and Experiments

method	dist	$C_2 a^2b^1$	D_3	$C_2 a^1b^2$	$[\text{Cu}(\text{en})_3]^{2+}$	$[\text{Cu}\{(\text{NH}_3)_2\text{sar}\}]^{4+ c}$
LDA restricted	Cu–N(1)	2.437		2.000	2.39(2) ^a /2.34(2) ^b	2.274(3)
	Cu–N(2)	2.053	2.166	2.233	}2.04(1) ^a /2.04(1) ^b	}2.114(3)
	Cu–N(3)	2.050		2.286		
LDA unrestricted	Cu–N(1)	2.433		1.999		
	Cu–N(2)	2.052	2.162	2.229		
	Cu–N(3)	2.047		2.280		
GGA restricted	Cu–N(1)	2.574		2.061		
	Cu–N(2)	2.130	2.249	2.331		
	Cu–N(3)	2.120		2.412		
GGA unrestricted	Cu–N(1)	2.563		2.064		
	Cu–N(2)	2.126	2.246	2.315		
	Cu–N(3)	2.115		2.396		

^a Reference 24; in en. ^b Reference 24; in water. ^c Reference 11.

Table 2. Calculated Total Energies (eV) for the Different Symmetries and Occupations

method	$C_2 a^2b^1$	$C_2 (D_3) a^2b^1$	D_3	$C_2 (D_3) a^1b^2$	$C_2 a^1b^2$
LDA restricted	–193.3091	–193.0499	–193.2283	–193.0561	–193.2590
LDA unrestricted	–193.5148	–193.2529	–193.3680	–193.2575	–193.4542
GGA restricted	–178.1660	–177.9235	–178.0888	–177.9303	–178.1271
GGA unrestricted	–178.4380	–178.1919	–178.2620	–178.1993	–178.3851

Q_θ . Thus, the three Jahn–Teller parameters E_{JT} , $2|\beta|$, and R_{JT} are obtained as follows:

$$E_{\text{JT}} = E(\rho_1, D_3) - E(\rho_1, C_2) \quad (5)$$

$$2|\beta| = |\{E(\rho_1, C_2) - E(\rho_1, D_3)\} - \{E(\rho_2, C_2) - E(\rho_2, D_3)\}| \quad (6)$$

$$= |E(\rho_1, C_2) - E(\rho_2, C_2)|$$

$$R_{\text{JT}} = Q(\rho_1, C_2) \quad (7)$$

It must be pointed out that the density functional calculations, in general, follow the inequality

$$|E(\rho_1, D_3)| \neq |E(\rho_2, D_3)| \quad (8)$$

mainly because of the distinct nature of the exchange-correlation functions involved in this type of calculations. This problem is solved in a pragmatic way by forcing equality of expression 8 as done in eq 6.

Results and Discussion

The calculation scheme for investigating the Jahn–Teller distortion of $[\text{Cu}\{(\text{NH}_3)_2\text{sar}\}](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$, using $\text{Cu}(\text{en})_3^{2+}$ as a model is depicted in Figure 2a. As far as DFT is concerned, one can assume that both e orbitals carry 1.5 electrons, thus leading to a totally symmetric electron distribution (ρ_0). This is represented in Figure 2a as $e_\theta^{1.5} e_\epsilon^{1.5}$. The second step of the calculation scheme consists of an unpaired electron occupying selectively one of the two degenerate e orbitals within the D_3 geometry. This is done by imposing a C_2 symmetry on the system within the ADF program, as shown in Figure 2b. Hereby, the two e orbitals are split into a and b orbitals which are populated as $b^2a^1(\rho_1)$ and $a^2b^1(\rho_2)$ in two separate calculations, providing the energies $E(\rho_1, D_3)$ and $E(\rho_2, D_3)$. Finally, we perform a complete (i.e., without constraints) geometry optimization on both C_2 cases corresponding to elongated and compressed geometries with two different energies $E(\rho_1, C_2)$ and $E(\rho_2, C_2)$.

The relevant bond lengths (Cu–N) obtained from all the calculations are summarized in Table 1. Notice first that changing the electronic distribution in high symmetry indeed leads to a change in geometry and nicely results in the JT distortion. The $C_2 a^2b^1$ configuration can be characterized as the tetragonally elongated form: one bond is lengthened by 0.27

Å/0.32 Å in LDA/GGA, and the two other bonds are shortened by 0.11 Å/0.125 Å in LDA/GGA. The a^1b^2 occupation in C_2 resulted in the compressed form, since we here obtained the opposite: two bonds are lengthened (0.09 Å/0.16 Å in LDA/GGA) and one is shortened (0.16 Å/0.14 Å in LDA/GGA) relative to the D_3 symmetry. Second, from the different total energies, listed in Table 2, we see that the lowest point on the adiabatic potential surface for $[\text{Cu}(\text{en})_3]^{2+}$ in C_2 symmetry corresponds to the a^2b^1 occupation, thus the elongated form.

It is well-known that the inclusion of gradient corrections leads to bond elongation compared to LDA results. A recent study on several Werner-type and organometallic complexes has shown the ability of the different functionals to calculate the geometries of these different types of molecules.²¹ Here it was shown that LDA tends to perform better for Werner-type complexes, as $[\text{Cu}(\text{en})_3]^{2+}$ in our case. Inclusion of spin polarization does not have as large an influence on the geometry as the functional does but leads, on the other hand, to lower total energies, since it introduces an extra degree of freedom into the minimum search (see Table 2). Comparing now with experiment reveals indeed that LDA performs better than GGA since there is a good agreement between the calculated geometry of our minimum ($C_2 a^2b^1$) and the experimental values of $[\text{Cu}(\text{en})_3]^{2+}$.

The Jahn–Teller stabilization energy (E_{JT}) and barrier height ($2|\beta|$) have been calculated from the results of the complete DF calculation scheme and by using eqs 5 and 6. On the other hand, the Jahn–Teller radii (R_{JT}) for two different conformations have been calculated from the geometrical parameters (Table 1) and by using the equation²²

$$R_{\text{JT}}^2 = \sum_{i=1}^6 (\Delta d_i)^2 \quad (9)$$

where $\Delta d_i = d_i - d_0$, d_i is the distance from the central metal ion to the i th ligand, and d_0 is the average metal–ligand distance. In experiment, the Jahn–Teller stabilization energy E_{JT} is

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Table 3. Jahn–Teller Parameters, as Obtained from Experiments and Calculations

	E_{JT} (cm ⁻¹)	$4E_{JT}$ (cm ⁻¹)	$2 \beta $ (cm ⁻¹)	R_{JT} (Å)
	Experimental			
[Cu{(NH ₃) ₂ sar}] ⁴⁺	2125 ^a	8500 ^b	143 ^d	0.195 ^d
[Cu(en) ₃] ²⁺	2050 ^a	8200 ^c	102 ^c	0.41 ^e
	Calculated			
LDA restricted	2091	8522	404	0.447
LDA unrestricted	2112	8629	489	0.445
GGA restricted	1956	7809	314	0.522
GGA unrestricted	1985	7895	427	0.514

^a Jahn–Teller energy calculated from the first electronic d–d transition using $\Delta E = 4E_{JT}$. ^b Reference 11. ^c Reference 25. ^d Reference 9. ^e Reference 24.

actually estimated from optical absorption spectroscopy from the energy ΔE of the transition between the split levels of the ²E state of the parent *D*₃ complex, since (see Figure 1) $\Delta E \cong 4E_{JT}$.²³ This approach to the potential parameter E_{JT} is tested by calculating the electronic transition using the Δ SCF procedure for a one-electron excitation corresponding to an (²A ↔ ²B) transition.

The results from all calculations for the obtained absolute minimum (*C*₂ a²b¹) along with the experimental values are summarized in Table 3. The Jahn–Teller stabilization energy for this compressed configuration is calculated at ~2100 cm⁻¹ with the LDA functional which is in good agreement with the experimental values. Also the calculated excitation energy ($4E_{JT}$)

from LDA agrees nicely with the observed transition energy. We wish to point out that the calculated values of E_{JT} do agree with both approaches, meaning that the theoretical results of both methods are consistent. On the other hand, the calculated barrier height ($2|\beta|$), which is a second-order effect of vibronic coupling, is estimated to be higher than the experimental value (300–400 cm⁻¹, instead of 100–150 cm⁻¹). Though we do not calculate $2|\beta|$ accurately, it is gratifying to note the prediction of correct order of magnitude, the parameter being second order in nature. It must be mentioned that the experimental value for ($2|\beta|$) as given in Table 3 is derived from EPR measurements and may be considered as a qualitative one; for an accurate estimation of the Jahn–Teller potential barrier, one must perform relaxation measurements. The predicted value for R_{JT} agrees well with the observed one for [Cu(en)₃]²⁺, which does correspond with the calculation model. However, the experimental value of R_{JT} for the cage complex is much smaller than the one predicted and observed for [Cu(en)₃]²⁺. The reason for this discrepancy is most probably due to a restricted JT distortion imposed by the cage. Indeed, the three “en” fragments of the cage are held together by additional bonds linking them together.

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