

reduction in the electron density at the Pt center, and thus it is possible that a dative bond between the electron-rich Pt(0) and the electron-deficient Zr(IV) exists. Such an interaction would be comparable to the $d^{10} \rightarrow d^0$ dative bond between Cu(I) and Ti(IV) observed in the complex $[\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{PPh}_2)_2\text{Cu}]\text{BF}_4$.²² In the more closely related complex $(\text{C}_5\text{H}_5)_2\text{Th}(\mu\text{-PPh}_2)_2\text{Ni}(\text{CO})_2$,²⁶ a short Th-Ni distance has been observed crystallographically. The implication of a metal-metal interaction in the Th-Ni species can be extended to the present compounds. Other workers have recently confirmed the presence of metal-metal dative bonds in the related Hf/Pd heterobimetallic complexes by crystallographic methods as well as molecular orbital calculations.³⁷ Thus it appears that **13** best represents the nature of the metal-phosphorus core of these compounds.



(37) Baker, R. T., personal communication.

The results described herein demonstrate a convenient synthetic route to heterobimetallic complexes in which two widely diverse transition metals are brought into close proximity. The utilization of **1** as a "metallo ligand" allows the preparation of heterobimetallic complexes, providing an alternative to the "bridge-assisted-dianion" approach of Geoffroy.^{2,9,12,14-17,20} The unique reactivity patterns that arise from the metal-metal interaction in these complexes are the subject of our current work.

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Factors Influencing Jahn-Teller Distortions in Six-Coordinate Copper(II) and Low-Spin Nickel(II) Complexes

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A simple method of calculating the Jahn-Teller distortions of copper(II) complexes to first order is described, and this is shown to predict ligand displacements generally somewhat smaller than those observed experimentally. The effects of anharmonicity in the vibrational potential, second-order electronic corrections, and d-s mixing on the potential surface are discussed, and the inclusion of these leads to calculated geometries and other Jahn-Teller parameters of typical copper(II) complexes in reasonable agreement with experiment. It is suggested that the electronic and geometric structures of spin-paired nickel(II) complexes may be considered to be derived from a Jahn-Teller distortion of the ¹E_g excited state of a regular octahedral complex. This allows the in-plane bond lengths to be estimated satisfactorily and provides a rationalization of the fact that the axial bonds in such complexes are very long or absent.

Introduction

The role of the Jahn-Teller effect in influencing the molecular geometries and physical properties of transition-metal complexes has become increasingly apparent in recent years.¹⁻⁵ Moreover, although the importance of this effect on the structural chemistry of copper(II) has sometimes been queried,^{6,7} it is clear that, at least at low temperature, copper(II) complexes almost invariably adopt distorted geometries that are in agreement with the predictions of the Jahn-Teller theorem. At higher temperatures, dynamic fluctuations between the distorted complexes may occur and here again models based upon the Jahn-Teller theorem have been widely used to describe the spectroscopic and X-ray diffraction properties of such systems.⁸⁻¹¹

Despite the overall success of the theorem some aspects of the stereochemistry of copper(II) complexes still require clarification. In particular, the Jahn-Teller active vibrational mode of an octahedral complex of a d⁹ metal ion is doubly degenerate and, to first order, theory suggests not only that a compressed-tetragonal geometry is just as likely as the elongated stereochemistry which is invariably observed experimentally, at least at low temperature, but also that the geometry should oscillate dynamically between these extremes along a normal coordinate corresponding to an orthorhombic molecular symmetry. Several suggestions have been made of ways in which the simple model may be extended to bring it into better agreement with experiment. Öpik and Pryce proposed

the addition of an anharmonic term to the vibrational potential,¹² and the importance of this term has also been recognized by Bacci.¹³ The extension to second order of the electronic term in the total potential energy expression has been investigated quantitatively both by Ballhausen and Liehr¹⁴ and by Bacci,¹³ though this was found to stabilize a compressed rather than an elongated geometry. Finally, a number of research workers have independently suggested that the elongated-tetragonal geometry characteristic of six-coordinate copper(II) complexes results from configuration interaction between the 4s and 3d_{z²} metal orbitals.¹⁵⁻¹⁷

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The similarities between the structural chemistries of d^8 and d^9 complexes have been discussed previously by Burdett using a simple angular-overlap approach.¹⁸ It is well established that diamagnetic nickel(II) complexes generally adopt an essentially planar geometry, as opposed to the regular octahedral ligand arrangement common for paramagnetic complexes of this metal ion. It is also well-known that the occupancy of the d orbital directed along a metal–ligand bond influences its length—indeed the geometry of copper(II) complexes might be rationalized on this basis alone, with the fact that the axial bonds are longer than the equatorial ones being simply related to the double occupancy of the $d_{x^2-y^2}$ orbital as opposed to the single occupancy of d_{z^2} . Simplistic arguments of this kind, based just upon metal–ligand repulsions, are clearly inadequate to explain the geometry of low-spin nickel(II) complexes since on the basis of the d_{z^2} occupancy the axial bond lengths in these compounds might be expected to be similar to those in analogous copper(II) complexes. In practice, the axial bonds in low-spin nickel(II) complexes are always extremely long, and often axial ligation does not occur at all.¹⁹ Although not generally thought of in this way, the $^1A_{1g}$ electronic ground state of a planar nickel(II) complex is simply one component of the Jahn–Teller active 1E_g excited state of a regular octahedral complex, the distortion along the Jahn–Teller mode being sufficient to make this the ground state, and part of the purpose of the present paper is to point out that the stereochemistry of low-spin nickel(II) complexes may easily be rationalized within the framework of the Jahn–Teller theorem.

Recently, a simple way of relating the overall metal–ligand bond length in a complex to the occupancy of the d orbitals was described,²⁰ allowing the change in bond length accompanying a d-electron rearrangement to be estimated in terms of the d-orbital splitting and the force constant of the α_{1g} totally symmetric stretching mode. The purpose of the present paper is first to show that this simple model may readily be extended to displacements along the Jahn–Teller ϵ_g mode active in systems with an E_g electronic degeneracy and, second, to investigate the relative importance of the various perturbations proposed to explain the predominance of the elongated-tetragonal geometry observed experimentally for complexes of this kind.

Summary of the $E \times \epsilon$ Jahn–Teller Problem

Detailed treatments of the $E \times \epsilon$ Jahn–Teller coupling have appeared in several recent textbooks and review articles,^{1–5} so only a brief outline of the problem will be given here. Octahedral complexes having an electronic degeneracy in the e_g^* orbitals have a single Jahn–Teller-active normal mode of ϵ_g symmetry. The normal coordinates of the two components of this mode, Q_ϵ and Q_θ , are illustrated in Figure 1b, it being conventional to describe the relative proportions of these at any instant of time in terms of an angle ϕ as shown in Figure 1a. The relationship between the normal displacements Q_θ , Q_ϵ and individual ligand displacements δx etc. are given by¹⁰

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

$$Q_\epsilon = (1/2)(\delta_{x_1} + \delta_{x_2} - \delta_{y_3} - \delta_{y_4}) \quad (1b)$$

Here, the subscripts refer to an arbitrary ligand numbering system and the displacements are with respect to a regular octahedral geometry. For a copper(II) complex in which the Jahn–Teller stabilization energy is much greater than the energy of the ϵ_g active mode, the ground-state wave function ψ is coupled to the nuclear geometry via the relationship

$$\psi = d_{x^2-y^2} \cos(\phi/2) + d_{z^2} \sin(\phi/2)$$

An angle $\phi = 0^\circ$ thus corresponds to an elongated-tetragonal ligand geometry with the unpaired electron in $d_{x^2-y^2}$, while $\phi =$

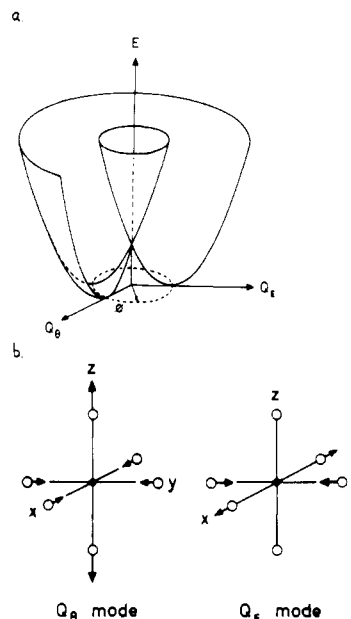


Figure 1. (a) "Mexican hat" potential surface. (b) Form of the two components of the ϵ_g Jahn–Teller active mode.

180° corresponds to the same nuclear displacements, but opposite in sign, i.e. a compressed-tetragonal geometry, with the unpaired electron in d_{z^2} . The overall nuclear displacement Q , sometimes called the Jahn–Teller radius ρ , is related to the displacements along the components Q_θ and Q_ϵ by

$$Q_\theta = Q \cos \phi \quad Q_\epsilon = Q \sin \phi$$

The basic driving force behind the Jahn–Teller distortion is the lowering in energy of the complex due to the unequal occupancy of the split components of the e_g^* orbitals, and this is expected to be approximately linear in nuclear displacement. Opposing this is the natural rise in energy that occurs whenever bonds are stretched or compressed, and to a first approximation this obeys the quadratic relationship of simple harmonic motion. The variation of the total energy of the system U as a function of the Jahn–Teller mode Q may thus be written

$$U = U_0 + \frac{f}{2}Q^2 - VQ \quad (2)$$

where f is the force constant of the ϵ_g mode of the parent octahedral complex and V is the constant indicating the amount by which the energy is lowered due to the unequal occupancy of the d orbitals. Since at equilibrium $dU/dQ = 0$, at this level of approximation the expected displacement along the Jahn–Teller mode is simply $Q = V/f$, with U being independent of ϕ . The potential surface of the complex now takes the form of a "Mexican hat" as illustrated in Figure 1a, the circle representing the energy minimum.

Derivation of the Electronic Coupling Constant V to First Order

Recently, it was shown that if it is assumed that the energy by which a d orbital is raised upon interaction with the ligands in a complex depends inversely upon some power n of the bond distance, then the change in overall bond length δr accompanying the rearrangement of m electrons between two d orbitals (or sets of d orbitals) separated in energy by Δ is given by the expression²⁰

$$\delta r \approx \frac{nm\Delta}{Nr_0^f}$$

where f is the force constant of the α_{1g} totally symmetric stretching mode, r_0 is the initial bond length, and N is the number of ligands in the complex. Both theory and experiment²¹ suggest that $n \approx$

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Table I. Structural and Spectroscopic Parameters of Jahn–Teller-Distorted Complexes Calculated with Neglect of Second-Order Electronic Effects, d–s Mixing, and Anharmonic Corrections to the Vibrational Potential

complex	input parameters			bond length changes, Å ^b				$E(d_{z^2} \rightarrow d_{x^2-y^2})$, cm ⁻¹	
	Δ' , cm ⁻¹	r_0 , Å	f , mdy ⁿ Å ⁻¹ ^a	calcd		obsd		calcd	obsd
				δ_x	$-2\delta_z$	δ_x	$-2\delta_z$		
Cu(H ₂ O) ₆ ²⁺	~11 500 ^c	2.10 ^d	0.57 ^e	0.08	0.16	0.11 ^d	0.23 ^d	4400	7500 ⁴⁴
Cu(C ₅ H ₅ NO) ₆ ²⁺	~11 500 ^c	2.09 ⁴²	0.57 ^e	0.08	0.16	0.12 ^f	0.27 ^f	4400	6050 ⁴⁵ 7400 ⁴⁶
Cu(NO ₂) ₆ ⁴⁻	12 000 ⁴	2.17 ⁴	0.64 ^g	0.07	0.14	0.09 ⁴	0.18 ⁴	4000	7200 ⁴
Cu(tach) ₂ ^{2+h}	11 400 ¹⁰	2.17 ¹⁰	0.64 ^g	0.07	0.14	0.11 ¹⁰	0.19 ¹⁰	3600	8800 ¹⁰
Ni(diamine) ₃ ²⁺ (¹ E _g)	11 600 ⁴⁹	2.12 ⁵⁰	0.71 ²³	0.13	0.25	~0.18 ⁱ	<i>i</i>	13900	~25000 ³²
Cr(NH ₃) ₆ ³⁺ (⁴ T _{2g}) ^j	22 300 ⁵²	2.16 ⁵²	1.72 ⁵²	0.05	0.10	0.05 ⁵²	0.09 ⁵²	5600	
PtF ₆ ²⁻ (³ T _{1g}) ^k	~41 000 ^k	1.91 ^k	3.62 ^k	0.05	0.09	0.05 ⁵³	0.11 ⁵³	10000	

^a 1 mdyⁿ Å⁻¹ = 0.5035 × 10⁵ cm⁻¹ Å⁻². ^b Estimated by assuming the displacement to be along the Q_θ component of the ϵ_g mode (Figure 1). ^c The optical spectra of Cu(C₅H₅NO)₆²⁺ and Cu(H₂O)₆²⁺ suggest that the parent octahedral complexes have an energy separation between the e_g and t_{2g} orbital sets of $\Delta \approx 8550$ cm⁻¹. Assuming that the π interaction e_π is ~20% of the σ interaction, e_π implies that the e_g orbitals are raised in energy by $\Delta' \approx 11 500$ cm⁻¹. ^d Average of the values observed in five Tutton salts. ^e Deduced from the average of the values $\bar{\nu}(\epsilon_g) = 235$ and 228 cm⁻¹ observed for Ni(H₂O)₆²⁺ and Zn(H₂O)₆²⁺, respectively. ^f The force constant of Cu(C₅H₅NO)₆²⁺ is assumed to be equal to that of Cu(H₂O)₆²⁺. ^g Value in aqueous solution. ^h Force constant estimated as the average of those of Ni(NH₃)₆²⁺ and Zn(NH₃)₆²⁺; the overall force constant of Ni(NO₂)₆⁴⁻ is very similar to that of Ni(NH₃)₆²⁺. ⁱ $tach = cis,cis-1,3,5$ -triaminocyclohexane. ^j The difference in metal–nitrogen bond length between high- and low-spin nickel(II) complexes involving the same amine varies between 0.16 and 0.20 Å.^{50,51} ^k Distortion occurs in ⁴T_{2g} excited state; it is likely that here the displacement involves an axial compression, rather than an elongation. ^l Distortion occurs in the ³T_{1g} excited state; it is likely that here the displacement involves an axial compression, rather than an elongation. The value of $\Delta = 30 000$ cm⁻¹ reported for PtF₆²⁻ implies an e_g antibonding energy $\Delta' \approx 41 000$ cm⁻¹ assuming $e_\pi \approx 0.2e_\sigma$ in this complex.²²

5, and the use of this value yields estimates of δr in good agreement with crystal structure data for the molecular changes accompanying the high-spin ↔ low-spin interconversions of Fe(II) complexes and with the bond length changes associated with electronic transitions as estimated from the band-shape analysis of the spectra of a wide range of metal complexes. When similar reasoning is applied to the $E \times \epsilon$ Jahn–Teller problem, it is easily shown that to first order

$$V = \frac{nm\Delta'}{12^{1/2}r_0}$$

(see Appendix). Here, n and m are defined as above, with m in this case being the difference between the number of electrons in the split components of the e_g^* orbitals, and Δ' is the antibonding energy of the e_g^* orbitals in the hypothetical parent octahedral complex. Note that $\Delta' = \Delta$, the d orbital splitting between the e_g^* and t_{2g} orbitals only when π -bonding is negligible; for π -donor ligands such as Cl⁻ or H₂O it has been found that $e_\pi:e_\sigma = 1:5$, and as $\Delta = 3e_\sigma - 4e_\pi$, this implies the relationship $\Delta' \approx 1.36\Delta$.²² At this level of approximation the Q_θ and Q_ϵ components of the ϵ_g mode are energetically equivalent, as are the elongated- and compressed-tetragonal forms of the q_θ component. Considering just the Q_θ component yields the individual in-plane ligand displacements

$$\delta_x \approx \frac{nm\Delta'}{12^{1/2}r_0f} \quad (3)$$

with the axial displacements being twice this and opposite in sign (Figure 1b).

Comparison of the Simple Model with Experiment

Assuming a value of $n = 5$,²¹ the substitution of the appropriate force constants and ligand field splitting parameters of a range of complexes into eq 3 yields the calculated ligand displacements given in Table I. For the copper(II) complexes, the estimated nuclear displacements, although of the right order of magnitude, are some 40% smaller than those observed experimentally. Calculated energies of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions are ~60% lower than the measured values. It should be noted that since the model implies a linear dependence of the Jahn–Teller nuclear displacement on m , the difference in the number of electrons between

the d_{z^2} and $d_{x^2-y^2}$ orbitals, and since Δ' and f are expected to be quite similar for octahedral nickel(II) and copper complexes, this suggests the nuclear displacements as one goes from the ¹E_g to the ¹A_{1g} state of a nickel(II) complex should be approximately twice those in an analogous copper(II) complex. As far as the in-plane ligands go, the observed displacement is from 60 to 100% greater than that in similar copper(II) compounds. Moreover, the fact that the axial ligands are usually lost completely when a nickel(II) complex undergoes a high-spin → low-spin conversion may now be explained, at least in qualitative terms—the axial bonds lengthen to such an extent that entropy considerations and/or higher order electronic effects make it energetically favorable for these ligands to be lost from the coordination sphere.

In order to test the generality of the model, it was also used to estimate the Jahn–Teller distortions in the excited ⁴T_{2g} and ³T_{1g} electronic states of Cr(NH₃)₆³⁺ and PtF₆²⁻. It is thought that the ϵ_g mode dominates in the Jahn–Teller distortions of these excited states,⁵² though it is interesting to note that because of the electron configurations of the excited states the sense of the displacement is likely to be an axial compression rather than the elongation observed for copper(II) complexes. Here, the agreement between the calculated ligand displacements and those derived from band-shape analysis is much better, the distortions being considerably smaller than those estimated for the copper(II) complexes. This is largely because the model suggests that $\delta_x \propto \Delta'/f$, and as one goes from copper(II) to the higher valent chromium(III) and platinum(IV), the force constant of the ϵ_g mode increases more than does the d-orbital energy parameter Δ' (in general, at least for simple ligands such as NH₃, for trivalent metal ions the force constants of the ϵ_g and α_{1g} modes are similar, while for divalent ions that of the ϵ_g mode is significantly smaller than that of the α_{1g} totally symmetric stretching mode²³). In this context it should be noted that the observed Jahn–Teller distortion of the low-spin Co(NO₂)₆⁴⁻ ion ($Q = 0.21$ Å) is significantly less than that of the analogous Cu(NO₂)₆⁴⁻ ion ($Q = 0.32$ Å), though the Δ' value for the two ions is similar (~12 500 cm⁻¹).⁴ The displacement cannot presently be calculated for the cobalt(II) complex, as no good estimate of the ϵ_g force constant is available. This is expected to lie between that of Ni(NO₂)₆⁴⁻ and that of the low-spin complex Fe(NO₂)₆⁴⁻, but apparently no data are yet available for the latter complex. However, the model clearly suggests that the smaller Jahn–Teller displacement in Co(NO₂)₆⁴⁻ compared with that in Cu(NO₂)₆⁴⁻ is likely to be due to a larger ϵ_g force constant in the former complex.

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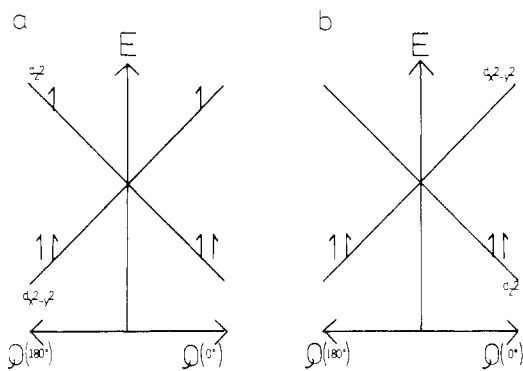


Figure 2. Variation of the d_{xy} and $d_{x^2-y^2}$ energies as a function of a displacement in the Q_θ normal mode for (a) the 2E_g state of copper(II) and (b) the 1E_g state of nickel(II). A displacement corresponding to $\phi = 180^\circ$ corresponds to an axially compressed and $\phi = 0^\circ$ to an axially elongated ligand geometry.

It should be noted that in considering the Jahn–Teller distortions of metal ions with electron configurations other than d^9 or d^1 interelectron repulsion will mean that the energy levels may no longer correspond to simple d-orbital occupancies such as those illustrated in Figure 2.²⁴ The general effect of this will be to reduce the value of m in eq 3 and hence mean that the ligand displacement will be less than that calculated. However, provided that the displacements are large, as is certainly always the case for low-spin d^8 systems, the “strong-field” approach inherent in the present model should remain valid.

Extension of the Model To Include Higher Order Vibrational and Electronic Terms and d–s Mixing

When it is assumed that the ϵ_g vibration is harmonic and that the d-orbital energies vary linearly with bond distance, then theory predicts that the result of the $E \times \epsilon$ coupling should be a structure that oscillates dynamically between compressed- and elongated-tetragonal geometries via orthorhombically distorted intermediates with the symmetry axis fluctuating between x , y , and z . This contrasts with experimental observation, which suggests that six-coordinate copper(II) complexes involving identical ligands invariably adopt an elongated-tetragonal geometry.²⁵ In the case of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, this is known to be the case not only in the solid state but also in solution,²⁶ and it is thought that the energy barrier to the cyclic interconversion between the tetragonal symmetry axes is of the order of a few hundred wavenumbers.²⁷ It has been recognized for some time that the addition of an anharmonic term to the vibrational potential and the extension of the electronic potential function to second order would each destroy the equivalence of the two components of the ϵ_g mode.^{12–14} The physical reason for this discrimination is the fact that while in the Q_e component of the mode all four ligands move by an equal amount, the axial ligands move twice the distance of the in-plane ligands in the Q_θ component (Figure 1b). The underlying cause of the anharmonicity in a stretching vibration is generally taken to be the fact that the energy rises more steeply when a bond is compressed than is the case when it is stretched. In the present context this means both that the Q_e component of the vibration should be essentially harmonic and that for equal displacements of the Q_θ mode the tetragonally compressed geometry will have a higher energy than the elongated geometry. Similarly, when

the power dependence of the ligand–d-orbital interaction is taken into account, discrimination will occur between the compressed and elongated displacements of the Q_θ component, while the Q_e component will be unaffected compared with a simple linear dependence. However, since the interaction stabilizes the system, it is clear that in this case the effect of a second-order electronic term in the total potential will be to lower the energy of the compressed- rather than the elongated-tetragonal geometry. Finally, it has been proposed that the configuration interaction between the $4s$ and $3d_{z^2}$ orbitals which is expected to accompany the nuclear displacement of the Q_θ component, but not that of the Q_e component, should tend to stabilize the elongated rather than the compressed geometry, since this produces a greater electron occupancy of the stabilized orbital.^{15–17} The above effects should thus make the total energy of the system dependent upon the relative contributions of the Q_e and Q_θ components to the nuclear displacement. That is, U will now depend upon ϕ , and the potential surface will become “warped” to give a minimum (or saddle point) at $\phi = 0^\circ$, with a corresponding saddle point (or minimum) at $\phi = 180^\circ$. Entirely equivalent “warping” will of course also occur centered at $\phi = 120$ and 300° , and 240 and 60° , corresponding to the symmetry axes being x and y rather than z . The amount by which the warping lowers the energy of the potential surface is conventionally represented by the parameter β , the energy barrier to the interconversion of the z , x , and y symmetry axes thus being 2β . An attempt will now be made to quantify the above contributions to the potential.

Anharmonic Correction to the Vibrational Potential

The change in total potential energy of two bonded atoms as a function of the bond distance is generally represented by a Morse function of the form⁵⁶

$$U = D_e(1 - e^{-CQ})^2 \quad (4)$$

where D_e is the bond dissociation energy. If D_e is expressed in cm^{-1} , the constant C in \AA^{-1} is given by

$$C = 0.2435(\mu \bar{\nu} x_e)^{1/2} \quad (5)$$

where μ is in units of atomic mass and $\bar{\nu} x_e$ is the anharmonicity constant of the vibration in cm^{-1} . Expansion of eq 4 yields

$$U = D_e(C^2Q^2 - C^3Q^3 + 7C^4Q^4/12\dots) \quad (6)$$

It may be seen that the Morse parameters are related to the force constant f appropriate to simple harmonic motion by

$$f = 2D_e C^2 \quad (7)$$

and that to third order in Q the potential energy is given by

$$U = f/2Q^2 + V_3Q^3 \quad (8)$$

where $V_3 = -Cf/2$. The only direct experimental data on the anharmonicity of the Jahn–Teller ϵ_g mode of which we are aware was obtained from the luminescence spectrum of PtF_6^{2-} , for which $\bar{\nu} x_e = 1.65 \text{ cm}^{-1}$.⁵⁴ Substitution of this in eq 4, together with $\mu = 19$ (the atomic mass of F), yields the estimate $C = 1.36 \text{ \AA}^{-1}$. Assuming that x_e remains approximately constant, as one goes from a complex of a tetravalent ion such as PtF_6^{2-} , where $\bar{\nu}(\epsilon_g) = 540 \text{ cm}^{-1}$, to one of a divalent metal ion, where $\bar{\nu}(\epsilon_g) \approx 250 \text{ cm}^{-1}$, the value of C should decrease to $\sim 0.9 \text{ \AA}^{-1}$.

Considerably more experimental data are available concerning the totally symmetric α_{1g} mode, and the way in which the force constant of this varies with distance provides a further way in which the anharmonicity constant may be estimated. Equation 8 is of the form $U = f'/2Q^2$, where $f' = f(1 - CQ)$, so that f' is in effect a force constant that varies as a function of Q ; thus, $C = (1 - f'/f)/Q$, where f' is the observed force constant following a displacement Q . Estimates of f'/f and Q for the ground and excited electronic states of a range of metal complexes are available from the analysis of the vibrational structure observed in electronic spectra,^{20,29} and substitution of the appropriate values in the above

(24) The Jahn–Teller stabilization of the split 1E_g state is in fact due to an off-diagonal matrix element coupling the ${}^1A_{1g}$ component of this level with the ${}^1A_{1g}$ state derived from the 1G free ion term. The relevant matrix elements are given in: Hitchman, M. A. *Inorg. Chem.* **1972**, *11*, 2387.

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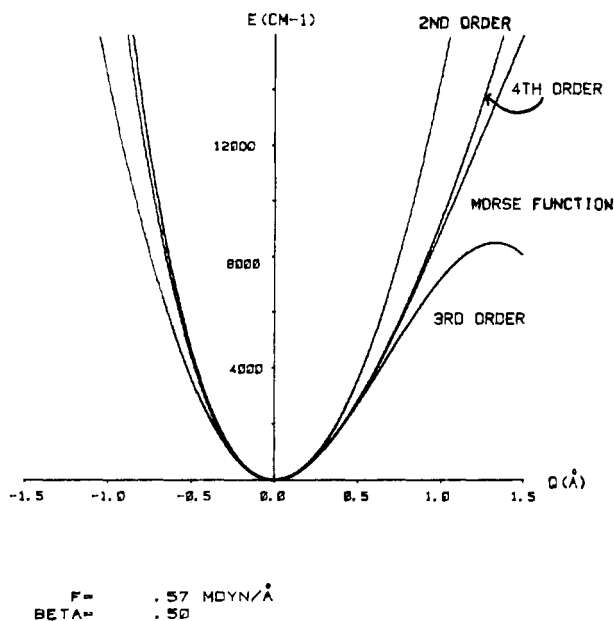


Figure 3. Comparison of vibrational potentials calculated to second, third, and fourth order with Morse function. See text for the definition of the mathematical expressions involved (eq 4-8).

equation yields the overall value $C = 1.0 \pm 0.4 \text{ \AA}^{-1}$. Since both are stretching vibrations, it is clear that the anharmonicity constant of the Q_θ component of the ϵ_g mode should have the same sign as that of the α_{1g} mode. However, the nature of the normal coordinate of the former vibration (Figure 1b) makes it likely that the magnitude of the anharmonicity constant could well be less than that of the corresponding α_{1g} mode. The general conclusion to be drawn from the above estimates is thus that C probably lies in the range $0.25\text{--}1.0 \text{ \AA}^{-1}$ for the ϵ_g vibration of an octahedral complex of a divalent metal, with a somewhat higher value for a similar complex of a trivalent metal.

It is of interest to see at what stage eq 8 deviates significantly from a Morse potential, and this may be seen for the values $f = 0.57 \text{ mdyN \AA}^{-1}$ and $C = 0.5 \text{ \AA}^{-1}$ typical of the ϵ_g mode of an octahedral complex of a divalent complex of a divalent metal ion in Figure 3. Under these circumstances truncation of the expansion of the Morse function at Q^3 is justified for $Q < \sim 0.5 \text{ \AA}$. However, for higher values of C it is necessary to include the fourth-order term in the expansion (eq 6) unless the range of Q to be investigated is quite small ($Q < \sim 0.25 \text{ \AA}$). It should also be stressed that all the above conclusions apply only to ML_6 isolated units; when coupling with the surrounding lattice is to be significant, this may drastically affect the anharmonicity of the vibrational potential (see General Conclusions).

Second-Order Corrections to the Electronic Potential and the Effect of d-s Mixing

Within the framework of the present model the term due to second-order electronic effects V_2 is obtained quite simply from the binomial expansion of the expression relating the d-orbital energies to bond distance (see Appendix). It should be noted that second-order terms occur which alter that the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals equally. These are not included in V_2 since in effect they are already taken into account in the force constant of the vibrational mode (they also contribute here for complexes having no electronic degeneracy in the e_g^* orbitals). The electronic contribution to the Jahn-Teller potential reflects the energy difference between the electronic states in which the odd electron (or electrons for the 1E_g state of d^8 systems) occupies the d_{z^2} or $d_{x^2-y^2}$ orbitals, measured as a function of the displacement in Q . As with the anharmonicity correction, V_2 is then zero for a displacement along the Q_e component of the ϵ_g mode. It may be noted that both the first- and second-order electronic contributions V and V_2 depend linearly on the σ -antibonding energy Δ' , typical values being $8200 \text{ cm}^{-1} \text{ \AA}^{-1}$ and $3400 \text{ cm}^{-1} \text{ \AA}^{-2}$, respectively, for

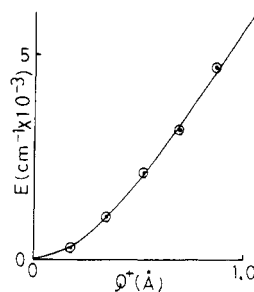


Figure 4. Polynomial curve $C_1Q + C_2Q^2 + C_3Q^3$ with $C_1 = 0.047 \times 10^3 \text{ cm}^{-1}$, $C_2 = 4.84 \times 10^3 \text{ cm}^{-1}$, and $C_3 = -2.04 \times 10^3 \text{ cm}^{-1}$ compared with calculated energies of depression of the d_{z^2} orbital for various positive displacements along the Q_θ normal mode. The energy depressions were estimated by using the method given in ref 32 and diatomic overlap integrals⁷ given by Smith.

$\Delta' = 12000 \text{ cm}^{-1}$ and $r_0 = 2.1 \text{ \AA}$. These values are quite similar to those estimated for CuCl_6^{4-} by Bacci¹³ using the angular-overlap approach ($V = 9540 \text{ cm}^{-1} \text{ \AA}^{-1}$, $V_2 = 3815 \text{ cm}^{-1} \text{ \AA}^{-2}$). This is to be expected, as it has been pointed out that the diatomic overlap integrals, upon which V and V_2 depend within the framework of the angular-overlap model, vary approximately as the fifth power of the bond distance,^{21,30} as assumed also in the present treatment.

Recent measurements of the electronic spectra and magnetic properties of planar, four-coordinate complexes have shown that the d_{z^2} orbital is $5000\text{--}10000 \text{ cm}^{-1}$ lower in energy than simple bonding theories would suggest.³¹⁻³⁴ It has been pointed out that the d_{z^2} orbital is effectively nonbonding in these complexes,³⁵ although just a simple consideration of the shapes of the d_{z^2} and $d_{x^2-y^2}$ orbitals requires that the former orbital is raised to one-third the energy of the latter by σ -interaction with the ligands. It has been suggested that the depression of the d_{z^2} orbital is probably due to configuration interaction with the empty metal s orbital, and this effect has been investigated quantitatively by Smith³⁶ using the angular-overlap model. The energy depression is then proportional to $\{[S_d(xy)][S_s(xy)] - [S_d(z)][S_s(z)]\}^2$, where $S_d(xy)$, $S_s(xy)$, etc. are the group overlaps between the metal d and s orbitals and the ligand orbitals situated along the axis (in parentheses). Several people have pointed out that as the interaction lowers the energy of the d_{z^2} orbital and since for a Jahn-Teller active complex this is occupied by more electrons for an axially elongated than for an axially compressed geometry (Figure 2), the effect of d - s mixing should be to stabilize a displacement toward the former stereochemistry.¹⁵⁻¹⁷ In order to quantify this, the overlaps $S_d(xy)$ etc. reported by Smith⁷ for Cl^- and Cu^+ were used to calculate the energy depression of d_{z^2} as a function of Q_θ (corresponding to $\phi = 0^\circ$ in Figure 1a) assuming an average Cu-Cl bond distance of 2.5 \AA . The resulting points were fitted to a polynomial of the form $C_1Q + C_2Q^2 + C_3Q^3$, the best fit (Figure 4) being obtained with the values $C_1 = 0.047 \times 10^3 \text{ cm}^{-1}$, $C_2 = 4.84 \times 10^3 \text{ cm}^{-1}$, and $C_3 = -2.04 \times 10^3 \text{ cm}^{-1}$ with Q measured in angstroms. To a good approximation this effect can therefore be represented by a general expression of the form $F_{ds} = k(C_2Q^2 + C_3Q^3)$, with the term Q^3 being significant only for values of $Q > \sim 0.3 \text{ \AA}$. Here the parameter k has been introduced to take into account the dependence of the d - s mixing on the strength of the metal-ligand interaction and the difference in the number of electrons between the two d orbitals m , being given the value $k = m\Delta' \times 10^{-4} \text{ cm}^{-1}$; i.e., $k = m$ for a complex with $\Delta' = 10000 \text{ cm}^{-1}$. The curve has been normalized to give agreement with the depression of $\sim 5000 \text{ cm}^{-1}$ deduced from the

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Table II. Jahn–Teller Parameters Estimated Including Second-Order Electronic Effects, d–s Mixing, and Anharmonic Corrections to the Vibrational Potential

complex	bond length changes, Å ^a				$E(d_{z^2} \rightarrow d_{x^2-y^2})$, cm ⁻¹		2β , cm ^{-1 b}
	calcd ^b		obsd ^b		calcd ^b	obsd ^b	
	δ_x	$-2\delta_z$	δ_x	$-2\delta_z$			
Cu(H ₂ O) ₆ ²⁺	0.13	0.26	0.11	0.23	7572	7500	671
Cu(C ₅ H ₅ NO) ₆ ²⁺	0.13	0.26	0.12	0.23	7608	6050	672
						7400	
Cu(NO ₂) ₆ ⁴⁻	0.11	0.22	0.09	0.18	6717	7200	587
Cu(tach) ₂ ^{2+ c}	0.10	0.21	0.10	0.19	5857	8800	498
Ni(diamine) ₃ ²⁺ (¹ E _g)	0.20	0.40	~0.18	<i>d</i>	19670	~25000	1600
Cr(NH ₃) ₆ ³⁺ (⁴ T _{2g})	0.07	0.13	0.05	0.09	7165		499
PtF ₆ ²⁻ (³ T _{1g})	0.06	0.12	0.05	0.11	13342	14900	741

^aIn each case the calculated bond length changes are such that the in-plane ligands (*x*) move closer to the metal. The observed changes follow this pattern except for the excited states of Cr(NH₃)₆³⁺ and PtF₆²⁻, where it is thought that interelectron repulsion stabilizes a compressed-tetragonal geometry.^{52,53} ^bCalculated by using eq 9 with anharmonicity, second-order electronic, and d–s mixing parameters defined as in the text and input data as listed in Table I. An anharmonicity parameter of $C = 0.5$ was used, the vibrational potential being carried to third order in every case except Ni(diamine)₃²⁺, for which it was found necessary to include the fourth-order correction (eq 6). See Table I for references to observed parameters. ^ctach = *cis,cis*-1,3,5-triaminocyclohexane. ^dAxial ligands are often absent in low-spin nickel(II) complexes; when present, the axial bonds are always very long.⁵¹

Table III. Effect of Varying the Higher Order Corrections on the Jahn–Teller Parameters of Cu(NO₂)₆⁴⁻

<i>C</i>	higher order correction parameters ^a			calcd Jahn–Teller parameters ^b			
	V_2 , cm ⁻¹	C_2 , cm ⁻¹	C_3 , cm ⁻¹	δ_x , Å ^c	$-2\delta_z$, Å ^c	$E(d_{z^2} \rightarrow d_{x^2-y^2})$, cm ⁻¹	2β , cm ^{-1 c}
0.25	3186	5808	-2447	0.09	0.19	5290	390
0.5	3186	5808	-2447	0.10	0.21	6200	550
1.0	3186	5808	-2447	0.14	0.29	8750	1000
0.5	0.0	0.0	0.0	0.09	0.18	4980	260
0.0	3186	0.0	0.0	0.06	0.12	-3030	-400
0.0	0.0	5808	-2447	0.10	0.20	6690	680

^aSee text for definition of parameters. ^bCalculated by using eq 9 plus the fourth-order correction to the vibrational potential defined as in eq 6. ^cA positive value of 2β indicates that the elongated-tetragonal geometry is more stable than the compressed-tetragonal geometry. In this case, the in-plane ligands (*x*) are displaced inward and the axial ligands (*z*) outward; when 2β is negative, these displacements are reversed.

electronic spectrum of planar, four-coordinate CuCl₄²⁻.³¹ Overlap parameters were also calculated by using Cu–N overlap integrals assuming an average bond length of 2.2 Å, and very similar values were obtained for the constants C_1 , C_2 , and C_3 . As with the second-order electronic effect, only the contribution directly relevant to the Jahn–Teller problem has been taken into account in the present model. That is, only effects due to the inequivalent occupancy of the d_{z^2} and $d_{x^2-y^2}$ orbitals have been included, it being assumed that other effects, which would also occur, for instance, in corresponding octahedral Ni(II) and Zn(II) complexes, are included in the vibrational force constants. However, it is interesting to note that since d–s mixing depresses only the d_{z^2} orbital in energy, it will tend to destabilize a regular octahedral geometry in favor of a tetragonally symmetric one even for ions with orbitally nondegenerate ground states. Pseudo-Jahn–Teller distortions of this kind have recently been discussed in detail by Bersuker.³ While d–s mixing is expected to be small for metal ions such as Ni²⁺ and Zn²⁺ and will simply cause a slight decrease in the force constant of the Q_θ component of the ϵ_g mode, it will increase dramatically when the metal *s* orbital approaches the filled d_{z^2} orbital in energy and is presumably an important factor contributing to the tetragonally compressed geometries often observed for Cu(I) and Hg(II) complexes.

Calculation of Jahn–Teller Distortion Parameters

It has been shown that after the second-order electronic term V_2 and the anharmonic correction C are included, the potential energies of the two electron states derived from the ²E_g level of an octahedral copper(II) complex are given by the expression⁵⁵

$$U(\pm) = U_0 \pm VQ \left(1 + \frac{V_2^2 Q^2}{V^2} - \frac{2V_2 Q \cos 3\phi}{V} \right)^{1/2} + \frac{F}{2} Q^2 - C_f Q^3 \cos 3\phi \pm F_{ds} \cos 3\phi \quad (9)$$

Here, the effect of the d–s mixing, parametrized by F_{ds} as described above, has been added to the normal equation. The energies of the potential surfaces now depend upon the composition of the

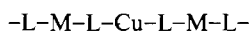
Jahn–Teller vibrational mode, as specified by the angle ϕ (Figure 1a), and the dependence is such that the energy of each surface will be maximized or minimized when the nuclear displacement is just along the Q_θ component, i.e., at $Q = 0$ or 180° (with corresponding symmetry-related inflections at 120° etc.). The Jahn–Teller surfaces of a copper(II) complex may therefore be estimated by calculating the variation of $U(\pm)$ as a function of Q for $\phi = 0$ and 180° , this corresponding to a section through the Mexican hat (Figure 1a). Substitution of the various correction factors estimated as discussed above leads to the calculated Jahn–Teller displacements indicated in Table II. The Jahn–Teller stabilization energy, energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition, and energy barrier 2β to the interconversion of *z*, *x*, and *y* as the symmetry axis are also shown in the table. A plot of the potential surface as a function of Q_θ is shown in Figure 5 with use of parameters appropriate to the Cu(H₂O)₆²⁺ ion, both with and without the various higher order corrections. It must be emphasized that the uncertainties in the higher order parameters are high, so that the calculations should be considered in general terms only, with little emphasis being placed on the numerical values of the results. To gain an idea of the sensitivity of the model to the input parameters, the calculations were performed for a range of anharmonicity constants, and the results for Cu(NO₂)₆⁴⁻ are shown in Table III, the individual effects of each of the higher order corrections also being indicated in the table. The effects of varying Δ' and f by 10% were also tested, and in each case this caused changes of 10–20% in δx and $E(d_{z^2} \rightarrow d_{x^2-y^2})$ and 20–30% in 2β .

General Conclusions

As expected, the most obvious result of the addition of the various second-order terms is to “warp” the Jahn–Teller potential surface, and in agreement with experimental observation the model predicts for all reasonable sets of input parameters that the sense of the warping is to stabilize an elongated-tetragonal geometry. The estimated energy barrier to the interconversion of the symmetry axis between the three Cartesian coordinates is a few

hundred wavenumbers, again in agreement with what limited experimental data are available.²⁷ It would appear that the basic reason an elongated- rather than a compressed-tetragonal geometry is preferred is because the three higher order contributions are comparable in magnitude, and two of these, the anharmonicity correction and the d-s mixing, tend to favor an outward displacement of the axial ligands (Table III). It is also apparent that the net effect of the higher order corrections is to produce a significant expansion in the equilibrium displacement of the Jahn-Teller normal coordinate compared with the predictions of the simple model, bringing the estimated geometries and calculated $d_{z^2} \rightarrow d_{x^2-y^2}$ transition energies for the copper(II) complexes into better agreement with experimental observations (Tables I and II).

Sensitivity of the Jahn-Teller Potential Surface to the Anharmonicity of the Vibrational Potential. For any particular metal ion the relative contributions of the second-order electronic and d-s mixing parameters to the Jahn-Teller potential surface are likely to remain approximately constant and independent of the environment of the complex. The same is not true of the anharmonicity correction to the vibrational potential. In this respect the present model is only really applicable to an isolated octahedral complex in which the coupling of the metal-ligand vibrations to the lattice is negligible. This should be a good approximation for Cu^{2+} in aqueous solution and a fair approximation for solid complexes containing species such as $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ or $\text{Cu}(\text{NO}_2)_6^{4-}$ but is clearly quite inappropriate to deal, for instance, with copper(II) ions doped into a continuous host lattice. When it is remembered that the physical cause of the anharmonicity correction is normally taken to be the fact that the total potential energy increases less steeply when a bond is stretched than when it is compressed, it would seem that when copper(II) is substituted into a continuous lattice of similar metal ions the anharmonicity correction should be rather small. This may be seen from the schematic diagram below, showing just one dimension of a continuous octahedral lattice. An elongation or shortening of the Cu-L bonds



causes an exactly equivalent effect, though opposite in sign, in the neighboring M-L bonds. In such a situation, therefore, the anharmonicity correction should have a rather small effect on the warping of the Jahn-Teller potential surface. If Cu^{2+} substitutes in a continuous lattice for a metal ion considerably larger than itself, the anharmonicity factor should have the same sign as that in an isolated complex, but substitution for a significantly smaller metal ion should produce an anharmonicity correction *opposite* in sign to that of an octahedral complex weakly coupled to the lattice. That is, in the latter situation the anharmonicity correction should actually tend to favor a compressed- rather than an elongated-tetragonal geometry. In general terms these predictions are in agreement with the fact that in solids containing isolated six-coordinate copper(II) complexes with oxygen donor ligands such as $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ²⁷ and $\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6^{2+}$ ⁴⁵ the warping energy 2β is quite high, whereas for Cu^{2+} doped into the continuous host lattices CaO and MgO a low warping barrier is apparently present. For the former complexes the EPR spectra show that exchange between the complexes localized in the three potential minima becomes slower than the EPR time scale upon cooling to temperatures below ~ 20 – 100 K, while for copper-doped MgO "tunneling" between the minima is sufficiently rapid to average the EPR spectra even at 1.2 K.^{37,38} However, it should be noted that while a detailed analysis of the spectra suggests that for Cu^{2+} in MgO very little warping of the potential surface occurs,³⁸ it is probable that for Cu^{2+} in CaO the surface is slightly warped to give minima at $\phi = 60, 180, \text{ and } 300^\circ$, corresponding to *compressed-tetragonal* ligand geometries, this trend being the opposite

of that suggested by the above arguments. For Ag^{2+} doped into SrO, CaO, and MgO, on the other hand, the EPR spectra suggest that in each case a tetragonally elongated geometry is most stable, with the warping being significant in SrO, intermediate in strength in CaO, and small in MgO, in agreement with the present model.³⁹ In this context it would be of interest to investigate the warping of the potential surface of Cu^{2+} doped into SrO.

Geometries of Low-Spin Complexes of d^8 Metal Ions. As discussed already, the $^1A_{1g}$ ground state of a diamagnetic complex of a metal ion with a d^8 electron configuration may be considered to be derived from the Jahn-Teller active 1E_g excited electronic state of the parent octahedral complex by distortion along the Q_6 normal mode. To first order, the ligand displacements are predicted to be twice those in the analogous complex of a d^9 metal ion, and this conclusion remains essentially unaltered by the inclusion of higher order terms. Comparison with experiment is difficult as virtually all nickel(II) complexes with monodentate ligands are high spin (cyanide forms four- and five-coordinate diamagnetic complexes with nickel(II) but the high covalency of these makes the application of the present model dubious). Inspection of the structural data available for complexes of the type $\text{Ni}(\text{diamine})_3^{2+}$ and $\text{Ni}(\text{diamine})_2\text{X}_2$, where the former are paramagnetic and the latter are sometimes diamagnetic, shows that the high-spin \rightarrow low-spin conversion is accompanied by a shortening of the in-plane Ni-N bond by ~ 0.16 – 0.20 Å.^{41,50,51} In reasonable agreement with the theoretical predictions. The model also predicts that the axial bonds should lengthen by ~ 0.4 Å, to ~ 2.5 Å for nickel(II) bonded to N, but in fact the axial bonds are always substantially longer than this (e.g. 2.8 Å in a diamagnetic Ni(II) macrocycle with coordinated perchlorate groups⁴⁰) and low-spin nickel(II) complexes are generally truly four-coordinate. Presumably, this is because the bond energy associated with the distant axial ligands axial ligands is usually insufficient to compensate for the lowering in energy from entropy factors and increased d-s configuration interaction that accompanies their loss. However, consideration of the geometry of low-spin d^8 complexes within the framework of the Jahn-Teller theorem does provide a simple explanation for the structural differences between these and corresponding d^9 complexes.

The stabilization of the $^1A_{1g}$ state compared with the parent 1E_g state is $2E_{JT}$, this being estimated as $\sim 11\,000$ cm^{-1} for the model complex involving six nitrogen donor atoms considered in the present calculations. The complex is predicted to be low spin if $2E_{JT}$ is greater than the spin pairing energy, which in the present case is simply the energy of the 1E_g excited state. Since $^1E_g \leftarrow ^3A_{2g} \approx 13\,000$ cm^{-1} for typical octahedral amine complexes of nickel(II),⁴² the high-spin state is expected to be slightly more stable than the low-spin state, in agreement with observation. Since E_{JT} largely depends on the ratio Δ/f , the low-spin state is favored for ligands producing a strong σ -antibonding interaction Δ' and the complex $\text{Ni}(\text{NO}_2)_6^{4-}$, for which the octahedral ligand field splitting $\approx 13\,000$ cm^{-1} ⁴³ could well lie close to the high-spin-low-spin crossover point (though it should be noted that E_{JT} depends only on the ligand σ -interaction, so that if the nitro groups in $\text{Ni}(\text{NO}_2)_6^{4-}$ act as π -acceptors, E_{JT} in this complex might be quite similar to that in a corresponding amine complex).

It might also sometimes prove fruitful to consider the reaction kinetics of low-spin d^8 complexes in terms of a Jahn-Teller potential surface, particularly when these are relatively ionic. For instance, in aqueous solution the coordination sphere of hydrated Pt^{2+} and Pd^{2+} ions is presumably a tetragonally elongated array of water molecules. Ligand exchange between the axial and in-plane ligands might then occur via the e_g Jahn-Teller active mode, with the rate-determining step being the overcoming of the

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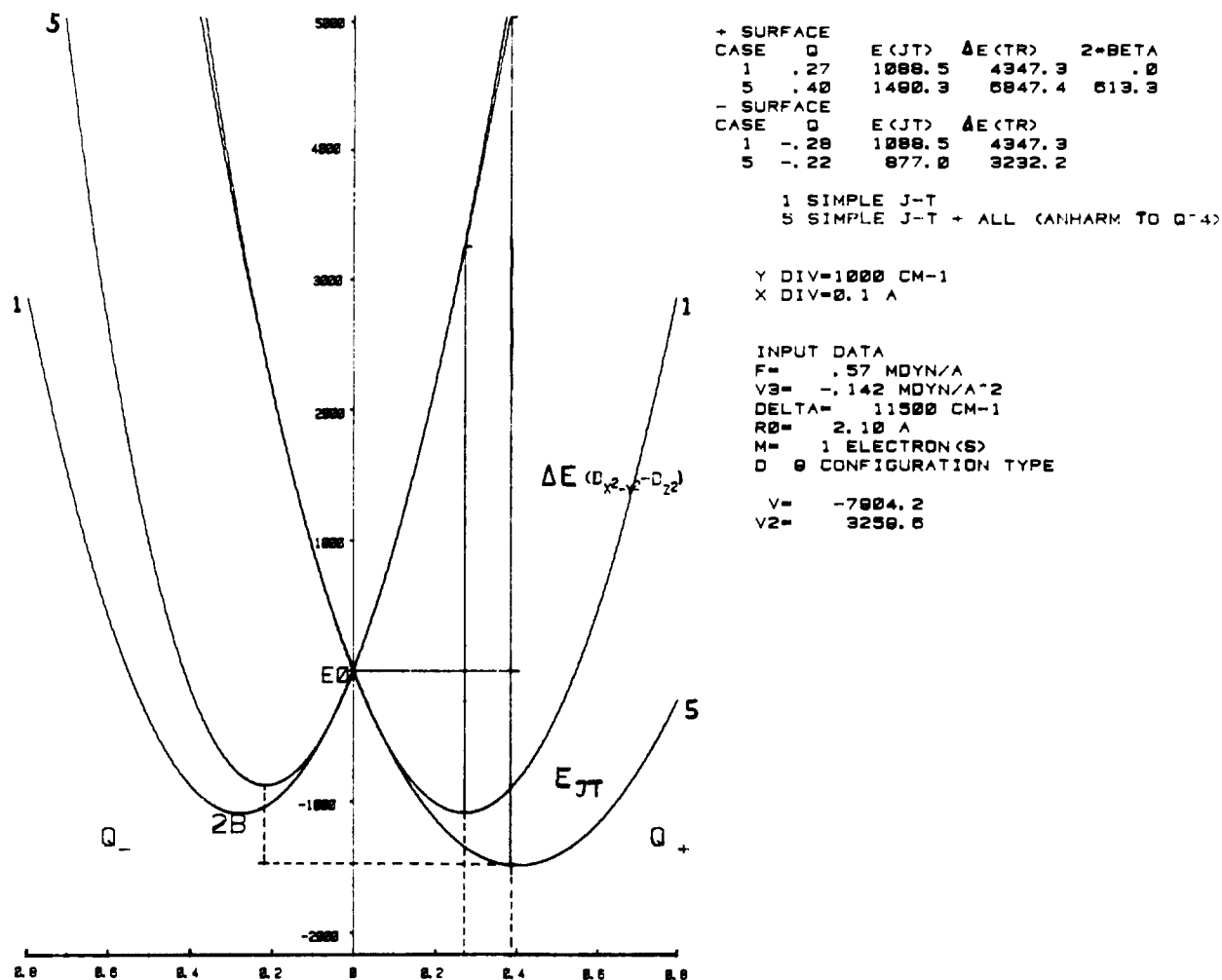


Figure 5. Jahn-Teller potential surfaces estimated for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ for radial displacements corresponding to $\phi = 0^\circ$ (Q_+) and $\phi = 180^\circ$ (Q_-) assuming simple harmonic motion and first-order electronic effects (1) and including anharmonic corrections to fourth order, second-order electronic effects, and d-s mixing (5).

warping barrier of the potential surface. It may be noted that the symmetry of this vibration requires that exchange should occur simultaneously for trans ligands, so that if ligand exchange does occur via this mechanism, when $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ is dissolved in isotopically labeled water (H_2O^*) the only significant intermediate in the replacement reaction should be *trans*- $\text{Pt}(\text{H}_2\text{O})_2(\text{H}_2\text{O}^*)_2^{2+}$.

Summary

A simple expression is derived for the linear electronic coupling constant of the $E \times \epsilon$ Jahn-Teller interaction, and this suggests distortions somewhat lower than those observed experimentally for a range of copper(II) complexes. The various factors that have been proposed as the likely cause of the fact that in the absence of lattice effects six-coordinate copper(II) complexes invariably adopt an elongated-tetragonal geometry, namely, second-order electronic effects, anharmonicity of the ϵ_g vibration, and configuration interaction between the d_{z^2} and $4s$ metal orbitals, have been investigated and found to be comparable in magnitude. It is pointed out that each of these corrections acts only on the Q_θ component of the ϵ_g mode and that the second-order electronic and anharmonicity corrections both depend upon the fact that the Q_θ component involves unequal ligand displacements, while for the Q_ϵ component the ligands move equal distances. Moreover, the underlying cause of the anharmonicity and the dependence of the d-orbital energies upon bond distance require that the former correction stabilize an elongated, and the latter a compressed, tetragonal geometry. The d-s mixing favors an outward displacement of the axial ligands, and calculations including all three corrections yield estimates of the geometries, $d_{z^2} \rightarrow d_{z^2-x^2}$ transition energies, and energy barriers to the fluxional interconversion of the symmetry axis between x , y , and z in reasonable agreement

with experiment. It is suggested that while the electronic and d-s mixing parameters are likely to vary little from one complex to another, the anharmonicity correction may be quite sensitive to the surroundings of a complex. In particular, the latter may be much reduced for Cu^{2+} doped into a continuous lattice, with a corresponding reduction in the "warping" of the brim of the Mexican hat potential surface.

It is pointed out that the geometries observed for low-spin d^8 complexes may be considered to be derived from the distortion of the Jahn-Teller active 1E_g excited state of the parent octahedral complex. The ligand displacements should then be approximately twice those observed in an analogous d^9 complex. This agrees with experiment as far as the in-plane ligands go, though in the case of the axial ligands, these are normally displaced to such an extent that they are lost from the coordination sphere in low-spin complexes of d^8 metal ions.

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Appendix: Derivation of the Electronic Contribution to the Potential

To first order, the Q_θ and Q_ϵ components of the ϵ_g mode have the same effect on the d orbitals, giving the Mexican hat potential surface shown in Figure 1a. To second order, the rim of the Mexican hat is "warped" to give energy minima and saddle points at angles ϕ corresponding to displacements in the Q_θ component alone. For this reason, and because the structures observed ex-

perimentally correspond to such displacements, the calculations of the coupling constants V and V_2 were carried out for displacements in the Q_θ component. The metal-ligand matrix elements specifying the relative effects of the various ligands in a complex distorted along both components of the ϵ_g mode are given in ref 44.

In the procedure given in ref 20 it is assumed that the σ -antibonding energy of a d-orbital Δ' varies inversely as the n th power of the bond distance. For a displacement Q along the Q_θ component of the ϵ_g mode (Figure 1b) at angle $\phi = 0^\circ$ (a tetragonal elongation) the energies of the $d_{x^2-y^2}$ and d_{z^2} orbitals are given by

$$E(d_{z^2}) = \frac{2}{3}\Delta' \left(1 + \frac{2CQ}{r_0}\right)^{-n} + \frac{1}{3}\Delta' \left(1 - \frac{CQ}{r_0}\right)^{-n} \quad (\text{A1a})$$

$$E(d_{x^2-y^2}) = \Delta' \left(1 - \frac{CQ}{r_0}\right)^{-n} \quad (\text{A1b})$$

where $C = 1/12^{1/2}$ is the appropriate normalization constant (see eq 1a of text). Expanding to second order gives

$$E(d_{z^2}) = \Delta' \left(1 - \frac{nCQ}{r_0} + \frac{3n(n+1)C^2Q^2}{2r_0^2}\right) \quad (\text{A2a})$$

$$E(d_{x^2-y^2}) = \Delta' \left(1 + \frac{nCQ}{r_0} + \frac{n(n+1)C^2Q^2}{2r_0^2}\right) \quad (\text{A2b})$$

The terms relevant to the Jahn-Teller distortion of the complex are those that discriminate in energy between $d_{x^2-y^2}$ and d_{z^2} ; the term in Q^2 affecting the baricenter of d_{z^2} and $d_{x^2-y^2}$ is effectively included in the force constant, since for the copper(II) complex this is estimated as the average of the corresponding nickel(II) and zinc(II) complexes. If the difference in the number of electrons between the two orbitals is m , the electronic contribution to the potential is

$$m[E(d_{z^2}) - E(d_{x^2-y^2})]/2 = \frac{-nm\Delta'Q}{12^{1/2}r_0} + \frac{m\Delta'n(n+1)Q^2}{24r_0^2} \quad (\text{A3})$$

A reversal in the electronic occupancy of the two orbitals simply reverses the sign of both contributions, and since it is conventional to define the first- and second-order electronic contributions V and V_2 in absolute terms, this yields the relationships

$$V = \frac{nm\Delta'}{12^{1/2}r_0} \quad V_2 = \frac{m\Delta'n(n+1)}{24r_0^2}$$

Registry No. Cu(H₂O)₆²⁺, 14946-74-8; Cu(C₅H₅NO)₆²⁺, 47839-68-9; Cu(NO₂)₆⁴⁻, 28111-94-6; Cu(tach)₂²⁺, 46934-10-5; Ni(diamine)₃²⁺, 15276-13-8; Cr(NH₃)₆³⁺, 14695-96-6; PtF₆²⁻, 16871-53-7.

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Kinetics and Mechanism of Chloride and Bromide Substitution of Diaquonickel(III) Macrocyclic Complexes

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The complex cations $[\text{NiM}_m(\text{OH}_2)_2]^{3+}$ ($M_m = [\alpha\text{-}C\text{-meso-}5,12\text{-dimethylcyclam}]$, $[\text{NiM}_r(\text{OH}_2)_2]^{3+}$ ($M_r = C\text{-rac-}5,12\text{-dimethylcyclam}$), and $[\text{NiE}_m(\text{OH}_2)_2]^{3+}$ ($E_m = C\text{-meso-}5,12\text{-diethylcyclam}$) (cyclam = 1,4,8,11-tetraazacyclotetradecane) react with Cl^- and Br^- in aqueous perchloric acid according to the equation $\text{NiL}(\text{OH}_2)_2^{3+} + \text{X}^- \rightleftharpoons \text{NiLX}(\text{OH}_2)_2^{2+}$ ($K = k_1/k_{-1}$). Stopped-flow studies provide details of forward and reverse rate constants: at 25 °C k_1 for the reaction of $[\text{NiM}_m]^{3+}$ with Cl^- is $2180 \pm 66 \text{ M}^{-1} \text{ s}^{-1}$ and for that with Br^- is $889 \pm 31 \text{ M}^{-1} \text{ s}^{-1}$; at 25 °C k_1 for the reaction of $[\text{NiE}_m]^{3+}$ with Cl^- is $(3.1 \pm 0.4) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and with Br^- is $(2.8 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$; at 13.4 °C, k_1 for the reaction of $[\text{NiM}_r]^{3+}$ with Cl^- is $(1.4 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The data are consistent with a dissociative mechanism, the effect of axial steric groups in the M_r ligand causing an increase in the rate. A second ligand and metal ion independent reaction has also been identified, which is postulated as a reorganization of the octahedral ions to more stable pentacoordinate complexes. ESR evidence is presented consistent with a more distorted geometry for the monochloro complex ions.

Although there has been considerable recent interest in the redox reactions of nickel(III) complexes,¹⁻⁴ there is still a dearth of information on the substitution reactions at these centers.⁵⁻⁷

Such studies are of interest, in that, whereas cobalt(III) complexes appear to react via dissociative-interchange^{8,9} mechanisms, many other trivalent metal ions show some associative character on

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