Correspondence

Totally Symmetric Metal–Nitrogen Stretching Vibrations of Ethylenediamine Chelate Complexes

AIC40710S

Sir:

There have been a large number of investigations of the vibrational spectra of bis- and tris(ethylenediamine) coordination complexes.[1–5] The more recent studies agree over the assignments of many of the important vibrational frequencies. In particular three investigations of the Raman spectra[3–5] of $M(en)_3{}^{n+}$ compounds assign the strong polarized metal-sensitive band at 450–600 cm^{-1} to a totally symmetric mode involving chiefly metal–nitrogen stretching motion and the polarized band at 280–320 cm^{-1} to a totally symmetric nitrogen–metal–nitrogen bending mode. The purpose of this correspondence is to point out that two studies of electronic spectra suggest that, in cobalt(III) and chromium(III) complexes, the vibration responsible for the 280–320-cm^{-1} band has at least as much metal–nitrogen stretching character as that for the 450–600-cm^{-1} band.

An X-ray crystal structure determination[6] of *d,l*-$2(Co(en)_3Cl_3)\cdot NaCl\cdot 6H_2O$ shows that the complex ion occupies a site of C_3 symmetry (excluding the hydrogens). If the puckering of the ethylenediamine rings is neglected, the point group symmetry of the ion is D_3. In D_3 symmetry the metal–nitrogen stretching coordinates form bases for $A_1 + A_2 + 2\,E$ representations, the nitrogen–metal–nitrogen bending coordinates form bases for $A_1 + A_2 + 2\,E$ representations, and the ring stretching and bending modes form bases for $4\,A_1 + 3\,A_2 + 7\,E$ representations. Although none of the normal coordinates can involve just one of these symmetry coordinates, it seems natural to assign the metal-sensitive vibrations by comparison with the corresponding hexaammine complexes where the M–N stretching modes occur in the 400–600-cm^{-1} range and N–M–N bending modes in the 200–300-cm^{-1} range[1] and previous assignments have used this analogy.

The electric dipole transition moment for a d–d transition $0 \rightarrow 0' + m\nu_u + n\nu_g$ (where ν_u and ν_g are ungerade and gerade normal modes, respectively) in a centrosymmetric metal complex is proportional to[7] $E^{(m)}{}_{0-0'}\langle 0|Q^m|m\nu_u\rangle\langle 0|n\nu_g\rangle$ where Q is the normal coordinate corresponding to ν_u and $E^{(m)}{}_{0-0'}$ is an electronic factor which decreases rapidly with increasing m. The first integral is very small unless $m = 1$. If the potential surfaces in states 0 and 0' are very similar, the second integral is very small unless $n = 0$.[7] A displacement of the potential surface of one electronic state with respect to the other along the coordinate corresponding to ν_g gives intensity to transitions with $n \geq 1$. Thus, if the equilibrium symmetry of both electronic states is the same, only totally symmetric vibrational modes can form progressions in the electronic spectrum.[7] The intensity of these progressions is given by[8]

$$I_n = [{}^1/_2\beta(\delta r)^2]^n I_0/n$$

where $\beta = 4\pi^2\nu_g cM/h$, δr is the change in the coordinate corresponding to ν_g, and M is the mass of the ligand (assumed monoatomic).

The formal u–g distinction disappears in a noncentrosymmetric complex, but since the perturbation of the atomic d orbitals is small, there is no essential change in the above argument except that the $m = 0$ transitions may acquire significant (or predominant) intensity.

Ballhausen and Dingle[9] have measured the ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ electronic absorption of a single crystal of *d,l*-$2(Co(en)_3Cl_3)\cdot NaCl\cdot 6H_2O$ at 4 K. The spectrum consists of an electronic origin plus three vibronic origins (i.e., transitions of the type $0 \rightarrow 0' + \nu_u$) each with up to four members of a progression in a totally symmetric vibration of 255 cm^{-1} based on them. Further members of these progressions and the other electronic origin are obscured by band broadening. The ${}^1A_{1g}$ and ${}^1T_{1g}$ states are derived almost exclusively from the $t_{2g}{}^6$ and $t_{2g}{}^5e_g$ configurations, respectively. The e_g orbitals are σ antibonding so that the Co–N bond lengths will be larger in the ${}^1T_{1g}$ state than in the ${}^1A_{1g}$ state and the force constants will be smaller. There will be changes in the magnitude of other totally symmetric symmetry coordinates but these are expected to be smaller since the N–Co–N angles and the ethylenediamine bond distances and angles are not *directly* affected. In the ${}^1T_{1g}$ state the molecule will therefore be displaced along those totally symmetric coordinates which involve a substantial contribution from the Co–N stretching symmetry coordinate relative to the ${}^1A_{1g}$ state. The ${}^1A_{1g} \rightarrow {}^1T_{1g}$ electronic spectrum shows that the potential surfaces of ${}^1A_{1g}$ and ${}^1T_{1g}$ states are displaced substantially along a normal coordinate corresponding to a normal mode of 255 cm^{-1} but no other displacements along totally symmetric coordinates were detected. We conclude that this 255-cm^{-1} mode in the ${}^1T_{1g}$ state has a greater Co–N stretching character than any other normal mode. The ground-state vibrational frequency corresponding to this mode occurs in the Raman spectrum[4] at 283 cm^{-1}. No progressions were observed in a mode corresponding to the 527-cm^{-1} ground-state vibration assigned previously[4] as the totally symmetric Co–N stretch. The three vibronic origins in the electronic spectrum involve vibrational frequencies of 185, 345, and ca. 400 cm^{-1} which are readily correlated with the 190-, 368-, and 438-cm^{-1} ground-state vibrational frequencies. For a vibronic origin to have high intensity it must involve substantial N–Co–N bending, C–N stretching, C–N–C bending, or C–N–H bending character so that the appreciable frequency shifts between the two states are expected. The corresponding vibrational modes that act as strong vibronic origins in the ${}^4A_{2g} \rightarrow {}^2E_g(O_h)$ absorption spectrum[10] of $2(Cr(en)_3Cl_3)\cdot KCl\cdot 6H_2O$ have wave numbers of 177, 335, and 406 cm^{-1}.

A possible objection to the above argument is that the ${}^1T_{1g}$ state of the $Co(en)_3{}^{3+}$ ion could be subject to a violent pseudo-Jahn–Teller effect involving interaction with the τ_{2g} modes and the progressions merely reflect the resultant distortion. If such a distortion is present, then it is surprising that the progression-forming mode and the vibronic origins are each 3–10% lower than in the ground state. Moreover the simplicity of the vibronic spectrum and the similarity of the positions and intensities of the vibronic origins to those in the ${}^4A_{2g} \rightarrow {}^2E_g$ absorption spectrum of the $Cr(en)_3{}^{3+}$ ion make such a distortion unlikely. If the vibronic interaction along the τ_{2g} coordinate is not *very* strong, then progressions in totally symmetric Co–N stretching modes should still be observed.

The second indication of the substantial metal–nitrogen stretching character in the 200–300-cm^{-1} mode comes from the luminescence spectrum[11] of the *trans*-$Cr(en)_2F_2{}^+$ ion. The ${}^4B_{1g}(D_{4h})$ ground state of this ion has an almost spherically symmetric d-electron distribution but in the ${}^2E_g(D_{4h})$ lowest excited state the tetragonal component of the crystal field results in a transfer of π-electron density from the *xz* and *yz* orbitals into the *xy* orbital.[11] In the ${}^2E_g$ state, therefore, the

Cr–F distance is shortened relative to the ground state and this results in a lengthening of the Cr–N bond length because of the reduction in the effective charge on the chromium. The $^2E_g \rightarrow {}^4B_{1g}$ luminescence spectrum of *trans*-[Cr(en)$_2$F$_2$]X (X = I, ClO$_4$) shows progressions in totally symmetric modes of 512 and 230 cm^{-1} both of which occur strongly in the Raman spectrum. Comparison of the vibrational spectra of these compounds with those of *trans*-Cr(en)$_2$X$_2$$^+$ (X = Cl, Br, I) and *trans*-Cr(py)$_4$F$_2$$^+$ shows that the 512-cm^{-1} band is essentially the α_{1g} Cr–F stretch so that the 230-cm^{-1} mode must involve substantial α_{1g} Cr–N stretching character. Progressions involving other Raman-active modes in the range 450–600 cm^{-1} were not detected.

These studies indicate that the totally symmetric modes in the range 280–320 cm^{-1} in tris(ethylenediamine) complexes and at somewhat lower frequency in D_{4h} bis(ethylenediamine) complexes have substantial metal–nitrogen stretching character. They do not show that the totally symmetric modes in the range 450–600 cm^{-1} do not involve a contribution from metal–nitrogen stretching character; indeed it would be difficult to explain the systematic variation of the frequency of these modes as the metal is changed[4,5] without invoking some metal–ligand stretching character. In both studies progressions in a totally symmetric mode of ca. 500 cm^{-1} would not have been detected if they were appreciably weaker than the observed progressions. It does seem probable however that the totally symmetric mode in the 220–320-cm^{-1} region of ethylenediamine complexes has at least as much contribution from the metal–nitrogen stretching coordinate as the 450–600-cm^{-1} mode. We attribute the difference between the hexaammine and tris(ethylenediamine) complexes in part to the greater mass of the ethylenediamine ligand but chiefly to strong coupling between the Co–N modes and the internal ethylenediamine modes which occur in the same spectral region.

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Registry No. Ethylenediamine, 107-15-3; cobalt, 7440-48-4; chromium, 7440-47-3.

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Twist Angle Calculations: Fact or Fantasy?

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Sir:

Descriptions of molecular structures are frequently given in terms of an idealized geometry. For example, in coordination chemistry a metal ion surrounded by six ligands is usually considered in terms of distortions from either an octahedral or trigonal-prismatic configuration. For bis(cyclopentadienyl)metal complexes, the relative orientation of the two five-membered rings is discussed in terms of the idealized "staggered" or "eclipsed" arrangements. In both these and many other cases, the deceptively simple problem arises of calculating the relative orientation of two approximately parallel plane faces. A variety of different methods have been used to calculate the so-called twist angle which, of course, ideally would be equivalent. However, in practice the value of the twist angle depends to a very large extent on the method of calculation. Since the difficulties involved in the twist angle calculation have not been presented nor apparently appreciated, we present the following discussion of this problem.

The calculation of the twist angle, ϕ, in octahedral complexes has been given in terms of the nonbonded contacts, s, the ligand bite, b, the metal ligand distances, a, and the distance between the two equilateral triangles, h.[1] However, the twist angle calculated by this method[1] is valid only if the two threefold faces are parallel, the metal atom lies on the line joining the centroids of the two faces, the three ligand bites are all equal, the six metal–ligand distances are all equal, and the nonbonded contacts are equal. Obviously, for the majority of octahedral complexes, one or more of these conditions will not hold, and then the twist angle will depend upon the choice of parameters used in the calculation. Problems with the idealized method have been discussed recently[2] with respect to the compression ratio for the two limiting cases. However, the effects of the deviations from ideality on the twist angle have not been considered.

The difficulties involved in calculating the twist angle between two n-fold faces can be appreciated by a consideration of the possibilities illustrated in Figure 1. In the general case we have two n-fold faces, face 1 and face 2, the centroids of which are C and C′. The faces need not be parallel but are inclined by an angle ω relative to each other. If a metal atom M is encompassed by the two faces, then the metal atom can be displaced by a distance Δ from the line defined by the two centroids C and C′. The twist angle ϕ_i can be calculated by a variety of methods and we shall define $\phi_i{}^n$ as the ith angle obtained from the nth method. We have considered the following six methods for computing: (1) the acute angle between the plane defined by L$_i$, C, and C′ and the plane defined by L′$_i$, C, C′; (2) the angle between the projection of the metal–ligand vectors M–L$_i$ and M–L′$_i$ on face 1; (3) the angle between the projection of the metal–ligand vectors M–L$_i$ and M–L′$_i$ on face 2; (4) the angle between the projection of the metal–ligand vectors M–L$_i$ and M–L′$_i$ on a plane orthogonal to the line defined by the two centroids; (5) the angle between the metal–ligand vectors M–L$_i$ and M–L′$_i$ projected on a plane normal to the line defined by M–C; (6) the angle between the metal–ligand vectors M–L$_i$ and M–L′$_i$ projected on a plane normal to the line defined by M–C′. Since the problem of calculating twist angles is not limited to octahedral complexes, we have calculated the angles $\phi_i{}^n$ for both octahedral complexes as well as ferrocene derivatives. The results are tabulated in Table I. The compounds given in Table I were chosen to illustrate the types of deviations from ideality which we frequently encountered.