

sensitive to such a change, ranging from 402 cm^{-1} ($R = \text{H}$) to 289 cm^{-1} ($R = \text{C}_3\text{H}_7$). This sensitivity of $\nu(\text{RhO})$ to R is surprising, bearing in mind the presumed near-constancy of the Rh-O bond length (cf. for six diruthenium tetracarboxylate complexes, the Ru-O distance is $2.01 \pm 0.01 \text{ \AA}$)³² in such complexes, a result that calls into question the uncritical usage of the simple empirical

relationship between metal-metal force constant and bond length more widely to metal-oxygen bonds.³³

Supplementary Material Available: Tables VIII-X, giving infrared data for $[\text{Rh}_2(\text{O}_2\text{CH})_4(\text{PPh}_3)_2]$, $[\text{Rh}_2(\text{O}_2\text{CC}_2\text{H}_5)_4(\text{PPh}_3)_2]$, and $[\text{Rh}_2(\text{O}_2\text{CC}_3\text{H}_7)_4(\text{PPh}_3)_2]$, respectively (6 pages). Ordering information is given on any current masthead page.

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Analysis of the Vibrational Fine Structure in the Electronic Spectrum of the Planar CuCl_4^{2-} Ion in *N*-(2-Ammonioethyl)morpholinium Tetrachlorocuprate(II): Evidence for a Pseudotetrahedral Distortion in the ${}^2A_{1g}$ Excited Electronic State

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The electronic spectrum of the planar CuCl_4^{2-} ion in *N*-(2-ammonioethyl)morpholinium tetrachlorocuprate(II) is reported. The temperature dependence of the band maximum of the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition suggests that the excited-state potential surface is distorted in the β_{20} out-of-plane bending vibration, with energy minima corresponding to two equivalent pseudotetrahedral geometries. However, the distortion from planarity is somewhat less than that proposed for the ${}^2A_{1g}(z^2)$ excited state of planar CuCl_4^{2-} in other lattices. The vibrational fine structure in the spectrum is consistent with an excited-state potential surface of this form, being incompatible with the simple model of vibronic coupling normally used to interpret Laporte-forbidden electronic transitions.

Introduction

Detailed analysis of the electronic spectra of transition-metal complexes can provide information that is of value in several areas of chemistry.¹ Simple, planar ions of the type MX_4^{2-} , where M is Pd, Pt, or Cu and X is a halide, have been particularly important in this respect.²⁻⁷ The low-temperature spectra of platinum(II) and palladium(II) chloride and bromide complexes show extensive fine structure, and analysis of this fine structure has provided a detailed picture of the nature of the vibrations inducing the intensity of the d-d transitions and the change in metal-ligand bond lengths accompanying the electronic excitations.² The spectrum of planar CuCl_4^{2-} is unusual for a number of reasons. Some bands increase dramatically in intensity as the temperature is raised from 10 to 290 K, and it has been inferred from this that the out-of-plane bending vibration is of very low energy.^{3,4} Also, the band maxima exhibit an anomalous red shift of up to $\sim 900 \text{ cm}^{-1}$ over the same temperature range, and in a recent study,⁵ it was shown that this implies that the complex has a potential surface with double minima corresponding to two equivalent pseudotetrahedral coordination geometries in each excited electronic state. For one compound this was confirmed by the analysis of a system of "hot" bands.⁷ The extent of the vibrational fine structure resolved in the spectrum of planar CuCl_4^{2-} at low temperature varies markedly from one crystal lattice to another. This fine structure has previously been interpreted by using the conventional model of vibronic coupling, with differences between the compounds being ascribed to coupling with different lattice modes.^{3,4} However, if, as has been proposed, the potential surfaces of the excited electronic states differ from that in the ground state in an intensity-inducing normal mode, then simple vibronic selection rules will break down. Moreover, it has been pointed out that the extent of the distortion in the excited state may well be lattice dependent,^{5,7} which could explain why the fine structure differs from one compound to another.

The compound *N*-(2-ammonioethyl)morpholinium tetrachlorocuprate(II), $(\text{Naem})\text{CuCl}_4$, is unusual in that the green

modification contains CuCl_4^{2-} ions of two kinds, one having a distorted tetrahedral geometry and the other a planar geometry.⁸ Recently, we presented an interpretation of the band energies and intensities of the distorted tetrahedral complex using the angular overlap model.⁶ The molecular spectrum of the planar complex in $(\text{Naem})\text{CuCl}_4$ shows well-resolved vibrational fine structure for the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition, the nature of which is quite incompatible with the simple model of vibronic intensity stealing in which the ground and excited states have identical potential surfaces except for a displacement in modes of α_{1g} symmetry. It is the subject of the present paper to show that these spectra are consistent with a model in which the excited state has a potential surface distorted in the β_{20} normal vibration to give two equivalent minima, each corresponding to a coordination geometry distorted slightly from planarity.

Experimental Section

The preparation and characterization of crystals of the green form of $(\text{Naem})\text{CuCl}_4$ have been described previously.^{6,8} Spectra of the prominent (10 $\bar{1}$) crystal face were recorded over a temperature range by using a Cary 17 spectrophotometer by a technique described elsewhere.⁹ Typical spectra with the electric vector of polarized light parallel to the crystal extinction directions are shown in Figure 1. The samples were cooled with a Cryodyne 21 refrigerator, and the crystal thickness, which

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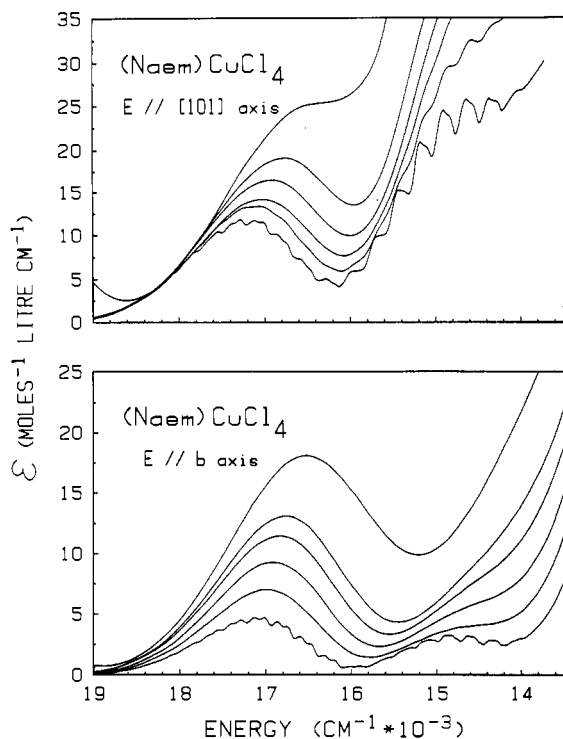


Figure 1. Temperature dependence of the spectrum of the (101) crystal face of $(\text{Naem})\text{CuCl}_4$ with the electric vector parallel to the b and [101] crystallographic axes. Spectra were measured at temperatures of 10, 60, 100, 140, 180, and 290 K and increased in intensity as the temperature was raised.

was used to derive the band intensities, was measured by using a graduated microscope eyepiece. The compound was found to convert to the yellow crystal modification⁹ moderately quickly at room temperature, so freshly grown crystals were used to record the spectra. Measurements were carried out on two separate crystals, and these were found to produce essentially identical results.

Results and Discussion

The unit cell of the green form of $(\text{Naem})\text{CuCl}_4$ contains two independent CuCl_4^{2-} ions.⁸ One of these is significantly distorted from planarity, with approximate D_{2d} symmetry, and this gives rise to the relatively intense bands centered at ~ 9000 and ~ 12000 cm^{-1} . The spectrum of this complex has been discussed elsewhere.⁶ The second CuCl_4^{2-} ion lies on a crystallographic inversion center and so is rigorously planar. The two Cu-Cl bonds differ slightly in length in this latter complex (224.0 and 231.4 pm),⁸ and this will cause the molecular x and y spectra to be inequivalent. The squared molecular projections when the electric vector of polarized light is parallel to the two extinction directions of the (101) crystal face are

$$[101]: 0.431x + 0.569y + 0.000z$$

$$b: 0.054x + 0.035y + 0.911z$$

where the x axis is parallel to the shorter Cu-Cl bond direction. Attempts were made to obtain data from a different crystal face, as this might allow the x and y spectra to be resolved. Spectra that differed from those shown in Figure 1 in the resolution of the vibrational structure and the position of the band at ~ 14500 cm^{-1} were obtained from sections cleaved from a large crystal. However, these faces could not be properly characterized nor could the reproducibility of the spectra be verified because of the unstable nature of the crystals. Thus, while there is tentative evidence for some in-plane anisotropy of the spectrum, this is only speculative and will be ignored in the present discussion, which will assume that the effective point group of the complex is D_{4h} .

Only two bands can be resolved in the spectral region within which the d-d transitions of planar CuCl_4^{2-} are expected (Figure 1). By analogy with the spectrum of this ion in other lattices,^{3,4} the band centered at ~ 17000 cm^{-1} is due to the transition ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$, while that at ~ 14500 cm^{-1} is due to ${}^2E_g(xz, yz)$

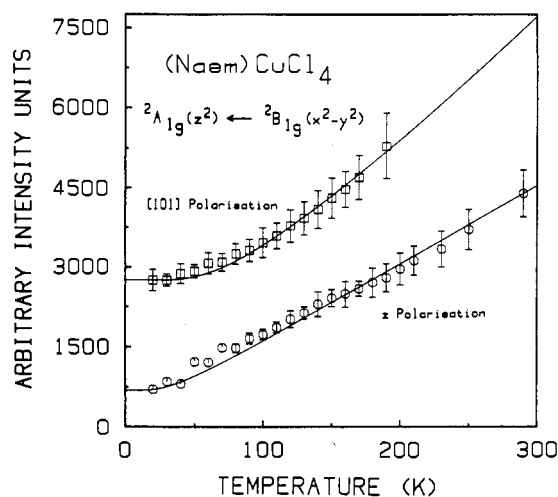


Figure 2. Variation of the intensity of the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition of $(\text{Naem})\text{CuCl}_4$ as a function of temperature in z and xy polarization. The optimum curves calculated by using eq 1 with "average" energies of the intensity-inducing vibrations of 64 (z) and 155 cm^{-1} (xy) are shown on the plots. The symbols for each polarization represent two independent sets of data, and the uncertainties in the data points were derived from the Gaussian analysis.

$\leftarrow {}^2B_{1g}(x^2 - y^2)$. The transition ${}^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2 - y^2)$, which is expected to occur as a weak band in xy polarization at ~ 12500 cm^{-1} is apparently obscured under the intense absorption due to the pseudotetrahedral CuCl_4^{2-} ion.⁶ The transition energies of the planar CuCl_4^{2-} ion in $(\text{Naem})\text{CuCl}_4$ are very similar to those reported for this complex in other lattices. The interpretation of the energy levels of these systems, in particular the anomalous energy of the ${}^2A_{1g}(z^2)$ state, has been discussed in detail elsewhere.^{3,4}

Variation of the Band Intensities with Temperature. The temperature dependence of the spectra over the temperature range 10–290 K is shown in Figure 1. For a centrosymmetric complex such as that considered here, the intensity of the "d-d" transitions is derived from higher energy charge-transfer states via coupling with *ungerade* vibrations. The theory of vibronic coupling¹⁰ suggests that the intensity I_T induced in a band by a vibration of frequency ν at temperature T is related to the intensity at 0 K, I_0 , by

$$I_T = I_0 \coth(h\nu/2kT) \quad (1)$$

In the derivation of this formula, the intensity variation depends only on the form of the ground state and is therefore unaffected by any distortion of the excited state potential surface.¹¹ The "best-fit" intensities of the transition to the ${}^2A_{1g}(z^2)$ excited state obtained by describing the spectra as the sum of a set of Gaussian curves were fitted to eq 1 by a least-squares procedure, and the results are shown in Figure 2. A description of this method has been given previously.^{3,4} Interference by the more intense bands of the pseudotetrahedral CuCl_4^{2-} ion (Figure 1) precluded any quantitative study of the temperature dependence of the transition to the ${}^2E_g(xz, yz)$ state.

For planar CuCl_4^{2-} the transition ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ in z polarization is allowed by coupling with the single mode of β_{2u} symmetry,^{3,4} and the slope of the line of best fit in Figure 2 suggests that this has an energy of 64 ± 3 cm^{-1} in $(\text{Naem})\text{CuCl}_4$. This is in excellent agreement with the energies found for the corresponding mode for the planar CuCl_4^{2-} ions in bis(methadonium) tetrachlorocuprate(II), $(\text{metH})_2\text{CuCl}_4$, (62 ± 6 cm^{-1}) and bis(creatinium) tetrachlorocuprate(II), $(\text{creat})_2\text{CuCl}_4$, (64 ± 4 cm^{-1}).⁴ The deviation of the experimental intensities in the low-temperature region from the behavior predicted by eq 1 for $(\text{Naem})\text{CuCl}_4$ (Figure 2) is similar to that observed for the other

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two salts.⁴ A detailed study⁵ of the spectrum of (metH)₂CuCl₄ has attributed this deviation to a slight anharmonicity in the β_{2u} potential surface, and a similar explanation is possible for (Naem)CuCl₄.¹²

The best least-squares fit to the variation in band intensity of the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ band in *xy* polarization was obtained for an energy of the inducing vibration of $155 \pm 10 \text{ cm}^{-1}$ (Figure 2). Again, this is very similar to the behavior of this transition in (metH)₂CuCl₄ and (creat)₂CuCl₄, where the corresponding energies were found to be 165 ± 25 and $155 \pm 10 \text{ cm}^{-1}$, respectively.⁴ Intensity is induced here by modes of ϵ_u symmetry, and infrared studies have shown that the planar CuCl₄²⁻ ion has two vibrations of this kind, one being predominantly a stretching vibration of energy $\sim 300 \text{ cm}^{-1}$ and the other being an in-plane bending mode of energy $\sim 180 \text{ cm}^{-1}$.⁴ The complicated nature of the lattice in (Naem)CuCl₄ precludes the identification of bands due to these vibrations in the infrared spectrum of the compound, though it appears that, as with the other two salts,⁴ the intensity is derived almost exclusively via coupling with the lower energy ϵ_u vibration, possibly with a small contribution from a low-energy lattice mode. The reason for the inactivity of the ϵ_u stretching vibration is unclear.

Temperature Dependence of the ${}^2A_{1g}$ Band Maximum. An unusual feature of the electronic spectra of compounds containing the planar CuCl₄²⁻ ion studied previously is the sizable red shift of the band maxima, which occurs upon raising the temperature from ~ 10 to 290 K .³⁻⁵ A detailed investigation of the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition of (metH)₂CuCl₄ suggested that this behavior, in conjunction with the shift in band maximum observed between *xy* and *z* polarization, is indicative of a significant distortion along the β_{2u} coordinate in the excited-state potential surface.⁵ A quantitative investigation⁵ suggested that the rearrangement of the d electrons is insufficient to explain the magnitude of the inferred distortion, and it was inferred that pseudo-Jahn-Teller coupling with a charge-transfer state may possibly act to amplify the distortion. It has recently been proposed that pseudo-Jahn-Teller coupling of this kind produces double-minima potential surfaces in the ground states of a number of six-coordinate copper(II) complexes.¹³

The variation with temperature of the band maxima of the "best-fit" gaussian curves of the above transition of (Naem)CuCl₄ is shown in Figure 3 for *z* and *xy* polarization; for the latter, only data up to 190 K are included, because of the poor resolution of the band at temperatures higher than this (Figure 1). The way in which the band maxima are expected to depend upon the form of the excited-state potential surface has been discussed elsewhere. Typical curves, calculated by the method described previously,⁵ are shown in Figure 3 for the case when the excited-state potential surface is identical with that of the ground state (except for a displacement in the α_{1g} totally symmetric mode), as well as if it is distorted by various amounts along the β_{2u} coordinate to take a form similar to that illustrated in Figure 4. Basically, this procedure involved calculating the relative intensities of the transitions from the various vibrational levels of the ground state to those of the excited state and using these to calculate the first moment or mean band position at various temperatures. A variational method similar to that described by Lohr¹⁴ was used to obtain the energies and wave functions of the relevant vibrational levels. Each potential surface was expressed as the sum of a fourth-order polynomial:

$$V(\xi) = \sum_{p=0}^4 a_p \xi^p \quad (2)$$

The vibrational Hamiltonian then has the form

$$H = -\frac{1}{2} \partial^2 / \partial \xi^2 + V(\xi) \quad (3)$$

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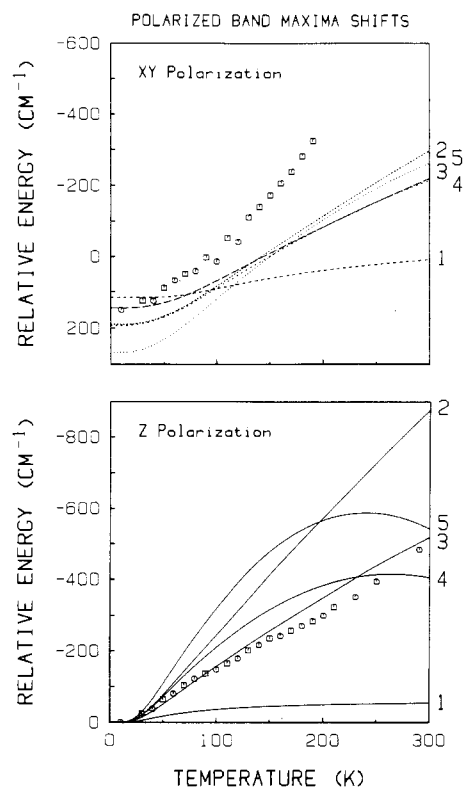


Figure 3. Variation of the band maximum of the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition of (Naem)CuCl₄ as a function of temperature in *z* and *xy* polarization. The different symbols represent different sets of data, and in each case the energy of the band maximum is measured relative to that in *z* polarization at 10 K . Curves calculated by using various excited-state potential surfaces are shown; see text and ref 5 for the method of calculation. The form of the potential function used to calculate the curves is as follows: curve 1, excited state identical with the ground state except for a displacement in the α_{1g} mode; curve 2, excited-state potential similar to that which reproduces both the polarized band maxima shifts and the low-temperature fine structure in the compound (metH)₂CuCl₄,^{5,7} defined with $h\nu = 64 \text{ cm}^{-1}$, the function used being $a_2 = -1.201$ and $a_4 = 0.0142$ ($\theta_{\min} = 10.0^\circ$; $E_{\min} = -1620 \text{ cm}^{-1}$); curve 3, excited-state potential defined as for curve 3 of the caption to Figure 5; curve 4, excited-state potential defined as for curve 4 of the caption to Figure 5; curve 5, excited-state potential as for curve 5 of the caption to Figure 5.

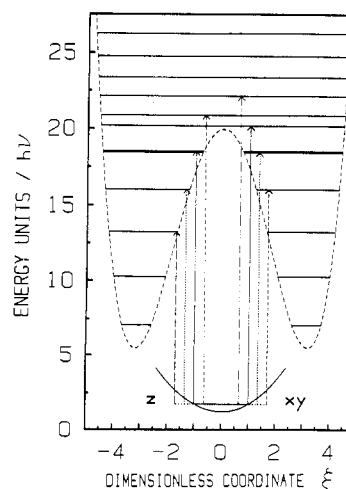


Figure 4. Potential surfaces of the ground and ${}^2A_{1g}(z^2)$ excited states of the planar CuCl₄²⁻ ion in (Naem)CuCl₄ in the β_{2u} coordinate. The distorted excited-state function is defined by the parameters given for curve 5 in the caption of Figure 5. The transitions responsible for the four most intense progressions in the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition at low temperature in *z* and *xy* polarization are identified.

This Hamiltonian was evaluated in a basis of harmonic oscillator wave functions characterized by a harmonic energy $h\nu$ and the

resulting secular equation solved. Here, ξ is a dimensionless coordinate related to the symmetry coordinates by

$$S = \xi/x \quad x = 1.722 \times 10^{-3}(Mh\nu)^{1/2} \text{ pm}^{-1} \quad (4)$$

In this expression $h\nu$ is in cm^{-1} , and the mass M is the inverse of the G matrix element appropriate to the symmetry coordinate of interest. For the α_{1g} and β_{2u} modes, this is the mass of one chlorine atom, whereas for the ϵ_u mode, a more complicated expression is required.⁵ The matrix elements of (3) are easily evaluated by published methods.¹⁵ After diagonalization of the secular equation with standard techniques, the energies are obtained in (nonintegral) units of $h\nu$ and the ground- and excited-state wave functions $|i\rangle$, $|j\rangle$ as linear combinations of the harmonic basis functions ϕ_n :

$$|i\rangle = \sum c_{ni}\phi_n \quad |j\rangle = \sum c_{nj}\phi_n \quad (5)$$

The overlaps between the components of (5) were then evaluated and used to calculate the desired Franck-Condon factors and transition probabilities, which in turn were used to find the mean energy of the band by the method of moments.¹⁴ A Boltzmann factor was used to weight the intensities according to the relative population of the vibrational levels of the ground state at each temperature. A basis size of ~ 120 was required to converge the wave functions of interest.

The changes in position of the band maximum are dominated by the inducing mode potentials, and in the ground state these were assumed to be harmonic functions in agreement with the temperature dependence of the intensity. The parameters defining these are referred to in the caption to Figure 3. From a previous study,⁵ the expected effect of the distortion in the β_{2u} potential in the excited state is to produce a surface with double minima (Figure 4). Each of these minima corresponds to a displacement of the chloride ligands away from the ground-state planar geometry toward a tetrahedral arrangement. The size of the distortion may be defined by the magnitude of the angle made by each Cu-Cl bond with the xy plane, θ_{\min} , and the depth of the wells with respect to the energy of the planar geometry, E_{\min} . These are related to the parameters of eq 2 by the following expressions:⁵

$$\theta_{\min} = (-b_2/2b_4)^{1/2} \quad E_{\min} = -(b_2^2/4b_4)$$

when the excited state is described by a simple quartic function. The coefficients b_i have the dimensions ($\text{cm}^{-1} \text{ deg}^{-2}$), and these are related to the dimensionless coefficients a_i of eq 2 by

$$h\nu a_i = (180/2\pi R x)^2 b_i$$

The normal and dimensionless coordinates are related by

$$\theta = (180/2\pi R x)\xi$$

Here R is the equilibrium bond length in picometers and x is given by eq 4. The excited state is displaced in the α_{1g} mode with respect to the ground state, as discussed below, but this does not affect the shifts in the band maxima. The potential surface of the excited state will also differ somewhat from that of the ground state in other normal modes. These differences have been estimated previously by a method based upon the angular overlap model,⁵ and the effects were included in the present calculations, though they have only a small influence on the shifts in the band maxima.

It is apparent (Figure 3, curves 1) that when the potential surface of the excited state is undistorted with respect to the ground state, as is assumed in the simple model of vibronic intensity stealing,¹⁰ the shift in band maximum that occurs in xy compared with z polarization is approximately equal to the energy difference between the inducing modes in the two polarizations, $\sim 120 \text{ cm}^{-1}$ in the present case. Moreover, the red shift upon warming to $\sim 290 \text{ K}$ is expected to be quite small, on the order of magnitude $h\nu$, the energy of the intensity-inducing vibration, which is $\sim 60 \text{ cm}^{-1}$ in z polarization in the present case. The observed red shift of $\sim 500 \text{ cm}^{-1}$ is significantly greater than this. When the excited-state potential is distorted in the β_{2u} mode, the size of the

red shift and the polarization dependence of the band maximum depend upon the magnitude of the distortion, as defined both by the size of the angle θ_{\min} and the depth of each well with respect to the undistorted geometry, E_{\min} (Figure 4). The comparatively modest red shift observed for $(\text{Naem})\text{CuCl}_4$ in z polarization implies that the excited state of the planar CuCl_4^{2-} ion in this lattice is distorted less in the β_{2u} coordinate than is the case for this complex in the other lattices that have been studied to date. While in $(\text{metH})_2\text{CuCl}_4$ the data are consistent with potential minima defined by $\theta_{\min} \approx 10.0^\circ$ and $E_{\min} \approx -1600 \text{ cm}^{-1}$, giving a red shift of $\sim 900 \text{ cm}^{-1}$ in z polarization (curve 2 of Figure 3 (z)) agrees with the experimental data of this complex), the red shift of $\sim 500 \text{ cm}^{-1}$ observed for $(\text{Naem})\text{CuCl}_4$ is consistent with considerably smaller distortion parameters ($\theta_{\min} \approx 7.0^\circ$ and $E_{\min} \approx -340 \text{ cm}^{-1}$, curve 3 of Figure 3 (z)).

The red shift of $\sim 450 \text{ cm}^{-1}$ observed in xy polarization on warming from 10 to 190 K (the highest temperature at which the band could be resolved satisfactorily) is considerably higher than is predicted by the present model even if a large distortion in the β_{2u} vibration is present in the excited state (curve 2 of Figure 3 (xy)). This is probably because the shift in band maximum is strongly influenced by the intensity-inducing mode, and in xy polarization this is the ϵ_u vibration, rather than the β_{2u} mode. The present calculations are based upon the assumption that the ϵ_u mode differs little in the excited state compared with the ground state, as estimated by using the angular overlap model.⁵ The large temperature dependence of the band maximum in xy polarization may therefore be indicative of a significant difference of the ϵ_u potential surface in the ${}^2A_{1g}(z^2)$ excited state.

As discussed below, the function giving optimum agreement with the temperature dependence in z polarization (curve 3 of Figure 3 (z)) does not generate spectral simulations that reproduce the double progressions observed in both z and xy polarizations. The double progression observed in z polarization can be simulated (curve 4 of Figure 5) with an upper potential surface with double minima corresponding to a distortion ($\theta_{\min} \approx 4.8^\circ$ and $E_{\min} \approx -440 \text{ cm}^{-1}$) quite similar to that giving optimum agreement with the shift in band maximum ($\theta_{\min} \approx 7.0^\circ$ and $E_{\min} \approx -340 \text{ cm}^{-1}$). However, such an excited-state surface implies a variation in band maximum with temperature increase that, while of the correct order of magnitude, exhibits a curved relationship, rather than the essentially linear one observed experimentally (curve 4, Figure 3 (z)). Such a potential surface does not predict the double progression observed in xy polarization. As already noted, poorer agreement with experiment is to be expected in xy polarization as the form of the potential surface in the ϵ_u intensity-inducing mode is unknown. The double progression can be simulated, albeit rather poorly (curve 5, Figure 6), by using a somewhat more distorted excited-state potential ($\theta_{\min} \approx 5.0^\circ$ and $E_{\min} \approx -930 \text{ cm}^{-1}$), though such a surface implies a shift of band maximum as a function of temperature in poor agreement with experiment (curve 5, Figure 3 (z)).

When the two minima in the excited-state potential surface are closely spaced, as is apparently the case in the present compound, features such as the low-temperature vibrational structure and the temperature dependence of the band maxima become very sensitive to the precise form of the ground- and excited-state surfaces. In the present model, these surfaces are represented by simple quartic functions, so that it is not surprising that the optimum simulation of the above features is not obtained by using a unique excited-state potential. Exploratory calculations were undertaken by using an anharmonic ground-state potential surface similar to that previously used⁵ to interpret the temperature dependence of the band intensity of $(\text{metH})_2\text{CuCl}_4$. These suggested that a slightly better fit to both the observed temperature dependence of the band maximum and the low-temperature fine structure in z polarization is possible.¹² Quantitative investigations¹² also suggested that both the calculated red shift and the simulated spectral detail in xy polarization can be significantly improved, with little change in the results in z polarization, if a slight distortion in the excited state along the ϵ_u coordinate producing a double minimum potential surface is present. However,

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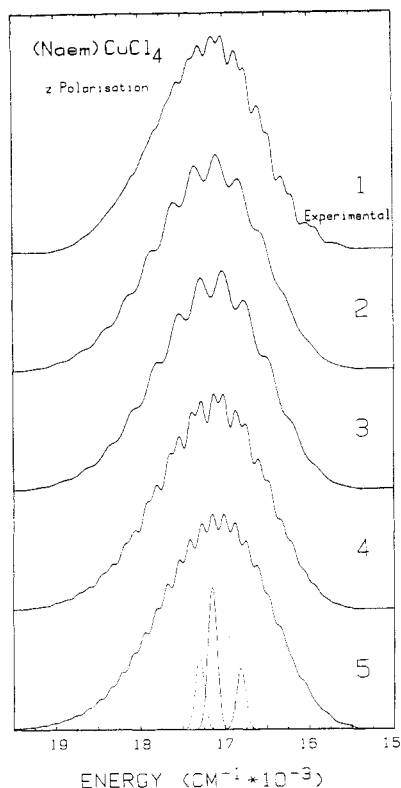


Figure 5. Observed (curve 1) and simulated (curves 2–5) band shapes of the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition at low temperature in z polarization. The estimated absorption due to lower energy transitions (Figure 1) has been removed from the observed spectrum. The potential surfaces used for the simulations were defined by using eq 2. In each case, the α_{1g} mode was defined with respect to a harmonic frequency of 275 cm^{-1} , by $a_2 = 0.5$ in the ground state and $a_2 = 0.469$ and $a_1 = -3.193$ ($\delta r = 10.0\text{ pm}$) in the excited state except for curve 5 where $a_1 = -3.113$ ($\delta r = 9.75\text{ pm}$). Curve 2 was obtained with the excited state identical with the ground state in the β_{2u} mode. For the remaining curves the following excited-state functions were used: curve 3, $a_2 = -0.514$ and $a_4 = 0.0124$ ($\theta_{\min} = 7.0^\circ$; $E_{\min} = -340\text{ cm}^{-1}$); curve 4, $a_2 = -1.415$ and $a_4 = 0.0728$ ($\theta_{\min} = 4.8^\circ$; $E_{\min} = -440\text{ cm}^{-1}$); curve 5, $a_2 = -2.757$ and $a_4 = 0.1307$ ($\theta_{\min} = 5.0^\circ$; $E_{\min} = -930\text{ cm}^{-1}$). These potentials were defined with respect to a harmonic energy of 64 cm^{-1} , as deduced from the temperature dependence of band intensity in z polarization. In the simulations, the basic half-width at half-height of each vibronic transition was 115, 90, 58, and 54 cm^{-1} for curves 2–5, respectively. For curve 5 the four most intense components of one double member of the α_{1g} progression are shown using line symbols that correspond to those used for the vertical Franck-Condon transitions responsible for the peaks indicated in Figure 4.

it is not apparent why such a distortion should occur, and this line of investigation was not pursued further.

Interpretation of the Vibrational Fine Structure. Although quite well-resolved fine structure is observed at low temperature on the band assigned to the ${}^2E_g(xz, yz) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition (Figure 1), it is impractical to attempt an interpretation of this at present, as the activities of the intensity-inducing modes are unknown. Moreover, this excited state is formally subject to a Jahn-Teller distortion, though this will be quenched to some extent by spin-orbit coupling and the rhombic component of the ligand field.

At 10 K the band due to the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition exhibits a well-resolved double progression in both z and xy polarization (Figure 1 and curves 1 of Figures 5 and 6). The interval of each progression, $\sim 267\text{ cm}^{-1}$, suggests that it occurs in the α_{1g} totally symmetric stretching vibration. The energy of this mode could not be measured directly from the Raman spectrum, as the compound is photochemically unstable at room temperature. However, the α_{1g} stretch occurs at $\sim 275\text{ cm}^{-1}$ in several other compounds containing planar CuCl_4^{2-} .^{3,4} A decrease in energy of this vibration in the excited state is expected, as an electron is promoted to the antibonding $B_{1g}(x^2 - y^2)$ orbital. Although it has little effect on the variation of the band maximum with

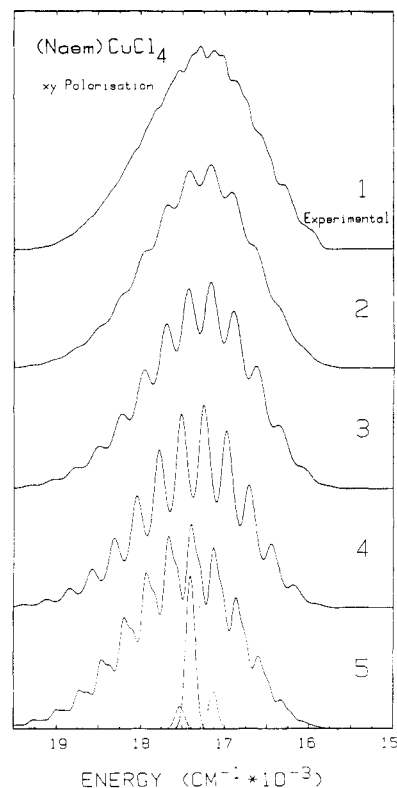


Figure 6. Observed (curve 1) and simulated (curves 2–5) band shapes of the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition at low temperature in xy polarization. The estimated absorption due to lower energy transitions (Figure 1) has been removed from the observed spectrum. The potential surfaces used for the simulations are identical with those defined for the corresponding curves in Figure 5. For curve 5 the four most intense components of one double member of the α_{1g} progression are shown by using line symbols that correspond to those used for the vertical Franck-Condon transitions responsible for the peaks indicated in Figure 4.

temperature, the displacement in the α_{1g} potential that accompanies the electronic transition is largely responsible for the shift in band maximum from the electronic origin. This potential was defined by the parameters $a_2 = 0.5$ in the ground state and $a_2 = 0.469$, $a_1 = -3.193$ in the excited state, corresponding to a lengthening of $\delta r = 10.0\text{ pm}$ in each Cu-Cl bond in the higher state. This change in bond distance is similar to those derived from the analysis of the corresponding band in the spectra of planar CuCl_4^{2-} ions in other lattices,^{3,4} and is also consistent with theoretical predictions.⁹

The fact that the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ band shows a double progression in z polarization is of particular significance, as only one vibration of the CuCl_4^{2-} ion is available to induce intensity in this polarization, that of β_{2u} symmetry. As both progressions are approximately equally intense (Figures 1 and 5), it is highly unlikely that one is caused by a lattice mode or is due to the formal symmetry of the complex being lower than that assumed in the present analysis. In fact, the large energy separation between the progressions, $\sim 130\text{ cm}^{-1}$, means that they cannot be built upon vibronic origins associated with different vibrations in the ground electronic state, as this would imply a temperature dependence quite incompatible with experiment. However, it has been pointed^{5,7} out that a large distortion of the excited-state potential surface relative to that of the ground state will cause the simple vibronic selection rules to break down, and this may lead to the observation of anomalous fine structure in the electronic spectrum.

In order to investigate the effect of a distortion in the excited-state β_{2u} potential upon the low-temperature vibrational fine structure, spectra were simulated for a range of potential functions. Typical spectra produced in this way are shown in curves 2–5 of Figures 5 and 6. In each simulation, the basic half-width of a transition between a vibrational level of the ground state and one of the excited state was chosen to produce optimum overall

agreement with the z -polarized spectrum, and the electronic origin was chosen to optimize the position of the corresponding band maximum. The experimental band shapes are also shown in Figures 5 and 6 (curves 1), after subtraction of the estimated absorption due to the lower energy transitions.

If the excited-state β_{2u} potential is identical with that of the ground state, a single progression is expected in z polarization, built upon a vibronic origin in which just one quantum of the β_{2u} mode is excited (curve 2 of Figure 5). In xy polarization, the same situation applies, except that here one quantum of the intensity-inducing ϵ_u mode is involved, and the higher energy of this ($\sim 180 \text{ cm}^{-1}$, compared with $\sim 60 \text{ cm}^{-1}$ for the β_{2u} mode) means that the band is shifted to higher energy by $\sim 120 \text{ cm}^{-1}$ (curve 2 of Figure 6). These simulations are in poor agreement with the observed bands. If a relatively large distortion in the excited-state β_{2u} coordinate is present, just a single progression in z polarization is expected as has indeed been observed for $(\text{metH})_2\text{CuCl}_4$.^{4,7} However, as described in detail elsewhere,^{5,7} each member of the α_{1g} progression is now itself a band composed of a β_{2u} progression, though the energy separation between members of the latter was found to be too small for these to be resolved.

As discussed previously, while the excited-state potential giving optimal agreement with the observed temperature dependence does not give rise to a calculated z spectrum showing a double progression (curve 3, Figure 5), a surface distorted somewhat less from the ground-state potential produces a simulation in good agreement with experiment (curve 4, Figure 5). However, the simulation in xy polarization using this function differs from that observed experimentally as it shows only a single progression (curve 4 of Figure 6). In order to reproduce a double progression in this polarization, it was necessary to increase the barrier energy between the minima of the excited-state potential (eq 2). The excited-state potential shown in Figure 4, with $\theta_{\text{min}} = 5.0^\circ$ and $E_{\text{min}} = -930 \text{ cm}^{-1}$ does reproduce this feature (curve 5 of Figure 6) and also produces a simulated z spectrum in good agreement with experiment (curve 5 of Figure 5), though the temperature variation of the band maximum calculated with this potential agrees poorly with that observed experimentally (curves 5 of Figure 3).

It is of interest to consider the cause of the well-defined double progression observed in the spectrum of $(\text{Naem})\text{CuCl}_4$, as this provides particularly strong evidence for a significant distortion in the excited-state potential surface. The present model suggests that this behavior is due to the breakdown of the selection rules governing the vibronic mechanism by which parity-forbidden electronic transitions gain intensity. These rules, which are derived by assuming that the excited-state potential surfaces are identical with those of the ground state except for a displacement in totally symmetric vibrations, require that the intensity-inducing modes change by 1 quantum in conjunction with the electronic transition.¹⁰ When the excited state potential surface is distorted in an intensity-inducing *ungerade* vibration, nonzero inducing overlaps occur for the excitation of multiple quanta of this mode. This gives rise to a band structure consisting of progressions in the α_{1g} mode built on a number of vibronic origins, with the precise pattern depending upon the energy spacings and wave functions of the vibrational levels of the inducing mode in the excited state. The four most intense components of one of the double peaks in the z spectrum of the planar complex in $(\text{Naem})\text{CuCl}_4$ simulated by using the excited-state potential producing optimum simulated spectra in both polarizations is shown in curve 5 of Figure 5. The particular vibrational levels are identified in Figure 4, with identical line symbols being used for the vertical Franck-Condon transition and for the band component it produces, as shown in Figure 5.

It should be noted that each of the four lowest levels shown in Figure 4 is in fact a pair of closely spaced vibrational energy levels. Group theory requires that for a centrosymmetric molecule the quantum number changes by an odd integer for a vibration-inducing intensity in an electronic transition, and for the transition in question excitations occur to the $\nu = 9, 7, 11$, and 5 vibrational levels of the β_{2u} mode of the excited electronic state, in order of decreasing intensity. It can be seen that the double progression

occurs because the maximum overlap between the lowest vibrational level of the ground state and the excited state levels takes place near the saddlepoint at $\theta = 0^\circ$ in the β_{2u} potential, where the latter levels are quite unevenly spaced (Figure 4). When the excited state β_{2u} potential is more highly distorted, maximum overlap occurs lower in the wells, giving rise to a more regular progression in the β_{2u} mode in which the individual components may not be resolved if the energy separations are relatively small.^{5,7}

Although the β_{2u} vibration does not induce intensity in xy polarization, the distortion means that nonzero Franck-Condon overlaps can occur in this mode for a range of excited-state vibrational levels (Figure 4) with group theory now dictating that transitions occur between levels differing by a multiple of 2 quanta in this vibration. Each of these transitions, plus 1 quantum of the intensity-inducing ϵ_u mode, acts as an origin for a progression in the α_{1g} mode. However, higher energy levels in the β_{2u} mode are involved in xy compared with z polarization ($0 \rightarrow 10, 8, 6$, and 12 in order of decreasing intensity; see Figure 4), and this contributes to the shift in position of the band maximum with polarization (Figures 5 and 6). Agreement between the simulated and observed band shape is not as good in xy polarization as it is in z polarization, but as already mentioned, this is to be expected, as in the former case the precise form of the excited-state potential surface in the intensity-inducing ϵ_u mode is unknown. Moreover, the degeneracy of this vibration will be removed by the inequivalence of the Cu-Cl bond lengths. This effect, which was not included in the calculations, would broaden the components of the xy spectrum, producing a simulation in better agreement with experiment (Figure 6).

The simulations were found to be quite sensitive to the form of the potential function when the excited state is similar to that shown in Figure 4, so that even small changes in the values of θ_{min} or E_{min} produced significant changes in the calculated spectra. While it was considered impractical to investigate all possible excited-state potential surfaces, it was found that the most important characteristic of the spectra, the doubling of the α_{1g} progression in z polarization, could only be reproduced if the excited-state β_{2u} potential minima are displaced by $\sim 8^\circ > \theta_{\text{min}} > \sim 4^\circ$.¹² This provides strong confirmation of the conclusion drawn from the temperature variation of the band maximum—that the equilibrium geometry of the ${}^2A_{1g}(z^2)$ excited state of the planar CuCl_4^{2-} ion in $(\text{Naem})\text{CuCl}_4$ is distorted from planarity, with this distortion being somewhat less than that which occurs in the excited state of this ion in other lattices.^{5,7} The reason for this difference in the excited-state equilibrium potential is not clear, though it is not unexpected that the geometry of the CuCl_4^{2-} ion in the excited state should be lattice dependent, as this complex exhibits such a wide range of stereochemistries in the ground state (the distortion angle θ varies between 0° and $\sim 30^\circ$ in solid tetrachlorocuprates).^{6,16}

Conclusions

While it has not been possible to simulate all the experimental features of the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition of $(\text{Naem})\text{CuCl}_4$ by using a unique set of ground- and excited-state potential functions, it has been shown that both the shift in band maximum with increasing temperature in z polarization and, in particular, the double vibrational progression observed at low temperature are consistent with an excited state slightly distorted to give a double minimum potential surface corresponding to two, equivalent, pseudotetrahedral ligand arrangements.

Previous interpretations of the electronic spectra of planar CuCl_4^{2-} ions have assumed that these can be interpreted by using conventional vibronic coupling theory.^{3,4} On this basis, the dramatic variation in the vibrational fine structure resolved in the low-temperature spectrum of this ion that occurs from one lattice to another was rationalized in terms of differences in coupling with lattice modes. The present work suggests that the form of the excited-state potential surface also strongly influences the nature of the fine structure resolved in the spectra and implies

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that this aspect of the previous interpretations should be reevaluated. Moreover, while planar CuCl_4^{2-} is unusual because of the very low energy of the intensity-inducing β_{2u} mode, the present results suggest that caution should be exercised in the application of the simple model of vibronic coupling in other systems.

There has recently been considerable interest in the temperature-dependent EPR spectra observed for various Cu(II) complexes,¹⁷ and the CuCl_4^{2-} ion has been proposed as a model for biologically important systems of this kind.¹⁸ It has been suggested that the unusual behavior of these systems may be caused

by a highly anharmonic potential surface in the ground state of the complexes.^{17,19} The present studies suggest that the anomalous temperature dependence of the optical spectrum of planar CuCl_4^{2-} is strongly influenced by the form of the excited-state potential surfaces, and we are considering the implications that this may have on the interpretation of temperature-dependent EPR parameters.

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Intervalence Transfer in Pentaammineruthenium Complexes of α,ω -Dipyridyl Polyenes

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Binuclear complexes containing the pentaammineruthenium(II) moiety linked to α,ω -dipyridyl polyenes have been prepared. The systems investigated have two, three, or four conjugated double bonds connecting the pyridyl moieties, and the metal-metal distance ranges from 15.8 to 20.6 Å. The electrochemical and spectroscopic properties of the complexes are described. Progressive oxidation gives rise to mixed-valence compounds exhibiting an intervalence transition in the near-IR region. The best resolution of these intervalence transitions with respect to the nearby charge-transfer transition is realized with nitrobenzene as solvent. The electronic coupling parameter is calculated from the intensity of the intervalence band and is shown to decrease only by ca. 30% when going from two to four double bonds.

Introduction

The experimental and theoretical study of long-distance electron transfer is a very active current research topic. The consequences of this process are of crucial importance in domains such as biology,¹ solid-state chemistry,² inorganic reaction mechanisms,³ and finally the emerging field of molecular electronics.⁴ In particular, the question of the rate of decay of the electronic interaction between the two redox sites as a function of distance has received considerable attention.⁵⁻⁹

In the course of a general program devoted to molecular electronics, we have undertaken the synthesis of new model systems in which two redox sites are linked by a conjugated pathway.¹⁰ The aims of this investigation are the following.

(i) We wish to show the possibility of long-distance electron transfer in or near the ground state. This would lead to the synthesis of "molecular wires" allowing the intramolecular propagation of electrons between a donor and acceptor site. In this respect, Lehn and co-workers have recently synthesized "caroviologens" with redox sites separated by a long conjugated chain.¹¹

(ii) We wish to investigate the possibility of "molecular switching" by a conformational change. As a prerequisite for this, the synthesis of sufficiently long bridging ligands appears necessary in order to ensure that the electron transfer really proceeds through bonds and not through space. The electron-transfer rate will then be influenced by the properties of the intramolecular medium and could probably be changed by a variation in the geometrical or energetic properties of the system.

Here we describe the electron-transfer ability of α,ω -dipyridyl polyenes of the general type $\text{py}(\text{CHCH})_n\text{py}$ (py = pyridyl) in which $n = 2-4$. In the following, these ligands will be denoted **2**, **3**, and **4**, respectively. The metal sites coordinated to the pyridine ends of these ligands are $\text{Ru}(\text{NH}_3)_5^{2+/3+}$ moieties, giving

binuclear complexes denoted as 2_{Ru} , 3_{Ru} , and 4_{Ru} , respectively (see Figure 1). According to the pioneering work of Taube,¹² Meyer,¹³ and others, pentaammineruthenium groups are particularly well suited for this purpose. Indeed, the two oxidation states 2+ and 3+ are stable and are easily interconverted at a reasonable redox potential. In addition, with NH_3 as ancillary ligands, ruthenium(II) is a strong π donor and interacts efficiently with the π acceptor bridging ligand. This is a favorable factor for the transmission of the electronic interaction.

The present systems thus represent a development of the work already performed by Sutton and Taube^{14,15} and Meyer and co-workers¹⁶ using 4,4'-bipyridine (**0**) and dipyridylethylene (**1**) bridging ligands.

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