Inorg. Chem. **1986**, *25*, 3273-3281 **3273**

Contribution from the Chemistry Department,
University of Tasmania, Hobart, Tasmania 7001, Australia

Electronic "d–d" Spectra of the Planar $CuCl_4^{2-}$ Ions in Bis(methadonium) Tetrachlorocuprate(II) and Bis(creatininium) Tetrachlorocuprate(II): Analysis of the Temperature Dependence and Vibrational Fine Structure

Robbie G. McDonald and Michael A. Hitchman*

Received December 18, 1985

The electronic spectra in the range 1000–450 nm of single crystals of (methadonium)$_2$CuCl$_4$ and (creatininium)$_2$CuCl$_4$ are reported. The band polarizations suggest a d-orbital energy sequence $d_{x^2-y^2} >> d_{xy} > d_{xz,yz} > d_{z^2}$ for the planar $CuCl_4^{2-}$ ions present in the compounds. Vibrational fine structure is observed at low temperature in the spectrum of the methadonium salt, and this is analyzed in terms of displacements in the α_{1g} totally symmetric breathing mode for the equilibrium nuclear geometries of the $^2A_{1g}(z^2)$ and $^2B_{2g}(xy)$ excited states, these being in good agreement with simple theoretical predictions. The observed temperature dependence of the band intensities is interpreted as being due to vibronic coupling, the inferred energies of the active u vibrational modes being in broad agreement with the infrared spectra of the complexes and the polarization behavior of the vibrational structure of the methadonium salt. The band maxima undergo anomalously large red shifts on going from 10 to 290 K, and the possibility is explored that this is caused by a temperature-dependent low-symmetry component of the ligand field, this being derived from the thermal population of excited vibrational levels of the out-of-plane bending mode of β_{2u} symmetry, which carries the complex from a planar toward a distorted-tetrahedral geometry. However, quantitative agreement with the observed temperature dependence of the band maxima for a simple model based on this concept is only obtained by using an energy of the β_{2u} mode significantly less than that implied by the temperature dependence of the band maxima.

Introduction

The $CuCl_4^{2-}$ ion is precluded from adopting a regular tetrahedral geometry by the Jahn–Teller theorem, the stereochemistry normally involving either a six-coordinate, tetragonally elongated structure with bridging ligands or a compressed tetrahedral geometry of D_{2d} symmetry.[1] To date, a truly four-coordinate, planar geometry for this ion has been found in only three compounds: bis(*N*-methylphenethylammonium) tetrachlorocuprate(II) ((*N*-mpH)$_2$CuCl$_4$),[2] bis(creatininium) tetrachlorocuprate(II) ((creat)$_2$CuCl$_4$),[3] and bis(methadonium) tetrachlorocuprate(II) ((metH)$_2$CuCl$_4$).[4] The electronic spectrum of planar $CuCl_4^{2-}$ is of interest for several reasons. First, this complex has been the subject of numerous theoretical calculations, so that the assignment of the excited-state energies has been the subject of some controversy.[5] Second, chlorocuprates provide useful models for molecules of biological importance,[6] a recent comparison of the charge-transfer spectra of planar and pseudotetrahedral $CuCl_4^{2-}$ being particularly valuable in this respect.[7] Finally, the "d–d" spectrum of (*N*-mpH)$_2$CuCl$_4$, the only complex of this type studied previously in any detail, is unusual in showing extensive fine structure at low temperature,[8] due to coupling with metal–ligand and lattice vibrations, and this provided a unique opportunity to study the effects of vibronic coupling on the electronic spectrum of a simple complex.[9] However, because of the crystal packing in (*N*-mpH)$_2$CuCl$_4$, molecular spectra cannot be resolved accurately.[9] For this reason, and to investigate the influence of the crystal lattice on "d–d" spectra, we have measured the spectra of (creat)$_2$CuCl$_4$ and (metH)$_2$CuCl$_4$, both of which contain $CuCl_4^{2-}$ ions having an orientation in the crystal lattice favorable to the resolution of good molecular spectra (a preliminary report of the spectrum of the former complex has already been published[10]). The present paper describes the results of these studies, the conclusions being compared with those reported previously for the analogous (*N*-mpH)$_2$CuCl$_4$ complex.[9] Particular attention has been paid to the anomalously large changes in the intensity and positions of the "d–d" bands which occur on warming from 10 to 290 K.

Experimental Methods

Large, green platelike crystals of (creat)$_2$CuCl$_4$ and (metH)$_2$CuCl$_4$ were grown as described previously,[3,4] and both complexes were found to have satisfactory analyses. Electronic spectra were measured by using a Cary 17 spectrophotometer, the crystals being mounted by a technique already described.[9,11] The crystals were cooled with a Cryodyne Model 21 cryostat fitted with an Oxford Instruments temperature controller and sensor. As in this arrangement the sample is held in a vacuum, particular care was taken to ensure that the crystals were in good thermal contact with the cooling block and the system was tested by measuring the spectrum of a crystal of (*N*-mpH)$_2$CuCl$_4$ for which data was also available with the sample held in cold helium gas. It is estimated that the sample temperature in the present studies is known to an accuracy of better than ~4 K.

Both complexes crystallized with the (100) crystal face well developed, the morphology being deduced by using optical goniometry and confirmed by EPR spectroscopy. Optical spectra were recorded for several crystals of each complex with the electric vector of polarized light parallel to the *b* and *c* crystal axes for various temperatures between 10 and 290 K. Molar extinction coefficients were deduced by measuring each crystal thickness with a graduated microscope eyepiece. Each spectrum consisted of three bands, and the "best-fit" Gaussian components were deduced by a nonlinear least-squares procedure. Base line corrections were estimated by removing the crystal and recording the "spectrum" of the copper mask upon which the crystal was mounted.[11] Typical experimental points and the "best-fit" curves are shown in Figures 1 and 2. The data were also fitted to skewed Gaussian curves, as suggested by Jørgensen,[12] the resulting band areas and maxima being not significantly different from those obtained with symmetrical Gaussian components.

Infrared spectra were measured by using a Digilab FTS 20E infrared spectrometer, and Raman spectra by using a Cary 82 spectrometer using the 514-nm excitation line of an argon/krypton laser. The peaks due to the $CuCl_4^{2-}$ units were identified by comparison with the spectra of the corresponding cation hydrochloride.

Results and Discussion

Vibrational Energies of the $CuCl_4^{2-}$ Ions. If the slight difference between the Cu–Cl bond lengths is neglected, the planar $CuCl_4^{2-}$ ion has seven normal vibrations.[13] The energies of these in

---

* To whom correspondence should be addressed.

[1] Smith, D. W. *Coord. Chem. Rev.* **1976**, *21*, 93.

[2] Harlow, R. L.; Wells, W. J., III; Watt, G. W.; Simonsen, S. H. *Inorg. Chem.* **1974**, *13*, 2106.

[3] Udupa, M. R.; Krebs, B. *Inorg. Chim. Acta* **1979**, *3*, 241.

[4] Nelson, H. C.; Simonsen, S. H.; Watt, G. W. *J. Chem. Soc., Chem. Commun.* **1979**, 632.

[5] Ros, P.; Schuit, G. C. A. *Theor. Chim. Acta* **1966**, *4*, 1. Demuynek, J.; Veillard, A. *Chem. Phys. Lett.* **1970**, *6*, 204. Trappeniers, N. J.; de Brouchiêre, G.; Ten Seldam, C. A. *Chem. Phys. Lett.* **1971**, *8*, 327. Demuynek, J.; Veillard, A.; Wahlgren, U. *J. Am. Chem. Soc.* **1973**, *95*, 5563. Correa de Mello, P.; Hehenberger, M.; Larsson, S.; Zernes, M. *J. Am. Chem. Soc.* **1980**, *102*, 1278.

[6] Solomon, E. I.; Hare, J. W.; Dooley, D. M.; Dawson, J. H.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 168.

[7] Desjardins, S. R.; Penfield, K. W.; Cohen, S. L.; Musselman, R. L.; Solomon, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 4590.

[8] Cassidy, P.; Hitchman, M. A. *J. Chem. Soc., Chem. Commun.* **1975**, 837.

[9] Hitchman, M. A.; Cassidy, P. J. *Inorg. Chem.* **1979**, *18*, 1745.

[10] Hitchman, M. A. *J. Chem. Soc., Chem. Commun.* **1979**, 973.

[11] Hitchman, M. A. *Transition Met. Chem.* (N.Y.) **1985**, *9*.

[12] Jørgensen, C. K. *Acta Chem. Scand.* **1954**, *8*, 1495.

[13] Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1963; p 113.

0020-1669/86/1325-3273$01.50/0

Table I. Vibrational Energies of the $CuCl_4^{2-}$ Ions

mode (D_{4h} sym)	activity	type	vibr energy, cm^{-1} K_2PtCl_4[a]	$(N\text{-mpH})_2CuCl_4$[b]	$(metH)_2CuCl_4$	$(creat)_2CuCl_4$
ν_1 (α_{1g})	R	sym str	329 s	276 s	275 s	290 s
ν_2 (β_{1g})	R	str	302 w	209 vw	195 w	*c*
ν_3 (α_{2u})	IR	out-of-plane bend	173	158 s	159 s	150 s
ν_4 (β_{2g})	R	in-plane bend	194 mw	182 s	181 s	202 s
ν_5 (β_{2u})		out-of-plane bend				
ν_6 (ϵ_u)	IR	str	325	314 s 285 s	303 s 281 s	308 s 290 s
ν_7 (ϵ_u)	IR	in-plane bend	195	193 s	179 s 177 s	188 s

[a] Ferraro, J. R. *J. Chem. Phys.* **1970**, *53*, 117. Hendra, P. J. *Spectrochim. Acta, Part A* **1967**, *23A*, 2871. Note that the assignements for ν_2 and ν_4 are as proposed in: Harrison, T. G.; Patterson, H. H.; Godfrey, J. J. *Inorg. Chem.* **1976**, *15*, 1291. [b] Reference 9 and present work. [c] Not observed.

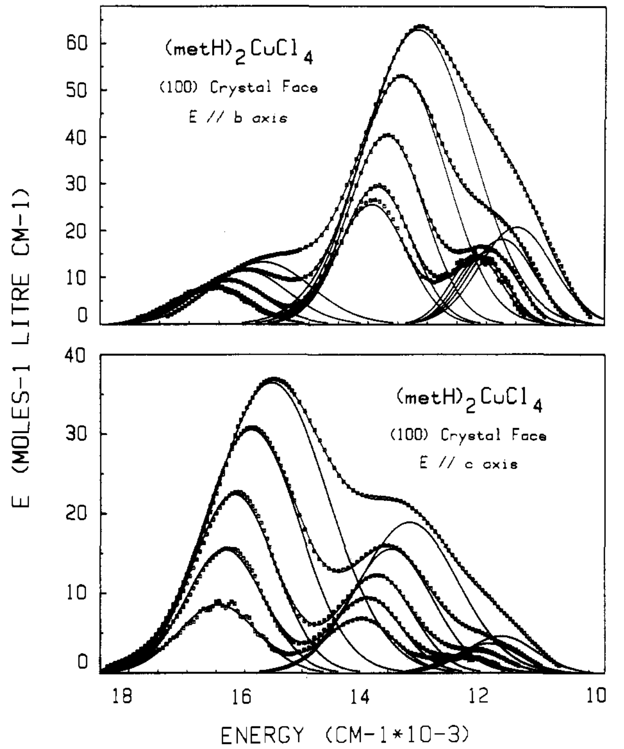


Figure 1. Spectra of the (100) crystal face of $(metH)_2CuCl_4$ with the electric vector of light parallel to the *b* and *c* crystal axes. Experimental points and the "best-fit" Gaussian curves are shown for temperatures of 10, 60, 100, 200 and 290 K, the intensity at each band maximum increasing as a function of temperature.

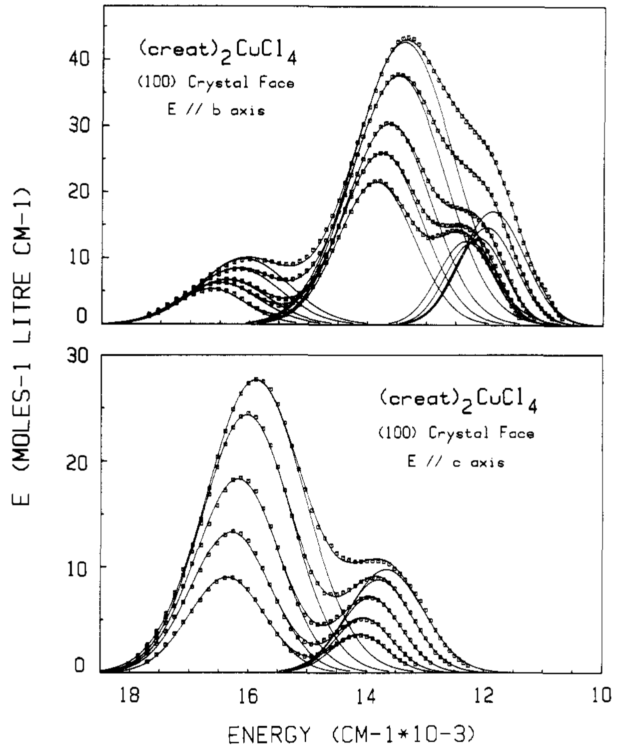


Figure 2. Spectra of the (100) crystal face of $(creat)_2CuCl_4$ with the electric vector of light parallel to the *b* and *c* crystal axes. Experimental points and the "best-fit" Gaussian curves are shown for temperatures of 10, 50, 90, 140 and 180 K, the intensity of each band maximum increasing as a function of temperature.

$(metH)_2CuCl_4$ and $(creat)_2CuCl_4$ are listed in Table I. The assignments were made by analogy with those of $PtCl_4^{2-}$ and $(N\text{-mpH})_2CuCl_4$, the vibrational energies of which are shown also for comparison. The out-of-plane bending mode of β_{2u} symmetry is both infrared and Raman inactive. As vibronic coupling with this mode has an important influence on the electronic spectrum of the $CuCl_4^{2-}$ ion, the energy of the vibration was estimated by normal coordinate analysis.[14] The calculated energy of $\bar{\nu}(\beta_{2u}) = {\sim}75$ cm^{-1} is quite similar to the value obtained by analysis of the optical spectrum (see below). The α_{1g} stretching mode occurs at slightly higher energy (290 cm^{-1}) in the creatininium salt than in those of the other two cations (275 and 276 cm^{-1}), and this may reflect the shorter Cu–Cl bond lengths in the former compound (225.1 pm as opposed to 226.5 and 226.8 pm). If the energy of the stretching vibration were to vary as about the sixth power of the bond length, a shift of the above amount would be expected.

Crystal Packing of the Complexes. Both $(metH)_2CuCl_4$ and $(creat)_2CuCl_4$ contain $CuCl_4^{2-}$ groups centered on crystallographic inversion points so that the metal and halide ions must in each case be coplanar. Although the crystallographic point group of each $CuCl_4^{2-}$ ion is no higher than C_i the only significant departure from a local D_{4h} point group is a slight inequivalence of the two Cu–Cl bond lengths (228.3 and 225.3 pm in $(metH)_2CuCl_4$[4] and 226.8 and 223.3 pm in $(creat)_2CuCl_4$[3]). In $(metH)_2CuCl_4$ the regions above and below the $CuCl_4^{2-}$ plane are devoid of ligand atoms,[4] while in $(creat)_2CuCl_4$ the closest axial contact is with an oxygen atom 364 pm from the copper(II) ion[3] so that the metal in both complexes is effectively four-coordinate. If the molecular *x* axis is defined to lie along the shorter Cu–Cl bonds, *z* defined to be orthogonal to the $CuCl_4^{2-}$ plane, and *y* defined to be orthogonal to *x* and *z*, the squares of the molecular projections made

Table II. Molecular Projections for the (100) Crystal Faces of the Complexes with the Electric Vector Parallel to the *b* and *c* Crystal Axes

compd	axis	molecular projections x^2	y^2	z^2
$(metH)_2CuCl_4$	*b*	0.21	0.73	0.06
	c	0.01	0.11	0.88
$(creat)_2CuCl_4$	*b*	0.98	0.01	0.01
	c	0.00	0.04	0.96

---

(14) M. J. Riley is thanked for carrying out these calculations. The computer program "Normal Coordinate Analysis" (*N.R.C.C. Bull.* **1976**, *No. 15*) was used for this purpose, good agreement being obtained with the energy of each other vibrational mode of the $CuCl_4^{2-}$ ion.

Table III. Vibronic Selection Rules for a Copper(II) Complex of D_{4h} Symmetry

transition	active vibr *xy*	active vibr *z*
$^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2-y^2)$	ϵ_u	
$^2E_g(xz,yz) \leftarrow {}^2B_{1g}(x^2-y^2)$	α_{2u}, β_{2u}	ϵ_u
$^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2-y^2)$	ϵ_u	β_{2u}

Table IV. Excited-State Energies (cm^{-1}) of Planar $CuCl_4^{2-}$ Ions

excited state	countercation *N*-mpH	metH *c*	metH *b*	creat *c*	creat *b*
$^2B_{2g}(xy)$	12480	12150		12320	
$^2E_g(xz,yz)$	14020, 14510	13960	14010	13880	14185
$^2A_{1g}(z^2)$	16990	16680	16440	16620	16360

by a vector parallel to the *b* and *c* crystal axes for the two complexes are listed in Table II.

Assignment of Excited States. The centrosymmetric nature of the chromophores in $(metH)_2CuCl_4$ and $(creat)_2CuCl_4$ means that the intensity of the "d–d" transitions must be induced by coupling with *u* vibrational modes.[11,15] Assuming that the effective point group for this vibronic coupling is D_{4h}, as was done previously for $(N\text{-mpH})_2CuCl_4$,[9] yields the symmetries of the vibrational modes allowing each electronic transition indicated in Table III. It should be noted that the transition $^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2-y^2)$ is allowed by vibrations of ϵ_u symmetry in *xy* polarization, rather than by those of α_{2u} and β_{2u} symmetry as stated incorrectly in ref 9. This transition is vibronically forbidden in *z* polarization, and for both complexes the electric vector is almost precisely along this direction when it is parallel to the *c* crystal axis (Table II). For both complexes the lowest energy band has a very low intensity in this polarization (Figures 1 and 2), confirming its assignment to the $^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2-y^2)$ transition as proposed for $(N\text{-mpH})_2CuCl_4$ on the basis of the poorly resolved molecular spectrum.[9] For $(creat)_2CuCl_4$, where the crystal spectra are virtually perfectly resolved into molecular components, the residual *z* intensity of the lowest energy band is negligible. The absence of any detectable intensity for this vibronically forbidden transition implies that, at least as far as this aspect of the spectra goes, the simple, oriented-gas model of vibronic coupling[11,15] operates quite effectively in $(creat)_2CuCl_4$. This contrasts with the interpretation of the temperature dependence and vibrational fine structure of some of the bands in these complexes, which imply that a significant fraction of the intensity is derived via coupling with lattice vibrational modes.

The assignment of the bands centered at ~14000 and ~16500 cm^{-1} follows that described previously for $(N\text{-mpH})_2CuCl_4$,[9] and the energies of the band maxima at 10 K in the *b* and *c* polarizations are given in Table IV, together with those of the (*N*-mpH) salt for comparison. The excited-state energies of the three complexes are very similar, so that the discussion given previously for $(N\text{-mpH})_2CuCl_4$[9] applies equally well for $(creat)_2CuCl_4$ and $(metH)_2CuCl_4$. The most interesting aspect of this is the unusually high energy of the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2-y^2)$ transition, which is apparently a characteristic feature of four-coordinate, planar complexes[16-18] and has been interpreted as being due to configuration interaction between the $a_{1g}(d_{z^2})$ and a_{1g} (4s) metal orbitals.[19]

Analysis of Vibrational Fine Structure. Vibrational fine structure has been observed in the electronic spectra of a number of metal complexes, and the theoretical interpretation of this has been treated in several books[20,21] and review articles.[11,15] For a centrosymmetric complex such as planar $CuCl_4^{2-}$, the "d–d" transitions are Laporte forbidden and derive their intensity from higher energy parity-allowed charge-transfer transitions via coupling with *u*-vibrational modes. In addition to the involvement of a single quantum of each active *u*-mode, any number of quanta of modes α_{1g} symmetry may be excited in an electronic transition. For excitations to orbitally degenerate electronic states, Jahn–Teller-active vibrations may also be involved in the transitions.[22-25] It has been suggested that the complex pattern expected if coupling with modes of the latter type occurs in addition to the coupling with those of α_{1g} symmetry may be the reason why vibrational fine structure is not resolved for the $^1E_g \leftarrow {}^1A_{1g}$ transition of $PtCl_4^{2-}$.[26] Similar arguments may perhaps explain the absence of vibrational structure on the $^2E_g(xz,yz) \leftarrow {}^2B_{1g}(x^2-y^2)$ transitions of $(metH)_2CuCl_4$ and $(creat)_2CuCl_4$ (Figures 1 and 2), though it should be noted that the orbital degeneracy is formally removed in these complexes by the slight inequivalent of the Cu–Cl bonds, and fine structure due to coupling with the α_{1g} mode is in fact observed on the transitions to the components of the $^2E_g(xz,yz)$ state in the analogous $(N\text{-mpH})_2CuCl_4$ complex.[9]

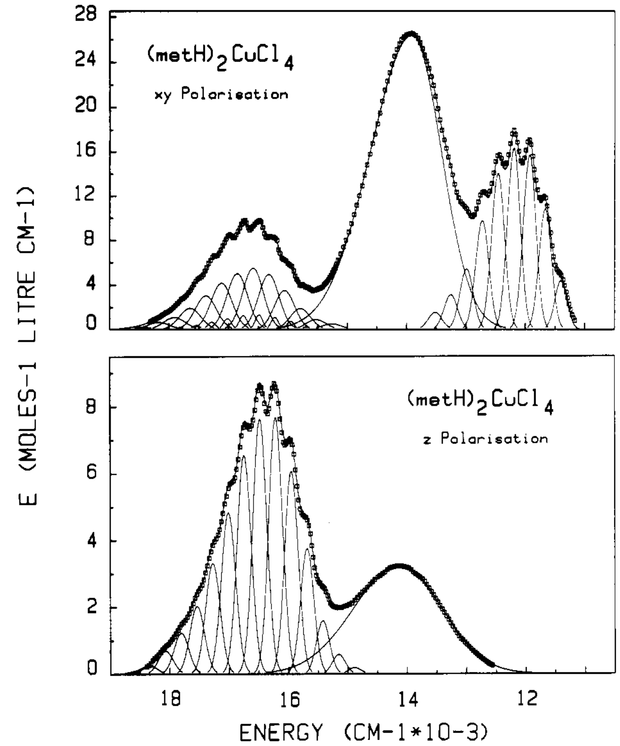


Figure 3. Electronic spectrum of $(metH)_2CuCl_4$ at 10 K showing resolution of lowest and highest energy bands into Gaussian vibrational components.

The low-temperature spectrum of $(metH)_2CuCl_4$ reveals vibrational structure for the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2-y^2)$ transition in both *xy* and *z* polarization, and for the $^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2-y^2)$ transition in *xy* polarization (Figure 3). For the former transition two progressions were resolved in *z* polarization. The theory of vibronic coupling[15] suggests that for transitions such as these the energy *E* of a progressional peak is given by

$$E = E_o + \bar{\nu}_u + n\bar{\nu}_{\alpha_{1g}} \quad (1)$$

---

(15) Flint, C. D. *Coord. Chem. Rev.* **1974**, *14*, 47. Cieślak-Golonka, M.; Bartecki, A. *Ibid.* **1980** *31*, 251.

(16) Mackey, D. J.; McMeeking, R. F.; Hitchman, M. A. *J. Chem. Soc., Dalton Trans.* **1979**, 299.

(17) Hitchman, M. A.; Bremner, J. B. *Inorg. Chim. Acta* **1978**, *27*, L61–L63.

(18) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1981**, *20*, 796.

(19) Smith, D. W. *Inorg. Chim. Acta* **1977**, *22*, 107. A minor error occurs in the expression for the $^2B_2 \rightarrow {}^2E$ transition energy quoted in this reference. The correct e_π coefficient is $\sin^2 2\theta - 2\cos^2 2\theta - 2\cos^2\theta$.

(20) Lever, A. B. P. Inorganic Electronic Spectroscopy, 2nd ed.; Elsevier: Amsterdam, 1984; Chapter 4.

(21) Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*; McGraw-Hill: New York, 1979.

(22) Solomon, E. I.; McClure, D. S. *Phys. Rev. B: Solid State* **1974**, *9*, 4690.

(23) Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1978**, *17*, 1729.

(24) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.

(25) Laurent, M. P.; Patterson, H. H.; Pike, W.; Engstrom, H. *Inorg. Chem.* **1981**, *20*, 372.

(26) Martin, D. S., Jr.; Tucker, M. A.; Kassman, A. J. *Inorg. Chem.* **1965**, *4*, 1682.

Table V. Parameters Obtained by Gaussian Analysis of the Bands in the Low-Temperature Spectrum of $(\mathrm{metH})_2\mathrm{CuCl}_4$

excited state	pol	vibr origin energy,[a] cm^{-1}	components half-width,[a] cm^{-1}
$^2\mathrm{A}_{1g}(z^2)$	xy	14 893 (5)	60 (10)[b]
	xy	14 994 (5)	195 (20)
$^2\mathrm{A}_{1g}(z^2)$	z	14 878 (10)	130 (5)
$^2\mathrm{B}_{2g}(xy)$	xy	11 403 (5)	120 (5)

[a] Values obtained by analysis of a typical crystal, with error limits in cm^{-1} indicated in parentheses. Analyses of other crystals yielded very similar results. [b] Progressional spacing held at a fixed value of 265 cm^{-1}.

where E_0 is the energy of the electronic origin, $\bar{\nu}_u$ is the energy of the u vibration inducing intensity, and n is the number of quanta of the α_{1g} mode of energy $\bar{\nu}_{\alpha_{1g}}$ that are excited. In order to determine accurately the relative positions and intensities of the vibronic components, a Gaussian analysis of the spectra was carried out. In this it was assumed that each progressional spacing was constant and that the half-width of each component increased progressively by $1.82n$ cm^{-1} compared with that of the initial member, due to the isotopic effects of chlorine on the spectrum.[9] The "best-fit" intensities of the components and their sum are compared with the experimental spectra in Figure 3, and the energies of the vibronic origins, half-widths, and progressional spacings are given in Table V.

In each case the progressional spacing is ~265 cm^{-1}, implying that the progression is in the α_{1g} totally symmetric stretching mode, which has an energy of ~275 cm^{-1} in the ground electronic state (Table I). The slight lowering in energy is consistent with the lengthening of the Cu–Cl bonds expected in each excited electronic state (see below). It should be noted that although the theory of vibronic coupling conventionally used to interpret fine structure on electronic transitions follows the above reasoning, an alternative model has been proposed in which the progression occurs in the u vibrational mode, inducing the intensity.[27,28] When the inducing mode is of ϵ_u symmetry, as has been the case in the system most widely studied previously, PtCl_4^{2-}, it is hard to distinguish between the two proposals, as one vibration of ϵ_u symmetry has an energy similar to that of the α_{1g} mode (Table I). However, the $^2\mathrm{A}_{1g}(z^2) \leftarrow {}^2\mathrm{B}_{1g}(x^2-y^2)$ transition in $(\mathrm{metH})_2\mathrm{CuCl}_4$ is allowed by coupling with the mode of β_{2u} symmetry, in z polarization, and the energy of this (~60 cm^{-1} from the temperature dependence of the band, ~75 cm^{-1} from normal coordinate analysis) is clearly far too low for this vibration to be responsible for the observed progression. Thus, at least in this case, it is apparent that the conventional interpretation of the vibrational structure is correct.

The $^2\mathrm{A}_{1g}(z^2) \leftarrow {}^2\mathrm{B}_{1g}(x^2-y^2)$ transition is allowed by vibrations of ϵ_u symmetry in xy polarization and β_{2u} symmetry in z polarization, so that the energies of the vibronic origins provide information about the relative energies of the inducing modes. The fact that a single progression is observed in z polarization implies that a single u mode dominates the intensity-stealing process. In agreement with this, planar CuCl_4^{2-} has a single mode of β_{2u} symmetry, and the temperature dependence of the band suggests that this has an energy of ~62 cm^{-1} (see following section). The vibronic origin energy of 14 878 cm^{-1} thus implies an electronic origin of ~14 816 cm^{-1} for this excited state. The vibronic origin energies of the two progressions observed in xy polarization imply energies of ~180 and ~80 cm^{-1} for the u modes, inducing intensity in the major and minor progressions, respectively. The energy of the former mode agrees well with that of the in-plane bending mode of ϵ_u symmetry (Table I). Presumably the weaker progression is due to coupling with a lattice mode of effective ϵ_u symmetry (a peak of moderate intensity occurs at 74 cm^{-1} in the infrared spectrum of $(\mathrm{metH})_2\mathrm{CuCl}_4$), or with the β_{2u} mode (energy ~60 cm^{-1} from the temperature dependence) despite the fact that this is not formally active in the xy polarization. It should be noted that although the minor progression was consistently found to be present in the spectra of good quality crystals when these were resolved along molecular axes, the very weak nature of the second progressions does mean that we cannot completely exclude the possibility that this is due to "contamination" of the xy spectrum by a small amount of z spectrum. It may be noted that a rather similar, though more extensive, pattern of vibrational fine structure has been observed for $(N\text{-mpH})_2\mathrm{CuCl}_4$.[9] Here the transitions to the $^2\mathrm{B}_{2g}(xy)$ and $^2\mathrm{E}_g(xz,yz)$ components consist of single progressions, while the $^2\mathrm{A}_{1g}(z^2)$ transition shows four progressions, a major one assigned to coupling with the lower energy metal–ligand ϵ_u mode and minor progressions built upon origins assigned to the excitation of lattice modes of effective ϵ_u symmetry. As with $(\mathrm{metH})_2\mathrm{CuCl}_4$, the component peaks of the bands in $(N\text{-mpH})_2\mathrm{CuCl}_4$ assigned to coupling with metal–ligand modes were considerably broader (half-widths 100–145 cm^{-1}) than those assigned to coupling with lattice modes (half-widths 20–30 cm^{-1}), though the reason for this difference is unclear.

The present spectra demonstrate that the lattice can have a profound influence on the resolution of vibrational fine structure in the electronic spectrum of a complex. The molecular geometries of the isolated CuCl_4^{2-} ions in $(N\text{-mpH})_2\mathrm{CuCl}_4$, $(\mathrm{metH})_2\mathrm{CuCl}_4$, and $(\mathrm{creat})_2\mathrm{CuCl}_4$ are virtually identical.[2-4] While the "d–d" transition energies and overall intensities and temperature dependences of the bands are very similar for the three complexes (Figures 1 and 2, and ref 9), the first complex shows extensive vibrational fine structure at low temperature, the second limited structure, and the third no structure at all. This cannot be due to poor resolution of the molecular spectra due to a crystal packing problem, as the molecular spectra are in fact best resolved in the creatinium salt. Clearly, the lattice strongly influences the vibrational fine structure without affecting the other spectral features significantly. The mechanism of this influence is not clear, though the temperature dependence of the bands in $(\mathrm{creat})_2\mathrm{CuCl}_4$ are quite similar to those in $(\mathrm{metH})_2\mathrm{CuCl}_4$ (see following section), suggesting that the effect of the lattice in the former complex may simply be to broaden the widths of the component peaks making up each band, rather than to contribute intensity via direct coupling with lattice modes. The profound influence which the lattice can have on the resolution of vibrational fine structure in optical spectra has also been noted for a range of complexes containing the $\mathrm{Ni(H_2O)_6}^{2+}$[29] and $\mathrm{Cr(NH_3)_6}^{3+}$ ions.[23]

Estimates of the Geometries of the Excited Electronic States. The relative intensities of the components of a band depend upon the displacement in the vibrational normal coordinate of the progression that accompanies the electron excitation. In the present case, the progression is in the totally symmetry α_{1g} breathing mode, and this is associated with an overall lengthening of each Cu–Cl bond as an electron is excited into the σ-antibonding $\mathrm{d}_{x^2-y^2}$ orbital. A convenient formula relating the absorption intensity I of the nth to the 0th member of a vibrational progression has been given by Yersin et al.[30]

$$\frac{I_n}{I_0} = \frac{E_n}{E_0}\left(\frac{R_n}{R_0}\right)^2 \tag{2}$$

where E is the energy of the relevant state and R is the vibrational overlap integral. These are given by

$$R_0 = [2\delta/(1+\delta^2)]^{1/2}\exp(-\tfrac{1}{2}\rho^2) \tag{3}$$

$$R_{n+1} = \frac{-2\delta D R_n - (2n)^{1/2}(\delta^2-1)R_{n-1}}{(\delta^2+1)[2(n+1)]^{1/2}} \tag{4}$$

where $\delta = (\bar{\nu}_1/\bar{\nu}_2)^{1/2}$, $D = C(m\nu_1)^{1/2}\Delta S$, and $\rho = D/(1+\delta^2)^{1/2}$. Here $\bar{\nu}_1$ and $\bar{\nu}_2$ are the vibrational frequencies in the ground and excited states, ΔS is the displacement along the normal coordinate,

---

(27) Hollebone, B. R. *Theor. Chim. Acta* **1980**, *56*, 45. This approach is discussed further in ref 20, pp 185–187.

(28) Hoggard, P. E.; Albin, M. *Inorg. Chem.* **1981**, *20*, 4413.

(29) Solomon, E. I.; Ballhausen, C. J. *Mol. Phys.* **1975**, *29*, 279.

(30) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951. Minor errors occur in the expressions quoted in this reference—in particular the value of the constant *C* is 0.1722: Zink, J. I., private communication. Errors also occur in ref 11, p 59, and ref 20, p 181; see: Henderson, J. R.; Muramoto, M.; Willett, R. A. *J. Chem. Phys.* **1964**, *41*, 580 and references therein.

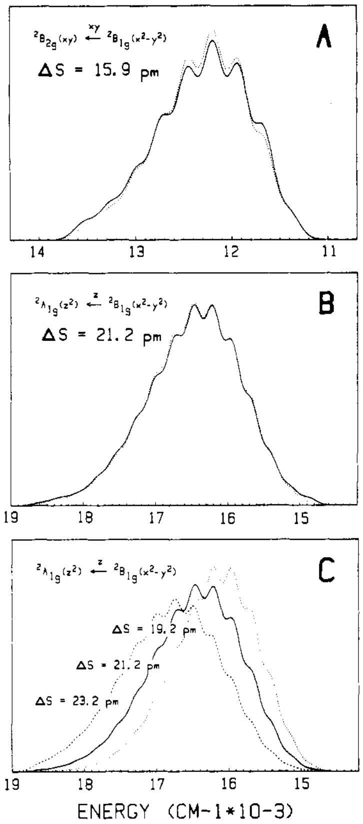


Figure 4. Band shapes derived from the Gaussian analysis of the *xy*-polarized $^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2 - y^2)$ (A) and the *z*-polarized $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ (B) transitions of (metH)$_2$CuCl$_4$ (full lines) compared with those calculated by using displacements of 15.9 and 21.2 pm (dashed lines), respectively, for displacements in the α_{1g} normal mode between the equilibrium nuclear geometries of the ground and excited electronic states. The sensitivity of the calculation is shown for the *z*-polarized $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition (C) where the band shape calculated with ΔS = 21.2 pm (full line) is compared with those estimated for changes of ΔS = 19.2 (dotted line) and 23.2 pm (dashed line).

and C is a constant. When the displacement occurs in the α_{1g} totally symmetric stretch, m is the mass of one ligand, and if this is in atomic mass units and ΔS is in Å, the constant C has the value 0.1722.[30]

Applying equations 2–4 to the estimates of the relative intensities of the components of the bands in (metH)$_2$CuCl$_4$ yields least-squares "best-fit" estimates of changes in the α_{1g} normal coordinate of 15.9 and 21.2 pm for transitions to the $^2B_{2g}(xy)$ and $^2A_{1g}(z^2)$ excited states in *xy* and *z* polarization, respectively. These correspond to changes of 7.9 and 10.6 pm in each Cu–Cl bond length, respectively.[11,30] The fit between the band shape deduced by Gaussian analysis of the observed spectra and that estimated by using eq 2–4 with the above bond length changes is shown in Figure 4 for the $^2B_{2g}(xy)$ and $^2A_{1g}(z^2)$ excited states. The estimated band shape is quite sensitive to the nuclear displacement, as may be seen for the curves calculated assuming values of ΔS = 19.2 and 23.2 pm for the latter transition.

The change in Cu–Cl bond length accompanying the excitation of an electron from the weakly antibonding d_{xy} and d_{z^2} orbitals to the more strongly antibonding $d_{x^2-y^2}$ orbital clearly depends on the difference in antibonding energy between the two orbitals, Δ, and inversely on the force constant f of the α_{1g} mode, which resists the displacement. It was recently shown[31] that if it is assumed that the d-orbital splitting in a complex varies inversely as some power n of the bond distance, then the expected change in bond length δr accompanying the d-electron rearrangement is given by the expression

$$\delta r \approx \frac{nm\Delta}{fNr_0} \tag{5}$$

where m is the number of electrons involved in the rearrangement, N is the number of ligands, and r_0 is the initial bond length (in the present cases $m = 1$, $N = 4$, and $r_0 = 227$ pm). This formula was found to give good agreement with the bond length changes deduced from the analysis of the electronic spectra of a wide range of metal complexes, as well as with the variation in bond lengths observed to accompany high ↔ low spin interconversions.[31] Simple theories[32] and experiment[33] both suggest that $n \approx 5$ for the "d–d" splitting in metal complexes, and the substitution of this value in eq 5, together with the appropriate transition energies (Table IV) and the force constant $f = 1.59$ mdyn Å^{-1} = 8.01 cm^{-1} pm^{-2} of the α_{1g} vibration in (metH)$_2$CuCl$_4$, yields the estimates δr = 8.5 and 11.4 pm for the transitions to the $^2B_{2g}(xy)$ and $^2A_{1g}(z^2)$ excited states, respectively, in excellent agreement with those from the analysis of the band shapes. The above interpretation ascribes the greater bond-length change associated with the excitation to the $^2A_{1g}(z^2)$ excited state to the larger difference in antibonding energy that occurs for this transition.

Temperature Dependence of the Bands. Variation of Band Intensities. For a vibronically allowed electronic transition activated by a single mode, the intensity is expected to increase as a function of temperature according to the relationship[11,15]

$$f_T = f_0 \coth\left(\frac{h\nu}{2kT}\right) \tag{6}$$

where h and k are the Planck and Boltzmann constants, f_0 and f_T are the oscillator strengths of the transition at 0 and T K, and ν is the frequency of the intensity-inducing vibration. This expression has been shown to be independent of the form of the excited-state potential surface,[34] though the intensity-inducing mode is assumed to be harmonic in the ground electronic state. The variations as a function of temperature of the intensities obtained by Gaussian analysis of the spectra of (metH)$_2$CuCl$_4$ and (creat)$_2$CuCl$_4$ are shown for each band in Figures 5 and 6. The effects of spin–orbit coupling and, in the case of (metH)$_2$CuCl$_4$, the minor corrections due to incomplete resolution of the crystal spectra into their molecular components as indicated in Table I were taken into account in these plots. For some transitions two modes may be responsible for inducing intensity. In these cases the variation of intensity as a function of temperature should take the form

$$f_T/f_0 = p_1 \coth\left(\frac{h\nu_1}{2kT}\right) + p_2 \coth\left(\frac{h\nu_2}{2kT}\right) \tag{7}$$

where f_0, f_T, h, and k are as before. Here, ν_i represents the frequency of the intensity-inducing vibration and p_i is the fraction of intensity produced by that mode at 0 K. The optimum curves calculated by using either eq 6 or 7 are shown in Figures 5 and 6, and the resulting estimates of p_i and the u mode energies are listed in Table VI.

The transition $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2-y^2)$ is allowed by modes of β_{2u} symmetry in z polarization, and only a single metal–ligand vibration has this symmetry for a planar complex. The observed temperature dependence of the band can be reproduced satisfactorily by using eq 6 for both the methadonium and creatininium salts, the energy of the β_{2u} mode giving optimum agreement with experiment, being 62 and 64 cm^{-1}, respectively. These values agree well both with one another and with the value of ~75 cm^{-1} obtained by the normal coordinate analysis of the planar CuCl$_4^{2-}$ ion. The transitions to the $^2B_{2g}(xy)$ and $^2A_{1g}(z^2)$ excited states in xy polarization and $^2E_g(xz,yz)$ in z polarization are each allowed by vibrations of ϵ_u symmetry. Two metal–ligand vibrations have this symmetry, one being an in-plane bend and the other an in-plane stretch. For the $^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition, although the average energy of the intensity-inducing mode cannot

---

(31) Hitchman, M. A. *Inorg. Chem.* **1982**, *21*, 821. The bond length change deduced from the analysis of the bandshape of planar CuCl$_4^{2-}$ is quoted incorrectly in this reference.

(32) Smith, D. W. *J. Chem. Phys.* **1969**, *50*, 2784. Bermejo, M.; Pueyo, L. *Ibid.* **1983**, *78*, 854.

(33) Drickamer, H. G. *J. Chem. Phys.* **1967**, *47*, 1880. Burns, G.; Axe, J. D. *Ibid.* **1966**, *45*, 4362.

(34) Lohr, L. L., Jr. *J. Chem. Phys.* **1969**, *50*, 4596.

Table VI

A. Average Energies of u Vibrational Modes Inducing Intensity into the "d–d" Transitions As Estimated from the Temperature Dependence of the Bands

excited state	pol	vibr sym	vibr energy,[a] cm^{-1} (metH)$_2$CuCl$_4$	vibr energy,[a] cm^{-1} (creat)$_2$CuCl$_4$
$^2B_{2g}(xy)$	xy	ϵ_u	200 (25)	205 (20)
$^2E_g(xz,yz)$	xy	β_{2u}, α_{2u}	100 (10)	110 (10)
	z	ϵ_u	110 (20)	85 (20)
$^2A_{1g}(z^2)$	xy	ϵ_u	165 (25)	155 (10)
	z	β_{2u}	62 (6)	64 (4)

B. Proportion of Intensity p_1 Induced at 0 K by the Higher Energy u Mode for Bands Where Two Modes Are Active

excited state	pol	(metH)$_2$CuCl$_4$ ν_1, cm^{-1}	(metH)$_2$CuCl$_4$ ν_2, cm^{-1}	(metH)$_2$CuCl$_4$ p_1	(creat)$_2$CuCl$_4$ ν_1, cm^{-1}	(creat)$_2$CuCl$_4$ ν_2, cm^{-1}	(creat)$_2$CuCl$_4$ p_1
$^2E_g(xz,yz)$	xy	159	62	0.62 (0.08)	150	64	0.75 (0.06)
$^2A_{1g}(z^2)$	xy	179	80	0.94 (0.05)			

[a] Estimated uncertainty indicated a parenthesis.

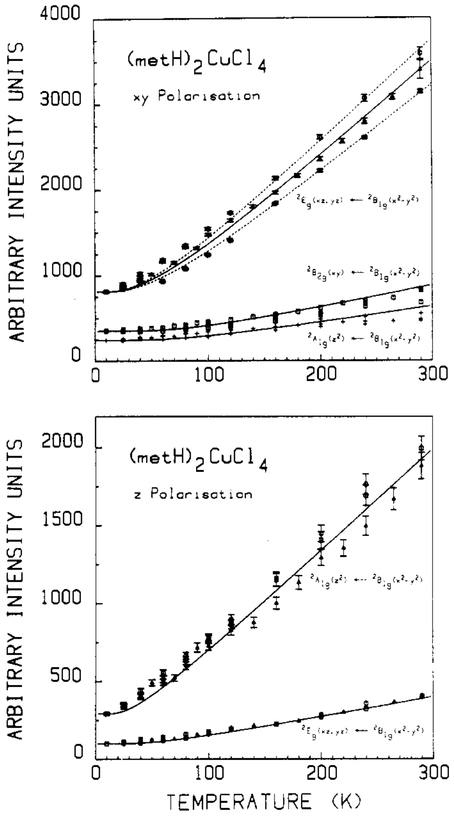


Figure 5. Variation of the intensities of the bands in the "d–d" spectra of (metH)$_2$CuCl$_4$ as deduced by Gaussian analysis at various temperatures. Error bars are shown where the uncertainty for most data points is larger than the symbol used to indicate the intensity. Measurements made on different crystals are distinguished by different symbols except for the lower intensity pair of transitions in xy polarization where this might cause confusion. The full lines show the variation in intensity calculated by using eq 6, where a single u mode is thought to dominate in the intensity mechanism, or eq 7, where two modes are thought to be active, the energies and relative activities of the vibrations being given in Table VI. The dashed lines show the calculated intensity variation of the $^2E_g(xz,yz) \leftarrow {}^2B_{1g}(x^2-y^2)$ transition in xy polarization for the range of proportions of the β_{2u} and α_{2u} modes indicated by the uncertainties in Table VI.

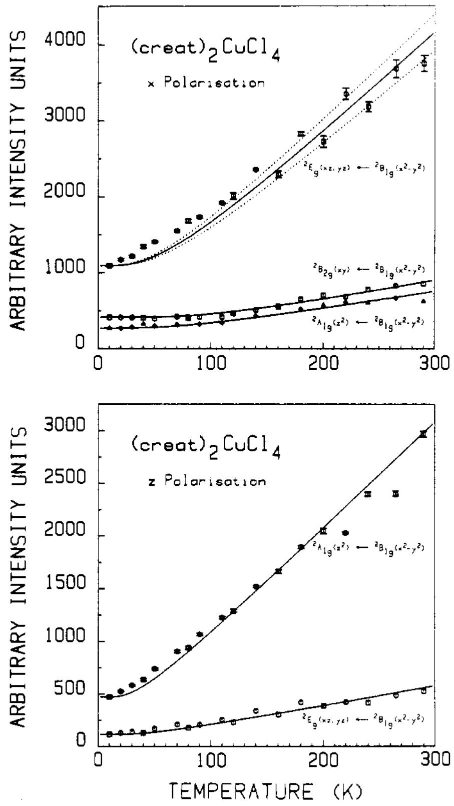


Figure 6. Variation of the intensities of the bands in the "d–d" spectra of (creat)$_2$CuCl$_4$ as deduced by Gaussian analysis at various temperatures. Error bars are shown where the uncertainty for most data points is larger than the symbol used to indicate the intensity, and measurements made on different crystals are distinguished by different symbols. The full lines show the variation in intensity calculated by using eq 6, where a single u mode is thought to dominate in the intensity mechanism, or eq 7, where two modes are thought to be active, the energies and relative activities being given in Table VI. The dashed lines show the calculated intensity variation of the $^2E_g(xz,yz) \leftarrow {}^2B_{1g}(x^2-y^2)$ transition in xy polarization for the range of proportions of the β_{2u} and α_{2u} modes indicated by the uncertainties in Table VI.

be deduced very accurately because of the weak nature of the band, the estimated value (~200 cm^{-1}) appears to be quite similar to that of the in-plane bend of ϵ_u symmetry (~180 cm^{-1}) for both salts, suggesting that in each compound the bulk of the intensity is derived by coupling with this vibration. The fact that a single u mode dominates in the intensity mechanism is in agreement with the observation that at low temperature this band is resolved into a progression built upon a single vibronic origin in the spectrum of (metH)$_2$CuCl$_4$ (Figure 3). For the transitions to the $^2A_{1g}(z^2)$ excited state in xy polarization the average energy of the intensity-inducing mode is ~165 cm^{-1} for the methadonium salt and ~155 cm^{-1} for the creatininium salt. This is lower than either metal–ligand mode of ϵ_u symmetry so that while it is likely that the bulk of the intensity is derived from coupling with the in-plane ϵ_u bending vibration, additional intensity must be induced by one or more lower energy modes. In the case of the methadonium salt, the band is in fact resolved at low temperature into progressions built upon two vibronic origins, and the relative energies of these imply coupling with the in-plane mode of ϵ_u symmetry of energy 180 cm^{-1} and a second mode of energy ~80 cm^{-1} (see preceding section). Assuming the total intensity to be the sum of that induced by coupling with these two modes, optimum agreement with the experimental temperature variation is obtained with the intensity at 0 K being derived ~94% from coupling with the metal–ligand ϵ_u bending vibration and ~6% from the lattice mode of effective ϵ_u symmetry. This is in good agreement with the relative areas of the two progressions, these being ~93% and ~7%, respectively. In the analogous (N-mpH)$_2$CuCl$_4$ complex, modes of this kind with energies as low as ~20 cm^{-1} were found to contribute to the intensity of the

$$^2A_{1g}(z^2) \xleftarrow{xy} {}^2B_{1g}(x^2 - y^2)$$

transition, and while these had only a very small effect near 0 K, their low energy meant that they significantly influenced the intensity at high temperature.[9] For the transition to the $^2E(xz,yz)$ excited state in z polarization the average energy of the intensity-inducing modes is quite low, ~110 cm^{-1} for both complexes. Because of the relatively low intensity of this band (Figures 1 and 2), the temperature-variation data is rather inaccurate, and this fact, combined with the lack of vibrational fine structure on the band, precludes any meaningful quantitative analysis of the number and energies of the intensity-inducing modes. However, it does seem likely that, as with the other transitions activated by vibrations of ϵ_u symmetry, the lower energy in-plane metal–ligand stretch is active, with significant intensity also coming from low-energy lattice modes.

The transition $^2E_g(xz,yz) \leftarrow {}^2B_{1g}(x^2 - y^2)$ is allowed by vibrations of β_{2u} and α_{2u} symmetry in xy polarization, and analysis of the temperature dependence of the bands using eq 6 suggests an average energy of ~105 cm^{-1} for the u modes inducing intensity. This is approximately midway between the energy of the α_{2u} mode (~150 cm^{-1}) and that estimated for the β_{2u} mode (~60 cm^{-1}). Assuming that the intensity is derived just from these two modes, optimum agreement with the observed temperature dependence is obtained with ~60% and ~75% of the intensity at 0 K being derived by coupling with the α_{2u} mode for the methadonium and creatininium salts, respectively.

An alternative way of representing the temperature variation of the intensity of a vibronically allowed transition is by means of the expression

$$\coth^{-1}(f_T/f_0) = \frac{h\nu}{2kT} \tag{8}$$

This implies that a plot of coth^{-1} (f_T/f_0) against $1/T$ should yield a straight line passing through the origin, with a slope proportional to the frequency of the active u mode. A plot of this kind for the intensity data of the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition of the methadonium salt is shown in Figure 7. It may be seen that the coth^{-1} relationship is indeed obeyed, the "best-fit" straight line yielding an estimate of 53 cm^{-1} for the energy of the β_{2u} mode active in inducing intensity. It should be noted that this estimate is somewhat lower than that obtained by fitting the data to eq 6 (62 cm^{-1}). This is because the use of the coth^{-1} (f_T/f_0) vs. $1/T$ relationship places greater emphasis on the low-temperature data. As the uncertainty in f_T/f_0 increases at low temperature, as f_T approaches f_0, we feel that more reliable estimates of the energies of the intensity inducing vibrations are obtained by fitting the data to eq 6. When two vibrational modes are active in inducing intensity, as is the case for the transition $^2E(xz,yz) \leftarrow {}^2B_{1g}(x^2 - y^2)$ in xy polarization, then the intensity variation should obey

$$\coth^{-1}(f_T/f_0) = 0.5 \ln\left(\frac{\arg + 1}{\arg - 1}\right) \tag{9}$$

where

arg =

$$p_1(1 + e^{-h\nu_1/kT})(1 - e^{-h\nu_1/kT})^{-1} + p_2(1 + e^{-h\nu_2/kT})(1 - e^{-h\nu_2/kT})^{-1}$$

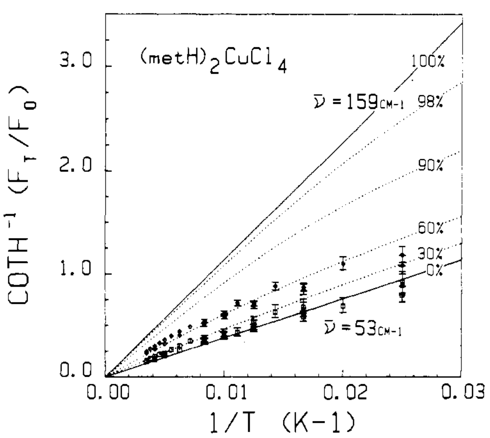


Figure 7. Plots of coth^{-1} (f_T/f_0) vs. $1/T$ for the z-polarized $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ and the xy-polarized $^2E_g(xz,yz) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transitions of (metH)$_2$CuCl$_4$. The full lines represent the temperature dependence calculated by assuming single u modes of energy 53 (lower line) and 159 cm^{-1} (upper line). The dotted lines give the calculated temperature dependence if both these modes are active in producing intensity with, in order of increasing slope, 30%, 60%, 90% and 98% of the intensity at 0 K induced by the higher energy vibration. Error bars are only shown for temperatures up to 120 K.

The plot of coth^{-1} (f_T/f_0) against $1/T$ is now expected to deviate from linearity (Figure 7), and this is indeed observed to be the case experimentally. Representing the data in this way suggests that the α_{2u} and β_{2u} modes are about equally effective in inducing intensity in the above transition at 0 K (Figure 7).

Intensities of the Bands Close to 0 K. In general terms, the spectra are considerably more intense in xy than in z polarization (Figures 1–3). As has been pointed out by Solomon et al.,[7] this is consistent with the fact that the "d–d" intensity is "stolen" largely from parity-allowed transitions of the same polarization, and for planar CuCl$_4^{2-}$ the xy-polarized charge-transfer transitions are far more intense than those of z polarization. It is also noteworthy that in both xy and z polarization the bands activated by the vibrations of β_{2u} and α_{2u} symmetry are more intense than those activated by the modes of ϵ_u symmetry. This may be related to the low energy of the former modes, which means that they have relatively large vibrational amplitudes. Although it might similarly be expected that the lower energy in-plane ϵ_u bend might induce more intensity than the higher energy stretching vibration of this symmetry, it is not clear why the latter vibration is apparently essentially inactive in the present complexes.

Shifts in Band Maxima as a Function of Temperature. One of the most interesting aspects of the "d–d" spectra of the present complexes is the significant shift of the band maxima to lower energy as the temperature is raised from 10 to 290 K (Figures 1 and 2), a feature which has already been commented on in the case of (creat)$_2$CuCl$_4$.[10] A shift to lower energy is indeed expected for transitions in which the intensity is derived by vibronic coupling, due to the contribution to the total intensity of "hot" bands built upon vibronic origins in which the vibrational quantum number V of the u mode of energy $\bar{\nu}$ decreases by 1 (i.e. $V_n \rightarrow V_{n-1}$) in conjunction with the electronic excitation.[11,15,35] This origin is ~$2\bar{\nu}$ lower in energy than that in which the vibrational quantum number increases by 1 ($V_n \rightarrow V_{n+1}$), the only kind of vibronic transition possible at 0 K. As these two types of transition contribute approximately equal amounts to the intensity, this provides an upper limit of ~$\bar{\nu}$ for the band maximum shift due to this mechanism. For the present compounds, this mechanism therefore predicts shifts of ~60–150 cm^{-1}, and decreases of this order of magnitude are indeed often observed in the electronic spectra of metal complexes on going from ~4 to ~290 K.[36,37] However, far larger shifts (~660–920 cm^{-1}) are observed for the present

---

(35) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; p 191.

(36) Holmes, O. G.; McClure, D. S. *J. Chem. Phys.* **1957**, *26*, 1686.

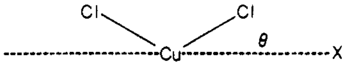
(37) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Inorg. Chem.* **1976**, *15*, 203.

compounds. Another possible mechanism for the observed red shifts could be a progressive increase in the metal–ligand bond lengths as the temperature is raised.[35] While this might perhaps be feasible for a continuous solid, for an isolated complex such as $CuCl_4^{2-}$ an increase of this kind corresponds to the thermal population of higher vibrational levels of the α_{1g} totally symmetric stretching mode, with this being significantly anharmonic. This mechanism has been considered quantitatively by Englman.[38] In the present case, however, the high energy of the α_{1g} mode ($\sim$280 cm^{-1}) means that excited vibrational levels of this will not be significantly populated in the temperature range under consideration; moreover, there is no evidence for any anharmonicity in the structure observed in the low-temperature spectra of $(metH)_2CuCl_4$ and $(N\text{-mpH})_2CuCl_4$.

A semiquantitative picture of a possible cause of the red shifts may be obtained by noting that the average nuclear geometry experienced by a d electron *at any instant of time* is not necessarily the *time-averaged* square-planar geometry, but rather the root-mean-square (rms) displacement along each normal coordinate. Usually, the amplitudes of normal vibrations are so small that considerations of this kind are irrelevant. However, in the present case, the energy of the β_{2u} mode is abnormally low. This means not only that its amplitude is large but also that highly excited vibrational levels may be thermally populated at relatively low temperatures. The β_{2u} vibration carries the $CuCl_4^{2-}$ ion toward a tetrahedral geometry, producing a ligand field of D_{2d} symmetry in which the d-orbital energy separations would be much smaller than those in the parent planar complex. On a simple, semiquantitative level, a possible cause of the "red shifts" is therefore that the d electrons experience a D_{2d} component to the ligand field, which increases progressively as the temperature is raised. A measure of the distortion is the average root-mean-square (rms) amplitude of the vibration at temperature T, and if the energy of the β_{2u} vibration is ν, this is given by[39]

$$\langle\theta^2\rangle^{1/2} = \left[\frac{h}{32\pi^2 cm\nu R^2}\coth\left(\frac{hc\nu}{2kT}\right)\right]^{1/2} \qquad (10)$$

where m is the mass of the ligand (amu) and R is the bond length (Å). Here θ is the angular distortion away from the time-averaged bond vectors:



The variation of the d-orbital energies as a function of θ is conveniently calculated by using the angular overlap model (aom) of the bonding in metal complexes, the appropriate expressions for the present situation having been given by Smith[19]

$$E(x^2 - y^2) = 3(\sin^4 \alpha)e_\sigma + (\sin^2 2\alpha)e_\pi \qquad (11a)$$

$$E(xy) = 4(\sin^2 \alpha)e_\pi \qquad (11b)$$

$$E(xz,yz) = \tfrac{3}{2}(\sin^2 2\alpha)e_\sigma + 2(\cos^2 \alpha + \cos^2 2\alpha)e_\pi \qquad (11c)$$

$$E(z^2) = (3\cos^2 \alpha - 1)^2 e_\sigma + 3(\sin^2 2\alpha)e_\pi - 4(3\cos^2 \alpha - 1)^2 e_{ds} \qquad (11d)$$

where $\alpha = \pi/2 - \theta$. Here, e_σ and e_π represent the energies by which the chloride ligands raise a d orbital by σ and π bonding, respectively, and e_{ds} represents the effect of the configuration interaction between the metal 4s and $3d_{z^2}$ orbitals.[19] The variation of the excited state energies as a function of θ calculated by using equation 11 is shown in Figure 8. Here, the transition energies observed for the planar complexes were used to obtain the metal–ligand bonding parameters, and it can be seen that the energies of the "d–d" transitions of the distorted $CuCl_4^{2-}$ ion present in Cs_2CuCl_4 (θ = 25°) are fitted satisfactorily by the calculated curves.

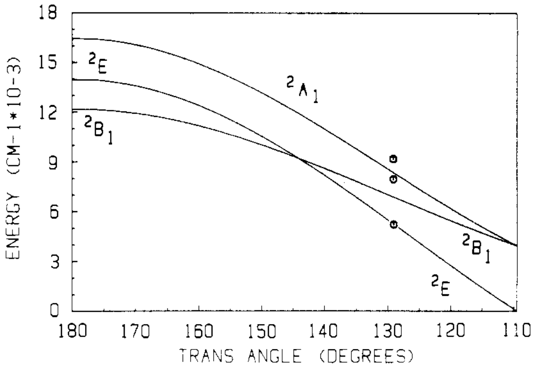


Figure 8. Variation of the d-orbital energies as a function of the ∠ClCuCl angle between trans chloride ions, calculated by using the angular overlap expressions given by Smith[19] using the parameters e_σ = 5250 cm^{-1}, e_π = 900 cm^{-1}, and e_{sd} = 1500 cm^{-1}. The transition energies observed for Cs_2CuCl_4[43] are shown in the diagram.

It is apparent that the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ and $^2E_g(xz,yz) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transitions are most sensitive to a distortion toward a tetrahedral geometry, the $^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition being much less affected. In agreement with the proposed explanation, the transition to the $^2A_{1g}(z^2)$ excited state exhibits the greatest red shift on warming from 10 to 290 K ($\sim$920 cm^{-1}), followed by the $^2E_g(xz,yz)$ state ($\sim$820 cm^{-1}), with the transition to the $^2B_{2g}(xy)$ state shifting least ($\sim$660 cm^{-1}), these changes being similar for the methadonium and creatininium salts. It is also noteworthy that the shift in each band maximum is essentially independent of polarization; that is, the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition, for instance, shows as large a shift in band maximum in xy polarization when it is activated by vibrations of ϵ_u symmetry, as in z polarization, when it is allowed by the β_{2u} mode implicated in the above model. This suggests that whatever factor causes the red shift of the band maxima, it is not directly related to the mechanism by which the bands gain intensity. However, it is clear that to explain the observed shifts by using the above model $\langle\theta^2\rangle^{1/2}$ is required to increase to $\sim$7.5° on warming from 10 to 295 K (Figure 8). This could only occur if the β_{2u} mode has an energy far lower than that suggested by the temperature dependence of the intensity of the bands activated by this vibration ($\sim$60 cm^{-1}). Substitution of $\bar{\nu} \approx 60$ cm^{-1} into eq 10 suggests a value of $\langle\theta^2\rangle^{1/2}$ = 1.11° at 0 K, rising to an average value of 2.93° and 290 K, and this implies shifts in band maxima of 80–120 cm^{-1} (Figure 8). A value $\bar{\nu} \sim 25$ cm^{-1} would produce shifts in band maxima as a function of temperature that agree with those observed experimentally, but this would imply that the intensities of those bands activated by this vibration should increase far more than is observed (a factor of 16.2 rather than the 6.7 that is observed).

Clearly, therefore, a marked discrepancy exists between the energy of the β_{2u} vibration derived from the band intensity variations ($\sim$60 cm^{-1}) and that obtained from the shift in the band maxima for the above model ($\sim$25 cm^{-1}). The vibrational energy inferred from the changes in band intensity must be considered more reliable, both because it relies on a well-established theoretical model and because it is supported by the analysis of the vibrational fine structure. Possibly, an entirely different mechanism from that outlined above is responsible for the red shifts in the band maxima. However, it seems to us unlikely that the relative ease with which the $CuCl_4^{2-}$ ion may be converted from the planar to the distorted-tetrahedral geometry, which is quantified by the low energy of the β_{2u} vibration, is unconnected with the anomalous influence of the temperature on the band positions. We are currently investigating two refinements of the above models to see whether the discrepancy can be removed: first, the possibility that the β_{2u} vibration is highly anharmonic; second, the possibility that the equilibrium nuclear geometry is displaced along the β_{2u} normal coordinate in the excited electronic states. It has been suggested that a change in geometry of this kind occurs in excited states of $Ni(CN)_4^{2-}$[40] and $PtCl_4^{2-}$.[41] While such an effect

---

(38) Englman, R. *Mol. Phys.* **1960**, *3*, 304.

(39) Cyvin, S. J. Molecular Vibrations and Mean Square Amplitudes; Elsevier Amsterdam, 1968, p 77.

(40) Ballhausen, C. J.; Bjerrum, N.; Dingle, R.; Erkis, K.; Hare, C. R. *Inorg. Chem.* **1965**, *4*, 514.

is forbidden to first order,[42] it is possible that higher order effects, combined with coupling to higher energy charge-transfer states, may be sufficient to produce such a displacement.

Conclusions

The overall energies, polarization behavior, vibrational fine structure, and temperature dependence of the bands observed in the electronic spectra of the planar $CuCl_4^{2-}$ ions in $(metH)_2CuCl_4$ and $(creat)_2CuCl_4$ may be explained reasonably well within the normal theoretical framework of vibronic coupling and ligand field theory described in previous publications. As with other similar complexes, the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transitions occur at unusually high energy, possibly due to configuration interaction between the metal $a_{1g}(d_{z^2})$ and $a_{1g}(4s)$ orbitals. Analysis of the vibrational structure observed on the transitions to the $^2B_{2g}(xy)$ and $^2A_{1g}(z^2)$ excited states of $(metH)_2CuCl_4$ suggests a lengthening of each Cu–Cl bond of ~8 and ~11 pm, respectively, in good agreement with theoretical predictions.

An unusual aspect of the spectra not readily explicable by using current simple theories is the abnormally large red shift observed for the band maxima of each "d–d" transition on warming from 10 to 290 K. An attempt has been made to explain these shifts in terms of a temperature-dependent low-symmetry component to the ligand field, this being caused by the low-energy β_{2u} vibration, which carries the complex from a planar toward a distorted-tetrahedral geometry. However, it was found that in order to explain the band maxima shifts in this way, the energy of the β_{2u} mode would have to be about half of the estimate of $\sim 60\ \mathrm{cm}^{-1}$ obtained from the analysis of the temperature dependence of the band intensities. The cause of this discrepancy is not clear.

Acknowledgment. The financial support of the Australian Research Grants Scheme is gratefully acknowledged. The Central Science Laboratory of the University of Tasmania is thanked for the loan of the cryostat used in the present work and Mark Riley is thanked for several useful discussions.

Registry No. $(metH)_2CuCl_4$, 72268-09-8; $(creat)_2CuCl_4$, 70602-46-9.

---

(41) Martin, D. S., Jr.; Tucker, M. A.; Kassman, A. J. *Inorg. Chem.* **1965**, *4*, 1682.

(42) We are concerned with the way in which the energy of an excited state ψ changes as the geometry alters from the equilibrium nuclear geometry of the ground state along a normal mode Q. This may be expressed as a power series:

$$\left\langle \psi \left| \left(\frac{\partial H}{\partial Q} \right)_0 \right| \psi \right\rangle Q + \left\langle \psi \left| \left(\frac{\partial^2 H}{\partial Q^2} \right)_0 \right| \psi \right\rangle Q^2 + \ldots$$

from which it follows that if ψ is nondegenerate, then Q must transform as α_{1g} for the linear term to be non-zero. Professor E. I. Solomon of Stanford University is thanked for pointing out this fact. However, it should be noted that this restriction does not apply to terms involving even powers: Q^2 etc.

(43) Deeth, R. J.; Hitchman, M. A.; Lehmann, G.; Sachs, H. *Inorg. Chem.* **1984**, *23*, 1310.

Contribution from the Departments of Chemistry, Texas A&M University, College Station, Texas 77843, and University of Delaware, Newark, Delaware 19716

Ligand Substitution Processes in Tetranuclear Carbonyl Clusters. 10. X-ray Structural Characterization of Products Resulting from Reactions of $Co_4(CO)_9$(tripod), tripod = $HC(PPh_2)_3$, with Phosphine Ligands

Donald J. Darensbourg,*[1a] David J. Zalewski,[1a] Arnold L. Rheingold,*[1b] and Rebecca L. Durney[1b]

Received January 28, 1986

The solid-state geometry of $Co_4(CO)_8(PMe_3)$(tripod) (I), $Co_4(CO)_7$(dppm)(tripod) (II), and $Co_4(CO)_7(PMe_3)_2$(tripod) (III) were determined by single-crystal X-ray diffraction studies. I crystallizes in an orthorhombic cell *Pbca* with a = 16.864 (5) Å, b = 16.989 (3) Å, and c = 34.676 (9) Å with eight molecules per unit cell. II crystallizes in a monoclinic cell $P2_1/c$ with a = 12.001 (4) Å, b = 21.955 (10) Å, c = 25.329 (9) Å, and β = 99.40 (3)° with four molecules per unit cell. III crystallizes in an orthorhombic cell $Pca2_1$ with a = 24.831 (6) Å, b = 11.999 (2) Å, and c = 19.191 (4) Å with four molecules per unit cell. The structures were refined to the following values: I to R = 0.0626 and R_w = 0.0589, II to R = 0.0900 and R_w = 0.0910, and III to R = 0.0706 and R_w = 0.0663. The solid-state structures were used to substantiate the solution structural assignments based on IR and ^{31}P and ^{13}C NMR spectroscopy and to assist in identifying the specific site of ligand dissociation in this series of clusters.

Introduction

As part of an extensive agenda to evaluate reaction pathways of polynuclear metal carbonyl derivatives, we have investigated ligand substitutional processes in tetranuclear group 9 metal species. Mechanistic aspects of carbon monoxide displacement reactions in $Co_4(CO)_{12}$ and its phosphine/phosphite derivatives have received much of our attention.[2] For example, the rates of CO dissociation in the sequential CO substitution reactions (eq 1) differed by less than 1 order of magnitude for all complexes

$$Co_4(CO)_{12} \xrightarrow[+L]{-CO} Co_4(CO)_{11}L \xrightarrow[+L]{-CO} Co_4(CO)_{10}L_2 \xrightarrow[+L]{-CO} Co_4(CO)_9L_3 \xrightarrow[+L]{-CO} Co_4(CO)_8L_4 \quad (1)$$

thus far examined. Furthermore, via ligand isotope double-labeling studies we were able to conclusively demonstrate that during ligand substitution reactions of $Co_4(CO)_{12}$ with phosphorus ligands to afford $Co_4(CO)_{11}L$ derivatives *no* cluster fragmentation occurs.[3]

Since ligand substitution processes involving metal carbonyls are often dependent on the nature and concentration of the incoming ligand (L) (eq 2),[4] rate parameters for the individual steps in eq 1 have been determined by employing ^{13}CO as incoming ligand. In this instance because of the low nucleophilicity of

$$\text{rate} = k_{\text{obsd}}[M_n(CO)_m] = (k_1 + k_2[L])[M_n(CO)_m] \quad (2)$$

carbon monoxide no ligand-dependent term ($k_2[L]$) is noted in the rate expression. Nevertheless, the ligand-independent pathway may be ascribed to either metal–metal bond fission or M–CO bond dissociation, assuming incoming ligand (L) trapping of the intermediate is fast relative to metal–metal bond re-formation. In efforts to assess the importance of metal–metal bond fission during ligand substitution reactions, where M–M bond cleavage does not lead to cluster fragmentation, rate data for CO displacement in $Co_4(CO)_9$(tripod) have been obtained.[5] In this derivative, which was initially synthesized by Osborn and co-workers,[6] one triangular

---

(1) (a) Texas A&M University. (b) University of Delaware.

(2) (a) Darensbourg, D. J.; Incorvia, M. J. *J. Organomet. Chem.* **1979**, *171*, 89. (b) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1980**, *19*, 2585. (c) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1981**, *20*, 1911. (d) Darensbourg, D. J.; Peterson, B. S.; Schmidt, R. E., Jr. *Organometallics* **1982**, *1*, 306.

(3) Darensbourg, D. J.; Zalewski, D. J. *Inorg. Chem.* **1984**, *23*, 4382.

(4) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.

(5) Darensbourg, D. J.; Zalewski, D. J.; Delord, T. *Organometallics* **1984**, *3*, 1210.

0020-1669/86/1325-3281$01.50/0