Electronic Spectrum and *d*-Orbital Energies of the Planar CuCl₄²⁻ Ion in Bis(creatininium) Tetrachlorocuprate

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Summary The low temperature, polarized electronic spectrum of the (100) crystal face of (creatininium)₂CuCl₄ is reported and interpreted in terms of a *d*-orbital energy sequence $d_{x^2-y^2} \gg d_{xy} > d_{xz} > d_{yz} > d_{z^2}$ for the planar CuCl₄²⁻ ion present in this compound; the marked temperature dependence of the spectrum and its comparison with that of the similar compound (PhCH₂CH₂-NH₂Me)₂CuCl₄ suggests that coupling both with lattice modes and an out-of-plane bonding mode of very low energy is important in the mechanism by which the electronic transitions gain intensity in compounds of this kind.

The electronic spectrum of planar CuCl₄²⁻ is of particular interest as the energy levels of this ion have been the subject of numerous theoretical studies, both of a sophisticated nature[1,2] and in testing simple models of the bonding in transition metal complexes.[3] Until recently, however, the only compound known to contain this ion with no axial ligand interaction was (PhCH₂CH₂NH₂Me)₂CuCl₄, (nmph)₂CuCl₄.[4] The electronic spectrum of this complex suggested *d*-orbital energies in agreement with simple theory except that the d_{z^2} orbital was *ca.* 5000 cm⁻¹ lower in energy than expected, this being rationalized in terms of the configuration interaction with the metal 4*s* orbital expected in a planar, truly 4-co-ordinate complex.[5] The spectrum was also unusual in showing extensive vibrational fine structure at low temperatures,[6,7] some of which was attributed to coupling with what are formally lattice modes.[7] However, the spectral analysis was hampered by the unfortunate crystal packing of the CuCl₄²⁻ groups, which did not allow the clear resolution of the crystal spectra into their molecular components. Recently, the
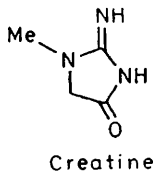
Creatine

crystal structure of a second compound containing planar CuCl₄²⁻ ions, (creatininium)₂CuCl₄, has been reported.[8] The dimensions of the CuCl₄²⁻ unit in this compound are virtually identical to those in (nmph)₂CuCl₄. Moreover, ligand interactions orthogonal to the plane of the complex in (creatininium)₂CuCl₄ are confined to two very distant oxygen atoms (Cu–O distances 3·64 Å) and the crystal packing allows the molecular spectra to be resolved quite readily. This compound therefore provides an ideal means of investigating the energy levels in simple systems such as CuCl₄²⁻, and how these are affected by the environment of the surrounding lattice and the presence of very distant axial ligands.

Green crystals of (creatininium)₂CuCl₄ were prepared by the method of Udopa and Krebs[8] and had a satisfactory analysis. The compound crystallized with the (100) face well developed and electronic spectra were recorded over a temperature range using a Cary 17 spectrophotometer with the electric vector of light parallel to the *b* and *c* crystal axes. Typical spectra are shown in the Figure.
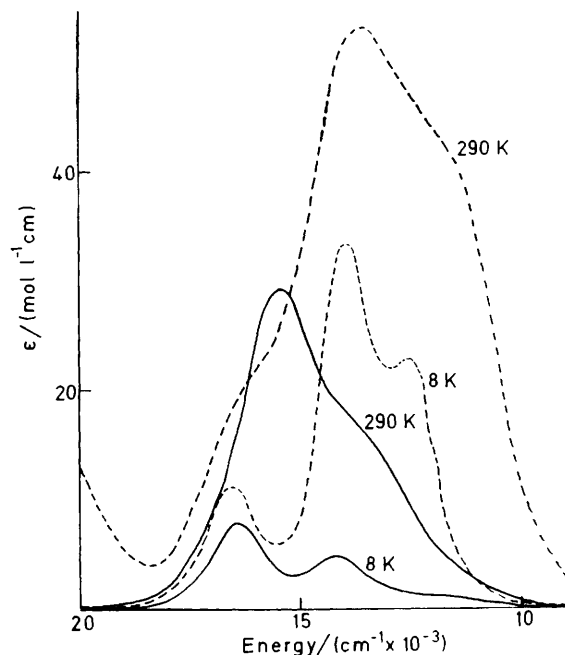
Figure. Electronic spectrum of the (100) crystal face of (creatininium)₂CuCl₄ measured at 290 and 8 K with the electric vector of light parallel to the *b* (– – – –) and *c* (——) crystal axes.

The complex crystallizes in the spacegroup P2₁/c with the unit cell parameters $a = 8·080$, $b = 7·831$, $c = 13·922$ Å, and $\beta = 113·77°$.[8] The CuCl₄²⁻ ion in (creatininium)₂CuCl₄ is rigorously centrosymmetric with Cu–Cl bond lengths of 2·233 and 2·268 Å and Cl–Cu–Cl angles of 89·9 and 90·1°. The complex thus belongs to the D_{2h} point group, with the departure from D_{4h} symmetry being due to the slight difference between the Cu–Cl bond distances. A molecular co-ordinate system was defined with *x* and *y* parallel to the shorter and longer Cu–Cl bonds and *z* orthogonal to these. The squares of the molecular projections made by a unit vector along the *b* and *c* crystal axes are $0·98x^2 + 0·01y^2 + 0·01z^2$ and $0·00x^2 + 0·04y^2 + 0·96z^2$, respectively, so that the *b* and *c* crystal spectra (Figure) correspond almost exactly to the *x* and *z* molecular spectra. The vibronic selection rules for a copper(II) complex with D_{2h} symmetry and a $^2A_g(x^2 - y^2)$ ground state are that transitions to the $^2B_{1g}(xy)$, $^2B_{2g}(xz)$,

and $^2B_{3g}(yz)$ states are forbidden in z, y, and x polarization, respectively (the d-orbital containing the unpaired electron being indicated in parentheses). The spectra at 8 K show peak maxima at 12,500, 13,840, and 16,530 cm^{-1} in x polarization and 14,185 and 16,390 cm^{-1} in z polarization. The selection rules therefore clearly suggest that the lowest energy peak is due to the transition $^2B_{1g}(xy) \leftarrow \, ^2A_g(x^2 - y^2)$. Since the departure from D_{4h} symmetry is small the $^2B_{2g}(xz)$ and $^2B_{3g}(yz)$ states are expected to occur close together, with the latter slightly higher in energy because of the stronger ligand perturbation along the x axis. As the central peak occurs at 13,840 cm^{-1} in x polarization when the transition $^2B_{2g}(xz) \leftarrow \, ^2A_g(x^2 - y^2)$ is allowed, and 14,185 cm^{-1} in z polarization when both this transition and that to the $^2B_{3g}(yz)$ state are allowed, this is consistent with the $^2B_{2g}(xz)$ state lying at 13,840 cm^{-1} and the $^2B_{3g}(yz)$ state being at $ca.$ 14,530 cm^{-1}. The highest energy peak is then assigned to the transition $^2A_g(z^2) \leftarrow \, ^2A_g(x^2 - y^2)$.

The excited state energies of (creatininium)$_2$CuCl$_4$ are quite similar to those in (nmph)$_2$CuCl$_4$ [$^2B_{1g}(xy) = 12,500$ cm^{-1}, $^2B_{2g}(xz) = 14,050$ cm^{-1}, $^2B_{3g}(yz) = 14,450$ cm^{-1}, $^2A_g(z^2) = 17,000$ cm^{-1}],[6] the observed sequence of d-orbitals agreeing with some theoretical calculations[1] but not with others.[2] The values $E(xy)$ 12,500 cm^{-1} and $E(xz,yz)$ $ca.$ 14,200 cm^{-1} suggest angular overlap parameters e_σ $ca.$ 5300 cm^{-1} and e_π $ca.$ 850 cm^{-1} for Cl$^-$ towards Cu^{II} in these complexes.[9] The high energy of the $^2A_g(z^2)$ state in planar complexes of this kind has been rationalized in terms of configuration interaction between the $a_{1g}(z^2)$ and $a_{1g}(4s)$ orbitals.[5] The magnitude of this depends on the difference in ligand interaction along the z and (xy) axes, which, because of the diffuse nature of the $4s$ orbital, is only expected to be significant when the axial bonds are very long or entirely absent as in (nmph)$_2$CuCl$_4$. In (creatininium)$_2$CuCl$_4$ the $^2A_g(z^2)$ state is 600 cm^{-1} lower in energy than that in (nmph)$_2$CuCl$_4$, which may indicate a weak interaction with the axial oxygen atoms (Cu–O distance 3·64 Å) in the former compound. This would correspond to a decrease of $ca.$ 5% in the magnitude of the coefficient of the $4s$ orbital in the $a_g(z^2)$ wavefunction[5] of (creatininium)$_2$CuCl$_4$ compared with the value of $ca.$ 0·25 estimated[7] for (nmph)$_2$CuCl$_4$.

The low-temperature spectrum of (creatininium)$_2$CuCl$_4$ differs markedly from that of (nmph)$_2$CuCl$_4$ in that it contains virtually no evidence of the extensive vibrational fine structure observed[6,7] for the latter compound. Only the lowest energy peak shows a barely discernible progression, the spacing of $ca.$ 260 cm^{-1} being similar to those observed in (nmph)$_2$CuCl$_4$ and suggesting that it involves excitation of the a_{1g} symmetric stretching mode. Since the geometries of the CuCl$_4$$^{2-}$ groups in the two compounds are virtually identical, this agrees with the supposition[7] that in (nmph)$_2$CuCl$_4$ coupling with what are formally lattice modes plays an important part in the vibronic intensity mechanism. As with (nmph)$_2$CuCl$_4$, the spectral peaks of (creatininium)$_2$CuCl$_4$ show marked decreases in intensity on cooling, and significant shifts of the band maxima to higher energy. The $^2A_g(z^2) \leftarrow \, ^2A_g(x^2 - y^2)$ transition is quite exceptional in this respect, the band maximum shifting by $ca.$ 1000 cm^{-1}. The crystal structure indicated an anomalously large temperature factor perpendicular to the CuCl$_4$$^{2-}$ plane for the chlorine atoms in (creatininium)$_2$-CuCl$_4$, suggesting either an out-of-plane bending mode of very low energy or a slight distortion towards a tetrahedral geometry, possibly dynamic in nature.[8] The excited state energies suggest that no tetrahedral distortion is present, at least at 8 K. The marked temperature dependence is consistent with the out-of-plane bending made of b_{2u} symmetry in the D_{4h} point group being active in inducing intensity and having a very low energy (much of the intensity in the spectrum of (nmph)$_2$CuCl$_4$ was also found to be derived from this mode, the energy in this case being $ca.$ 100 cm^{-1}).[7] It is hoped to clarify this point by making a detailed study of the electronic spectra of several crystal faces of (creatininium)$_2$CuCl$_4$ in the near future.

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