The *X*-Ray Crystal Structure and Electronic Energy Levels of the Square-pyramidal μ-Formato-monodiethylenetriaminecopper(II) Formate

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Summary The crystal structure of μ-formato-monodiethylenetriaminecopper(II) formate has been determined and shown to contain a square-pyramidal stereochemistry: the single-crystal electronic properties indicate a one-electron orbital sequence $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} > d_{yz}$ consistent with the low axial distortion present.

THE square-based pyramidal stereochemistry[1] is probably one of the most common geometries for complexes of the copper(II) ion and yet the ordering of the one-electron energy levels of the copper(II) ion in this geometry has not been clearly established.[2] Preliminary examination of the electronic properties of μ-formato-monodiethylenetriamine-copper(II) formate, particularly the presence of a "penta-ammine type" electronic reflectance spectrum[3] suggested a square-pyramidal stereochemistry. As the single-crystal electronic properties of the complex suggested that the local molecular axes were aligned parallel in the unit cell, the *X*-ray crystal structure of [Cu(dien)(HCO_2)]HCO_2 was determined [(dien) = diethylenetriamine].

The dark-blue crystals are orthorhombic (space group *Pnam*) with $a = 8{\cdot}954$, $b = 11{\cdot}640$, $c = 9{\cdot}676$ Å and $Z = 4$. 893 unique, non-zero reflections were estimated visually from single-crystal precession photographs, using Mo-K_α radiation, of the 0—4 layers precessing about *b*, *c*, and (0,1,1). Systematic absences in the *X*-ray spectra indicated that the space group was either $Pna2_1$ or *Pnam*, the latter being indicated from the three-dimensional Patterson synthesis and subsequently confirmed by the structure analysis. The structure was solved by normal heavy-atom methods, and refined by full-matrix least-squares techniques with individual isotropic thermal parameters. The present *R*-value is 0·079. The molecular structure is illustrated in Figure 1, together with the relevant bond lengths about the copper(II) ion. There are no discrete $[Cu(dien)(HCO_2)]^+$ ions in the crystal; chains of ions are formed about the 2_1 axes parallel to *a*; the copper(II) atoms are linked by formate groups in an *anti–syn* bridging arrangement.[4] Each $[Cu(dien)(HCO_2)]$ group possesses mirror symmetry (space group imposed) and the copper atom environment is essentially square-pyramidal. The copper atom is displaced 0·31 Å towards the apical oxygen atom from the mean plane of the three basal nitrogen atoms and basal oxygen atom. The local molecular axes (Figure 1) of the four molecules in the unit cell are aligned parallel. The second formate ion is present as a free ion in the unit cell.

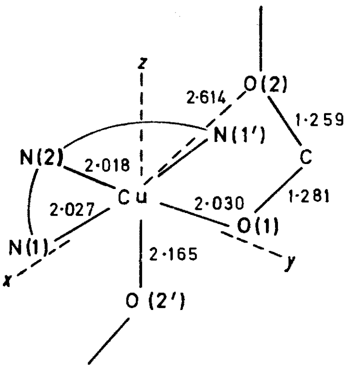

FIGURE 1. *The molecular structure of* $[Cu(dien)(HCO_2)]HCO_2$. σ, Cu–O, N = 0·007—0·009.

$<$N(1)–Cu–N(2) = 85·6°, $<$N(1)–Cu–N(1′) = 169·2°
$<$N(2)–Cu–O(1) = 152·8°, $<$N(1)–Cu–O(2′) = 94·5°
$<$N(2)–Cu–O(2′) = 111·6°, $<$O(1)–Cu–O(2′) = 95·7°
$<$O(1)–Cu–O(2) = 55·1°.

The room temperature magnetic moment ($\mu_{eff} = 1{\cdot}95$ B.M.) shows no evidence of exchange coupling[2,5] *via* the formate bridges. The single-crystal e.s.r. spectra gives three *g*-values, $g_1 = 2{\cdot}0341$, $g_2 = 2{\cdot}0939$, and $g_3 = 2{\cdot}2437$ which lie parallel to the *x*, *y*, and *z* axes respectively of the local molecular chromophore and suggest[2] a $d_{x^2-y^2}$ ground state. The polarised single-crystal electronic spectra are shown in Figure 2 and indicate an effective symmetry lower than axial (the strict crystallographic site symmetry is C_s). In view of the molecular structure an effective symmetry of C_{2v} is suggested. The assignment[6] of the electronic spectra is given in the Table. The most intense spectrum in each polarisation is readily assigned, the band at 14·2 kK is only indicated by Gaussian analysis of the *z*-polarised spectrum and is assigned as the electronically forbidden $d_{xy} \rightarrow d_{x^2-y^2}$ transition. This assignment yields the tentative one-electron orbital sequence $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} > d_{yz}$.

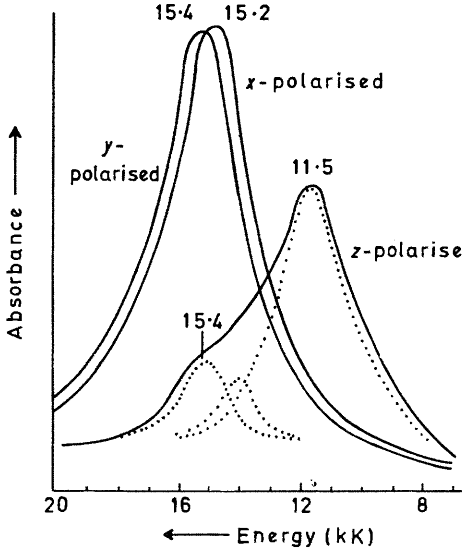

FIGURE 2. *The polarised single-crystal electronic spectra of* $[Cu(dien)(HCO_2)]HCO_2$. (· · · ·) *Gaussian analysis of z-polarised spectrum.*

The assignment of the electronic spectra of $[Cu(dien)\ (HCO_2)]HCO_2$ *with a* d_{x2-y2} *ground state in* C_{2v} *symmetry* (*kK*)

Transition	Energy	Transition	Energy
$d_{z^2} \rightarrow d_{x^2-y^2}$	11·5	$d_{xz} \rightarrow d_{x^2-y^2}$	15·2
[$d_{xy} \rightarrow d_{x^2-y^2}$	14·2]	$d_{yz} \rightarrow d_{x^2-y^2}$	15·4

This is the first clear example of the assignment of a copper(II) complex with a square pyramidal stereochemistry and the low energy[7] of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition (11·5 kK) supports the low tetragonal distortion[6,8] present in this stereochemistry due to the close approach of a single fifth ligand. The assignment of these spectra also substantiates the earlier suggestion,[3] on the basis of their electronic reflectance spectra, that the $Cu(NH_3)_5{}^{2+}$ and $[Cu(en)_2\text{-}NH_3]^{2+}$ cations have a square-pyramidal stereochemistry.

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