Single-crystal Electronic and Electron Spin Resonance Spectra of the Two Forms of Bis(nitrato)bis-(α-picoline)copper(II) and of Bis(nitrato)-mono(pyrazine)copper(II)

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The polarised single-crystal electronic and e.s.r. spectra of the two forms of bis(nitrato)bis-(α-picoline)copper(II) and of bis(nitrato)mono(pyrazine)copper(II) have been measured. The polarised single-crystal spectra of the first two complexes are assigned in an effective symmetry of C_{2v} and those of the last complex in D_{2h} symmetry. All three complexes yield the same one-electron orbital sequence, namely $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{xz}$, but with significant differences in the energies involved which are correlated with the different molecular structures present and in particular with the potential bonding role of the terminal nitrate oxygen atoms positioned off-the-z-axis.

THE electronic properties associated with the four-co-ordinate rhombic coplanar CuO_2N_2 chromophore, as in bis-(*N*-n-propylsalicylaldiminato)copper(II), have been described recently.[1] They are characterised by a high energy for the $d_{z^2}\rightarrow d_{x^2-y^2}$ transition and by evidence for significant out-of-the-plane π-bonding. A com-

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[1] R. J. Dudley, R. J. Fereday, B. J. Hathaway, and P. G. Hodgson, *J.C.S. Dalton*, 1972, 1341.

parable CuO_2N_2 chromophore also exists in the structure of *trans*-bis(monochloroacetato)bis-(α-picoline)copper(II) in which the co-ordination number is increased to six by the presence of two further oxygen atoms positioned off-the-*z*-axis (ref. 2, Figure 1A). The electronic properties[3] of Cu(α-pic)$_2$ $(ClCH_2CO_2)_2$ suggested that these off-the-*z*-axis oxygen atoms must be included in describing the tetragonality present.[4] The recent *X*-ray crystallographic determination of the structures of the two forms[5] (I) and (II) of bis(nitrato)bis-(α-picoline)copper(II) and of bis(nitrato)mono(pyrazine)copper(II)[6] (Figure 1) offer a further opportunity to examine the role[6,7] of these off-the-*z*-axis ligands especially as in the first two complexes the $CuO_2N_2O_2'$ chromophore is clearly non-centrosymmetric while in $Cu(NO_3)_2C_4H_4N_2$ it is centrosymmetric. The electronic properties of these three complexes (measured as described previously)[8-10] are now reported.

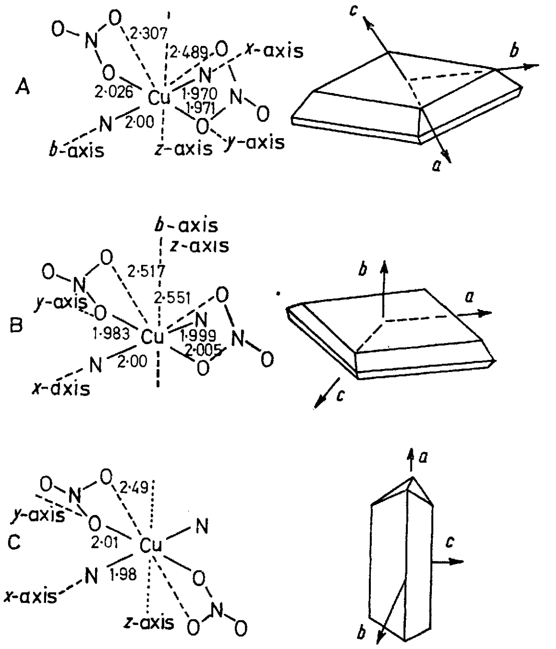

FIGURE 1 The molecular structures and crystal morphologies of A, Cu(α-pic)$_2$$(NO_3)_2$, cold form (I); B, Cu(α-pic)$_2$$(NO_3)_2$, hot form (II); and C, $Cu(NO_3)_2C_4H_4N_2$

EXPERIMENTAL

Preparation.—Cu(α-pic)$_2$$(NO_3)_2$ (I *and* II). The cold form (I) was prepared[5] by stirring $Cu(NO_3)_2,3H_2O$ (12·5 g) with 2,2-dimethoxypropane (25 cm^3) in methanol (200 cm^3) at room temperature for *ca.* 1 h. α-Picoline (10 cm^3) was then added and the solution allowed to stand. Purple crystals separated after 24 h. The hot form (II) was prepared as above except that the solution was boiled at each stage and the final hot solution was filtered through Celite (B.D.H.) before being set aside. Purple crystals separated after 24 h. $Cu(NO_3)_2C_4H_4N_2$ was prepared by the literature method[6] as royal blue crystals.

RESULTS AND DISCUSSION

E.s.r. Spectra.—The single-crystal e.s.r. spectra of all three complexes yielded three crystal *g*-factors (Table 1) with no evidence of hyperfine structure. The local molecular axes of the $CuO_2N_2O_2'$ chromophores of the different molecules in the unit cells of all three complexes[2,5,6] are not aligned strictly parallel, but in all three complexes the misalignments are so small[5,6] that they can be ignored and therefore the crystal *g*-factors are equated with the local molecular *g*-factors.

TABLE 1

The single-crystal and molecular *g*-factors for A, Cu(α-pic)$_2$$(NO_3)_2$, cold form (I); B, Cu(α-pic)$_2$$(NO_3)_2$, hot form (II); and C, $Cu(NO_3)_2C_4H_4N_2$[7]

	g_x	g_y	g_z	R
A	2·0563	2·0742	2·2740	0·0896
B	2·0619	2·0642	2·2830	0·0105
C	2·0543	2·0669	2·2714	0·0616

In all three complexes the values[11] of $R = (g_2 - g_1)/(g_3 - g_2)$ (Table 1) are very much less than unity and indicate predominately $d_{x^2-y^2}$ or d_{xy} ground states (rather than d_{z^2} ones) consistent with the elongated rhombic octahedral stereochemistries of the local $CuO_2N_2O_2'$ chromophores present. In the hot-form[5] of Cu(α-pic)$_2$$(NO_3)_2$ the *z*-molecular axis and the unique monoclinic crystal axis are virtually parallel and the correlation of the in-plane *g*-factors and the copper–ligand directions clearly indicate a $d_{x^2-y^2}$ ground state.[7] In neither of the two remaining complexes[5,6] is it possible to determine unambiguously the electronic ground states due to their

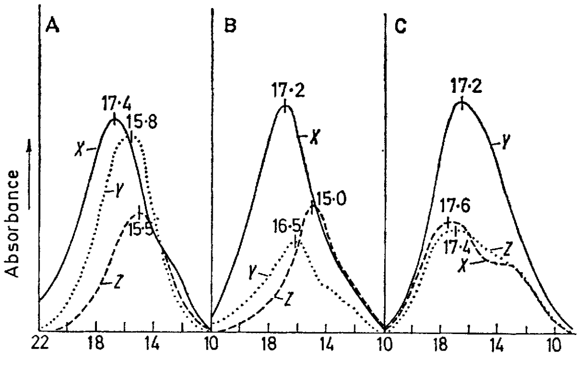

FIGURE 2 The polarised single-crystal electronic spectra of A, Cu(α-pic)$_2$$(NO_3)_2$; cold form (I); B, Cu(α-pic)$_2$$(NO_3)_2$, hot form (II); and C, $Cu(NO_3)_2C_4H_4N_2$

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[2] G. Davey and F. S. Stephens, *J. Chem. Soc.* (*A*), 1971, 1917.

[3] G. Davey, R. J. Dudley, and B. J. Hathaway, *J. Chem. Soc.* (*A*), 1971, 1446.

[4] B. J. Hathaway, *Structure and Bonding*, in the press.

[5] A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1970, 865; 1971, 253; *J.C.S. Dalton*, 1972, 58.

[6] A. Santoro, A. D. Mighell, and C. W. Reimann, *Acta Cryst.*, 1970, **B26**, 979.

[7] G. F. Kokoszka and C. W. Reinmann, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3229.

[8] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[9] B. J. Hathaway, P. Nicholls, and D. Barnard, *Spectrovision*, 1969, No. 22, 4.

[10] M. J. Buerger, ' Precession Method,' Wiley, New York, 1962.

[11] D. E. Billing, R. J. Dudley, B. J. Hathaway, and A. A. G. Tomlinson, *J. Chem. Soc.* (*A*), 1971, 1962.

respective crystal systems but the comparability of the g-factors (Table 1) and of their local molecular structures suggest that it is a reasonable assumption that $d_{x^2-y^2}$ ground states are also present in these complexes.

Electronic Spectra.—The polarised single-crystal electronic spectra of all three complexes are shown in Figure 2(A—C). In all cases the spectra were measured in the appropriate face parallel to the extinction directions and to the directions of the g-factors. As the misalignment of the local molecular axes is small in all three complexes, the crystal spectra are taken as equivalent to the local molecular spectra and are labelled accordingly in the Figures.

Assignment of the Electronic Spectra.—The crystallographic site symmetry [5,6] in both forms of Cu(α-pic)$_2$(NO$_3$)$_2$ is C_1 and in Cu(NO$_3$)$_2$C$_4$H$_4$N$_2$ it is C_{2h} but the marked polarisation of the electronic spectra and the rhombic g-factors in all three complexes suggest higher effective symmetries.[8] The approximate molecular symmetries of both forms of Cu(α-pic)$_2$(NO$_3$)$_2$ are C_{2v} (although D_2 cannot be ruled out) and that for Cu(NO$_3$)$_2$C$_4$H$_4$N$_2$ is D_{2h}. The electronic selection rules in C_{2v} and the vibronic selection rules in D_{2h}, both with $d_{x^2-y^2}$ ground states have been given previously [8] and tentative assignments of the electronic spectra of all three complexes are given in Table 2. All three complexes yield the same tentative one-electron orbital sequence $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{xz}$.

TABLE 2

The assignments of the electronic spectra of the two forms of Cu(α-pic)$_2$(NO$_3$)$_2$ in C_{2v} symmetry, of Cu(NO$_3$)$_2$C$_4$H$_4$N$_2$ in D_{2h} symmetry, with a $d_{x^2-y^2}$ ground state [along with the assignment of Cu(α-pic)$_2$(ClCH$_2$CO$_2$)$_2$ in D_{2h} symmetry] and the combined spin–orbit and orbital reduction parameters

	Cu(α-pic)$_2$(NO$_3$)$_2$			
	Cold form	Hot form	Cu(α-pic)$_2$(ClCH$_2$CO$_2$)$_2$ [3]	Cu(NO$_3$)$_2$C$_4$H$_4$N$_2$
Symmetry	C_{2v}	C_{2v}	D_{2h}	D_{2h}
$d_{z^2}\rightarrow d_{x^2-y^2}$	15·5	15·0	18·0	17·4
$d_{xy}\rightarrow d_{x^2-y^2}$	*ca.* 14·0	*ca.* 14·0	15·0	14·8
$d_{xz}\rightarrow d_{x^2-y^2}$	17·4	17·2	18·7	17·6
$d_{yz}\rightarrow d_{x^2-y^2}$	15·8	16·5	17·7	17·2
$r_{\parallel}$	0·77	0·76	0·78	0·78
$r_{\perp}$	0·81	0·81	0·80	0·80

Correlation of the Electronic Properties and Molecular Structure.—The electronic energy levels of the two forms of Cu(α-pic)$_2$(NO$_3$)$_2$,[5] of Cu(NO$_3$)$_2$C$_4$H$_4$N$_2$,[6] and of Cu(α-pic)$_2$(ClCH$_2$CO$_2$)$_2$ [2] are comparable and reflect the similarities in their molecular structures. The energies of the $d_{z^2}\rightarrow d_{x^2-y^2}$ transitions are significantly lower than that of 19·5 kK observed in the strictly rhombic coplanar CuO$_2$N$_2$ chromophore [1] of bis-(N-n-propylsalicylaldiminato)copper(II) and suggest that the CuO$_2$N$_2$ chromophores in the present complexes should not be considered as strictly rhombic coplanar but rather as six-co-ordinate with the two off-the-z-axis oxygen atoms contributing to some weak out-of-the-plane bonding.[6,7] This type of bonding has been suggested previously [3] for Cu(α-pic)$_2$(ClCH$_2$CO$_2$)$_2$ with the terminal carboxylate oxygens contributing to the out-of-plane bonding above and below the CuO$_2$N$_2$ plane (Figure 5, ref. 3) and the structure may be considered as being analogous to an elongated tetragonal octahedral stereochemistry.[8] In the two forms of Cu(α-pic)$_2$(NO$_3$)$_2$ the two terminal nitrate oxygen atoms contribute to the out-of-the-plane bonding above the CuO$_2$N$_2$ plane and this structure may be considered as being analogous to an elongated square pyramidal stereochemistry, a comparison which is further endorsed by the copper(II) ion occupying a position 0·11—0·17 Å above the plane of the four inplane ligands towards the two ' fifth ' oxygen ligands. This is a structural situation which is characteristic of many square pyramidal copper(II) complexes,[8] *e.g.*, {Cu(NH$_3$)$_4$-H$_2$O}SO$_4$.[12]

In all four complexes the $d_{xz}\rightarrow d_{x^2-y^2}$ and $d_{yz}\rightarrow d_{x^2-y^2}$ transitions are non-degenerate. The separation is smallest in Cu(NO$_3$)$_2$C$_4$H$_4$N$_2$ (0·4 kK) and greatest in the cold form of Cu(α-pic)$_2$(NO$_3$)$_2$ (1·6 kK). In each case this splitting between the d_{xz} and d_{yz} orbitals could arise from out-of-plane π-bonding but as there are no p-orbitals on the in-plane oxygen or nitrogen ligands suitably orientated [3,13,14] for out-of-plane π-bonding to these ligands, this is unlikely to be the origin of this splitting. A possible cause is a simple electrostatic consequence of these off-the-z-axis oxygen ligands on the d_{yz} orbital rather than the d_{xz}. This would account for the sense of the splitting, it being remembered that these orbitals cannot be involved in σ-bonding to the off-axis oxygen ligands (Figure 5b, ref. 13). The relatively large splitting in the cold form of Cu(α-pic)$_2$(NO$_3$)$_2$ may then be accounted for by the significantly closer approach of one of these off-axis oxygens to the copper(II) ion in this complex, namely 2·307 Å.

The relatively low energies of the $d_{xy}\rightarrow d_{x^2-y^2}$ transition in all four of the complexes in Table 2 are considered significant as the energy of this transition could reflect the presence of in-plane π-bonding to the oxygen and nitrogen ligands. In both forms of Cu(α-pic)$_2$(NO$_3$)$_2$ the vertical conformations [5] of the planes of both the nitrate groups and of the α-picoline rings cause p-orbitals of the

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[12] F. Mazzi, *Acta Cryst.*, 1955, **8**, 137; B. Morosin, *ibid.*, 1969, **24**, 19.

[13] D. E. Billing, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc.* (*A*), 1970, 1877.

[14] R. J. Dudley, B. J. Hathaway, and P. G. Hodgson, *J. Chem. Soc.* (*A*), 1971, 3355.

ligands to lie in the *xy*-plane suitably orientated for in-plane π-bonding to the d_{xy} orbital. In the other two complexes[2,6] only the *p*-orbitals of the oxygen ligands are favourably orientated and this is reflected in the slightly higher energies of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition.

Orbital Reduction Parameters.—By combining the electronic energy levels with the molecular *g*-factors and using the approximate[8] axial *g*-factor expressions we can evaluate the combined spin–orbit and orbital reduction factors for the complexes of this paper. The results are shown in Table 2 along with those previously obtained[3] for $Cu(\alpha\text{-pic})_2(ClCH_2CO_2)_2$. All four pairs of *r*-values are comparable, and similar in magnitude to the values obtained[8] for complexes containing CuO_x and CuN_x chromophores, despite[15] the fact that two of the present complexes lack a centre of symmetry. They are consistently higher than the values obtained[1] in three complexes containing the strictly rhombic coplanar CuO_2N_2 chromophore, *e.g.*, in $Cu(N\text{-n-prsalim})_2$ $r_\perp = 0{\cdot}71$ and $r_\parallel = 0{\cdot}69$—$0{\cdot}76$. This difference is consistent with the shorter copper–ligand bond-lengths observed[1] in these coplanar chromophores which would imply a more covalent bond. If the *r*-values of Table 2 are related to the corresponding molecular orbital coefficients,[8] the consistently high value of $r_\perp$ suggests that there is little or no out-of-the-plane π-bonding and as $r_\parallel$ is slightly lower than $r_\perp$ there may be a small but significant amount of in-plane π-bonding present in these complexes. This situation contrasts with that observed[1] in the rhombic coplanar chromophore of $Cu(N\text{-n-prsalim})_2$ where clear out-of-plane π-bonding was implied, and further supports the suggestion that the off-*z*-axis ligands present in the complexes of Table 2 are able to satisfy the out-of-the-plane bonding potential[8] of the CuO_2N_2 chromophore. These conclusions support those drawn from the correlations between the relative energies of the one-electron orbital levels and the molecular structures of these four complexes as discussed earlier.

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[15] D. Smith, *J. Chem. Soc. (A)*, 1970, 3108.