The Crystal Structure † of Bis(*NN*-Diethylethylenediamine)copper(II) Dinitrate and the Electronic Properties of some Square Planar CuN_4 Chromophores

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The crystal structure of the red isomer of $[Cu(deen)_2][NO_3]_2$ (1) (deen = *NN*-diethylethylenediamine) has been determined by *X*-ray diffraction using photographic techniques. The crystals are monoclinic, space group, $P2_1/n$, with $a = 9.76(5)$, $b = 12.81(5)$, $c = 8.24(5)$ Å, $\beta = 105.87(8)^\circ$, and $Z = 2$. The centrosymmetric CuN_4 chromophore is rhombic coplanar with Cu–N bond distances of 2.081(5) (tertiary nitrogen) and 2.011(5) Å (primary nitrogen). The conformations of the ethyl substituents effectively block the axial position of the CuN_4 chromophore and the nitrate ions exist as free ions in the lattice. The single-crystal electronic and e.s.r. spectra of (1) and of $Cs_2[Cu(succ)_4]\cdot 2H_2O$ (2) (succ = succinimido), are reported, correlated with the *X*-ray crystal structures of the complexes, and suggest the presence of significant in-plane π bonding in (2).

The existence of a strictly square (or rhombic) coplanar CuN_4 chromophore in copper(II) complexes is unusual [1,2] as additional ligands are usually involved to give a five-co-ordinate (square pyramidal) or six-co-ordinate (elongated tetragonal octahedral) stereochemistry.[3] The square coplanar stereochemistry is believed to exist in $Cs_2[Cu(succ)_4]\cdot 2H_2O$ (2) (succ = succinimido) [4] and $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2\cdot H_2O$ (3),[5] but in both complexes additional oxygen ligands may be involved in out-of-plane [2] bonding to the copper(II) ion: eight succinimide [4] oxygen atoms at 3.09 Å in (2) and two water molecules [5] at 2.88 Å in (3). The rhombic coplanar CuN_4 chromophore [6,7] exists in $[Cu(deen)_2][ClO_4]_2$ (4) (deen = *NN*-diethylethylenediamine) where co-ordination at the axial positions is blocked by the ethyl substituents, a situation that is also believed to exist [8] in $[Cu(deen)_2][NO_3]_2$ (1). As the latter occurs [8,9] in a red and purple high-temperature form, >160 °C, the crystal structure of (1) has been determined along with the electronic properties of (1) and (2).

Experimental

Preparation.—Complexes (1) and (2) were prepared by the literature methods,[10,11] and their composition confirmed by microanalysis.

Physical Properties.—The single-crystal e.s.r. and electronic spectra were determined [12,13] as previously described.

Crystal Data.—$C_{12}H_{32}CuN_6O_6$, $M = 419.6$, Monoclinic, $a = 9.76(5)$, $b = 12.81(5)$, $c = 8.24(5)$ Å, $\beta = 105.87(8)^\circ$, $U = 991$ Å^3, D_m (by flotation) = 1.41, $Z = 2$, $D_c = 1.43$ g cm^{-3}, $F(000) = 223$, Cu-K_α radiation, $\lambda = 1.5418$ Å, $\mu = 17.48$ cm^{-1}, space group $P2_1/n$, systematic absences confined to $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$).

Table 1. Fractional atomic co-ordinates for $[Cu(deen)_2][NO_3]_2$ (1)

Atom	*x*	*y*	*z*
Cu	1.000 00	0.000 00	0.000 00
N(1)	0.821 5(5)	0.069 2(4)	0.046 3(7)
N(2)	1.062 7(6)	0.147 4(4)	−0.023 9(8)
C(1)	0.835 2(8)	0.184 6(5)	0.028 1(10)
C(2)	0.990 9(8)	0.215 4(5)	0.075 3(10)
C(3)	0.823 5(8)	0.040 6(6)	0.223 8(9)
C(4)	0.693 4(9)	0.074 2(8)	0.280 5(11)
C(5)	0.688 1(7)	0.031 5(6)	−0.075 1(10)
C(6)	0.703 5(8)	0.022 4(6)	0.743 2(10)
N(3)	0.574 7(7)	0.748 5(5)	0.949 9(8)
O(1)	0.642 7(7)	0.768 6(5)	0.842 6(9)
O(2)	0.607 0(8)	0.796 4(5)	0.084 6(8)
O(3)	0.478 7(8)	0.683 3(6)	0.917 5(11)

Table 2. Bond lengths (Å) and angles (°) for $[Cu(deen)_2][NO_3]_2$ (1)

Cu–N(1)	2.081(5)	Cu–N(2)	2.011(5)
N(1)–C(1)	1.496(8)	N(1)–C(3)	1.502(9)
N(1)–C(5)	1.489(8)	N(2)–C(2)	1.495(8)
C(1)–C(2)	1.515(10)	C(3)–C(4)	1.529(10)
C(5)–C(6)	1.549(12)	N(3)–O(1)	1.268(9)
N(3)–O(2)	1.232(9)	N(3)–O(3)	1.228(9)
N(2)–Cu–N(1)	84.9(2)	C(1)–N(1)–Cu	107.5(4)
C(3)–N(1)–Cu	106.6(4)	C(3)–N(1)–C(1)	111.2(6)
C(5)–N(1)–Cu	111.1(4)	C(5)–N(1)–C(1)	109.8(5)
C(5)–N(1)–C(3)	110.6(5)	C(2)–N(2)–Cu	107.0(4)
C(2)–C(1)–N(1)	110.0(6)	C(1)–C(2)–N(2)	107.2(5)
C(4)–C(3)–N(1)	116.0(6)	C(6)–C(5)–N(1)	112.1(5)
O(2)–N(3)–O(1)	118.2(7)	O(3)–N(3)–O(1)	119.9(7)
O(3)–N(3)–O(2)	121.8(8)		

The intensity data were collected photographically at room temperature, using the equi-inclination Weissenberg technique, for the layers $hk0$—$hk7$ and $h0l$—$h2l$. Integrated spots were used and estimated visually: 1 165 non-zero unique reflections were collected. The intensities were corrected for Lorentz and polarization effects and placed on a common arbitrary scale by internal correlation. No correction for extinction or absorption was applied, and complex atomic scattering factors were employed.[14] The structure was solved by the heavy-atom method and successive Fourier synthesis. The refinement converged when the shift-to-error ratio of any parameter was less than 0.01, with a refined weighting scheme, $w = k/\sigma^2(F_o + gF_o^2)$, where the final k and g were 1.00 and 0.0225, respectively. Anisotropic thermal parameters were refined for all non-hydrogen atoms, calculated hydrogen positions were used, C–H and N–H distances of 1.08 Å, and fixed thermal parameters of 0.07 Å^2. The final R value was 0.079 and the highest residual electron density was <0.6 e Å^{-3}. The final atomic co-ordinates are given in Table 1, and the bond lengths and bond angles in Table 2. Figure 1 shows the molec-

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† *Supplementary data available* (No. SUP 23749, 12 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

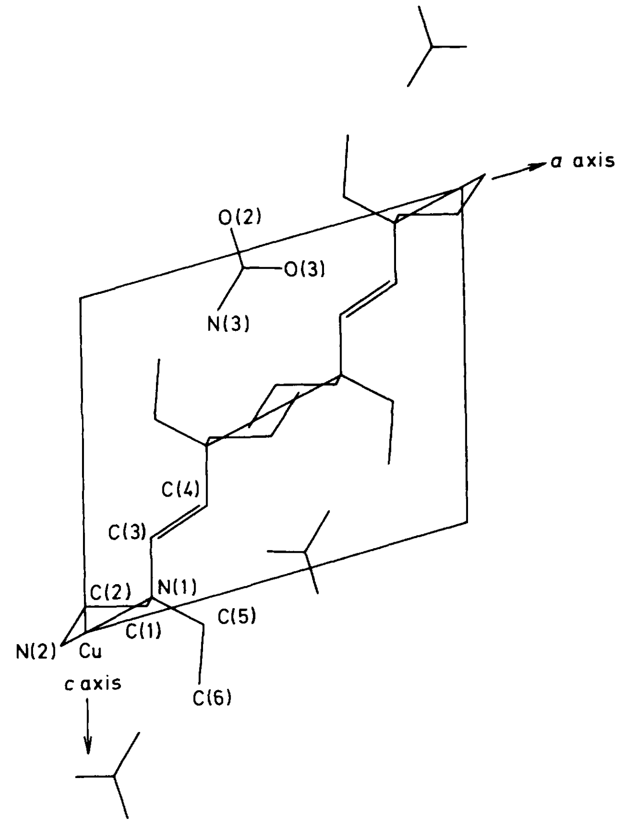

Figure 1. The molecular structure, atom numbering, and unit-cell packing viewed down the *b* axis for $[Cu(deen)_2][NO_3]_2$ (1)

ular structure of (1), the atom-numbering scheme used, and the packing viewed down the *b* axis.

Complex (2) crystallises [4] in a triclinic space group with the local molecular axes of the two molecules in the unit cell aligned parallel.

All calculations were carried out using the SHELX 76 [15] and XANADU (G. M. Sheldrick), PLUTO (S. Motherwell), and PUBTAB (K. Henrick) systems of programs and an IBM 4341 and VAX 11/780 computers.

E.S.R. Spectra.—The single-crystal e.s.r. spectra were determined using the six-position method [16] and three crystal *g* factors were obtained for each complex: $g_1 = 2.043$, $g_2 = 2.045$, and $g_3 = 2.174$ (± 0.001) for (1) and $g_1 = 2.043$, $g_2 = 2.050$, and $g_3 = 2.240$ (± 0.001) for (2).

Electronic Spectra.—The electronic reflectance spectra of (1) and (2) are shown in Figure 2(*a*), both spectra involve a high-energy band maximum and a weaker shoulder to low energy. The polarised single-crystal spectra [12] of (1) and (2) are shown in Figure 2(*b*) and (*c*), respectively. The polarised single-crystal spectrum of (1) was measured in the (1 1 0) face yielding the almost pure (84%) *z*-polarised spectrum, but due to the misalignment of the two symmetry related chromophores, only an *xy*-polarised spectrum was determined. The *xy*-polarised spectrum of (1) shows a clear shoulder at 18 700 cm^{-1}, not revealed in the reflectance spectrum. The polarised single-crystal spectrum of (2) was measured in the (0 0 1) face of the crystal and yielded the pure *z*-polarised spectrum and a mixture of the *xy* polarisation (65%*x* + 35% *y*); the *z*-polarised spectrum showed a clear maximum at 18 400 cm^{-1} not revealed in the reflectance spectrum.

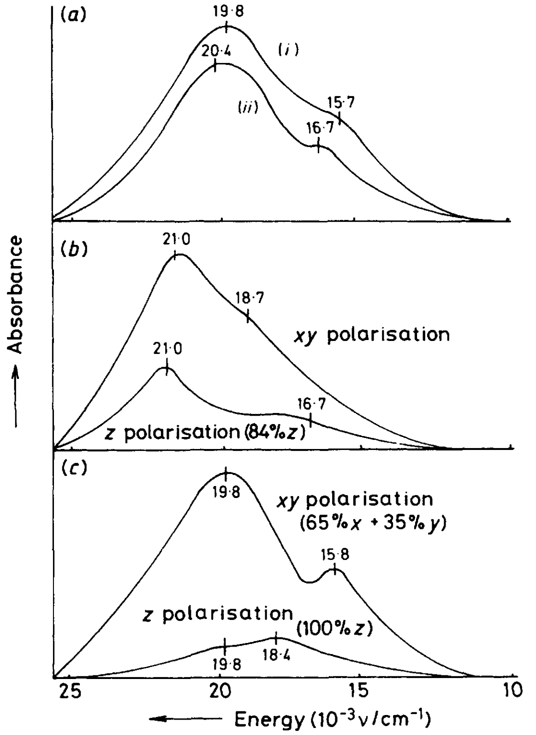

Figure 2. (*a*) The electronic reflectance spectra of (*i*) $Cs_2[Cu(succ)_4]\cdot 2H_2O$ and (*ii*) $[Cu(deen)_2][NO_3]_2$. The polarised single-crystal electronic spectra of (*b*) $[Cu(deen)_2][NO_3]_2$ and (*c*) $Cs_2[Cu(succ)_4]\cdot 2H_2O$ are also shown

Discussion

Crystal Structure.—The structure of (1) consists of discrete $[Cu(deen)_2]^{2+}$ cations and nitrate anions. The nitrate anions are planar (r.m.s.d. = 0.0039 Å), have no unusual bond distances or bond angles,[17] and are consistent with the presence of ionic nitrate ions in the lattice. The molecular structure of the $[Cu(deen)_2]^{2+}$ cation is shown in Figure 1; it is centrosymmetric and involves the copper(II) ion in a rhombic coplanar CuN_4 stereochemistry. The structure of the cation of (1) is essentially the same as that in (4) (see earlier) and the CuN_4 chromophore is in a strictly rhombic coplanar stereochemistry with no structural evidence for the semi-co-ordination [18] of the nitrate ions to the copper(II) ion. This crystallographic evidence for the non-co-ordinated environment of the nitrate ion of (1) is consistent with the i.r. spectroscopic evidence [8] for ionic nitrate ions in this complex.

E.S.R. Spectra.—The e.s.r. spectra [12] of both (1) and (2) are nearly axial ($g_3 \gg g_2 \approx g_1 > 2.0$) consistent with the elongated tetragonal octahedral stereochemistry. The two molecules in the monoclinic unit cell of (1) have their local molecular *z* axis aligned, but their *x* and *y* axes are misaligned ($2\alpha = 40°$) and it is not possible to specify the in-plane local molecular *g* factors from the observed crystal *g* factors. But as the anisotropy of the g_2 and g_1 local molecular *g* factors is likely to be small, their values are not expected to differ significantly from the observed crystal *g* values. As non-equivalent nitrogen ligand atoms are involved, rhombic in-plane *g* factors would be anticipated [12] which would most probably be orientated approximately along the Cu–N bond directions, giving rise to an approximately $d_{x^2-y^2}$ ground state.[12] In (2) the crystal *g* values are equivalent to the local molecular *g* values as the CuN_4 chromophores are aligned in the triclinic space group

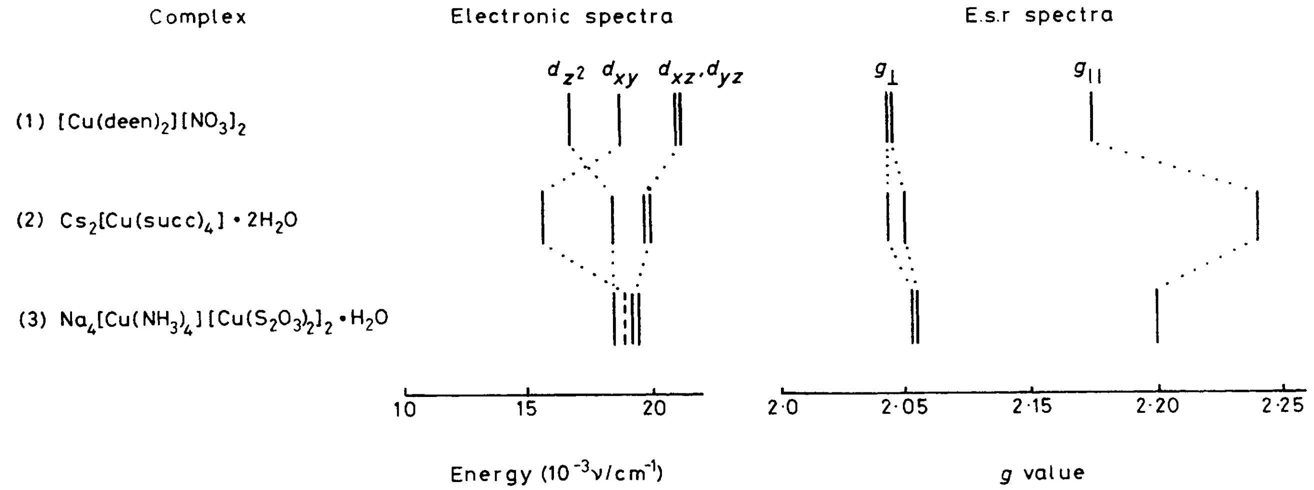

Figure 3. The single-crystal electronic energies and g values for three coplanar CuN_4 chromophore-containing complexes

Table 3. Tentative assignment of the electronic spectra (ν/cm^{-1}) of $[Cu(deen)_2][NO_3]_2$ (1) and $Cs_2[Cu(succ)_4]\cdot 2H_2O$ (2)

Transition	(2)	(1)
$d_{z^2} \longrightarrow d_{x^2-y^2}$	18 400	16 700
$d_{xy} \longrightarrow d_{x^2-y^2}$	15 800	18 700
$d_{xz} \longrightarrow d_{x^2-y^2}$ $d_{yz} \longrightarrow d_{x^2-y^2}$	19 800	21 000

$C\bar{1}$. The small but significant rhombic component in the g values is unexpected as the Cu–N distances are not significantly different.[14] The highest g value (g_3) in (1) is significantly lower than that in (2).

Electronic Spectra.—In both complexes (1) and (2) the band maxima in the electronic reflectance spectra lie above 19 000 cm^{-1}, at 20 400 and 19 800 cm^{-1}, respectively, consistent with the square (or rhombic) coplanar stereochemistry present.[1,2,12] The only other CuN_4 chromophore to have an electronic band maximum at such a high energy is that of (3)[1] with an observed band maximum at 19 200 cm^{-1}, which also involves an H_2O group at 2.88 Å along the z axis.[1,5] This suggests that the CuN_4 chromophore of (1) involves the least out-of-plane bonding of the three complexes (1)—(3). It also suggests that the two water groups in (3) at 2.88 Å and the eight oxygens in (2) at 3.30 Å[4] are involved in a small, but significant out-of-plane bonding to the copper(II) ion, sufficient to reduce the electronic band maximum to a lower energy in (3) and (2), than in (1). The reflectance spectra of both complexes [Figure 2(*a*)] show a low-energy shoulder, which is also at higher energy in (1) than in (2).

Only partial polarised spectra were obtained for both (1) and (2), Figure 2(*b*) and (*c*), respectively. Both the structure and the local molecular g factors of (2) deviate only slightly from a strict D_{4h} symmetry.[12] Since the complex is centrosymmetric, all of the *d–d* transitions are electronically forbidden and a vibronic mechanism must be invoked.[12] Assuming a $d_{x^2-y^2}$ ground state (which cannot be distinguished experimentally from a d_{xy} ground state in this symmetry), and the vibronic selection rules given previously,[12,19] a tentative assignment[19] of the electronic spectrum of (2) is given in Table 3. In (1), while the differences in the in-plane Cu–N bond distances suggest a D_{2h} effective symmetry the 40° misalignment in the CuN_4 plane makes it impossible to measure experimentally the anisotropy of the in-plane g factors or the separate x- and y-polarised electronic spectra. The closeness of the crystal g factors does suggest that the in-plane anisotropy of the g factors is small. As the xy-polarised spectrum, Figure 2(*b*), shows the presence of two peaks, this suggests that the effective symmetry of (1) is D_{4h}, despite the anisotropy of in-plane Cu–N distances. A tentative assignment of the electronic spectrum of (1) is also given in Table 3.

The assignment of the polarised single-crystal spectra of (1), (2), and (3) along with their single-crystal g values are summarised in Figure 3, for these three square (or rhombic) coplanar CuN_4 chromophores. In all three complexes relatively high-energy electronic energies occur in the range 21 000—19 000 cm^{-1}, and all three complexes have axial e.s.r. spectra. In (2) and (3) the d_{yz} and d_{xz} levels are not resolved, as would be expected for the strictly square coplanar CuN_4 chromophore present; in (1) there may be some splitting due to the non-equivalent Cu–N distances present, but it is not resolved in the polarised spectra. The average energy of the $d_{yz},d_{xz} \longrightarrow d_{x^2-y^2}$ transition decreases slightly in the sequence (1), (2), (3), which is reflected in the corresponding slight increase of the value of $g_\perp$ in the same sequence, Figure 3. This is not unexpected[12] as $g_\perp = 2 - 2r_\perp\lambda/\Delta(d_{yz},d_{xz} \longrightarrow d_{x^2-y^2})$, where $r_\perp$ is the combined orbital reduction parameter,[12] which should be comparable in these three complexes involving no out-of-plane π bonding. The energies of the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transitions in the three complexes are well defined and nearly 2 000 cm^{-1} lower in energy in (1) than in (2) and (3). As the energy of the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition reflects the tetragonal distortion[20] about the copper(II) ion this is surprising as there are no potential ligand atoms along the perpendicular to the CuN_4 plane in (1). The blocking carbon atoms of the ethyl groups of the deen ligands are well off this axis, at >3.0 Å, and the nearest nitrate oxygen atoms also lie well off this axis at >4.0 Å. Nevertheless, they must combine effectively to reduce the energy of the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition in (1) to less than that in (2) and (3). In (2) and (3) the relatively high energy of the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition implies that the eight succinimide oxygen atoms at 3.09 Å in (2) and the two water molecules at 2.88 Å along in z axis in (3) have little effect on the electronic energies of the CuN_4 chromophores present. The energy of the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition is the least well defined. In (3) it is not observed, but presumed to occur at 19 000—20 000 cm^{-1}; in (1) it is observed as a weak shoulder at 18 700 cm^{-1} and only well defined at 15 700 cm^{-1} in (2). The difference in energy of the

$d_{xy} \longrightarrow d_{x^2-y^2}$ transition for (2) and (3) of *ca.* 3 000 cm^{-1} is considerable and only slightly less, 2 000 cm^{-1}, in (1). It is reflected in a significantly higher value for $g_{\|}$ in (2) than in (3) and (1) (2.24, 2.20, and 2.175 respectively), as expected from the g value expression[12] $g_{\|} = 2.8\, r_{\|}\lambda/\Delta(d_{xy} \longrightarrow d_{x^2-y^2})$. This independent information on the low energy of the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition in (2) suggests that the difference must arise for a definite reason, namely the presence of in-plane π bonding in (2) that is absent in (1) and (3). In (2) the plane of the co-ordinated succinimide ligand is orientated at 90° to the CuN$_4$ plane, and involves a p_z orbital on the co-ordinated nitrogen of the succinimide ligand, which is thereby orientated in the CuN$_4$ plane, suitably aligned for in-plane π bonding to the copper(II) d_{xy} orbital. Such in-plane π bonding would then produce the lowering of the energy of the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition and hence the high value for $g_{\|}$ in (2), as observed.

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