

bidentate bridging role of the nitrate group (Nakamoto, 1978). The electronic reflectance spectrum of (I) has a broad peak centred at 15 000 cm⁻¹, with a weakly resolved shoulder at 10 200 cm⁻¹, consistent with its stereochemistry, and comparable with the electronic spectra of (II), which has a main band at 15 800 cm⁻¹ and a weakly resolved shoulder at 10 000 cm⁻¹ (Ray, Tyagi & Hathaway, 1982). The lower energy of the main band in (I) is then consistent with the slightly higher tetragonality of (I) than of (II), 0.785 and 0.765, respectively. The polycrystalline ESR spectrum of (I) is axial, $g_1 = 2.073$ and $g_{11} = 2.299$ and consistent with the elongated rhombic octahedral chromophore present, but due to some misalignment of the local molecular axes ($2\gamma = 80^\circ$), these g values do not equate with the local molecular g values (Hathaway & Billing, 1970).

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Structure of Bis[cyanatobis(di-2-pyridylamine)copper(II)] Sulfate Bis(di-2-pyridylamine) Monohydrate

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Abstract. [Cu(NCO)(C₁₀H₉N₃)₂](SO₄)_{0.5}·C₁₀H₉N₃·0.5H₂O, $M_r = 676.20$, monoclinic, $I2/c$ [equivalent positions: $\pm(x, y, z)$; $\pm(-x, y, \frac{1}{2}-z)$], $Z = 8$, $a = 17.688$ (3), $b = 20.596$ (4), $c = 17.519$ (2) Å, $\beta = 96.886$ (2)°, $V = 6336.17$ Å³, $D_m(\text{floatation}) = 1.42$ (6), $D_x = 1.417$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.733$ mm⁻¹, $T = 298$ K, $F(000) = 2792$, 1893 unique observed reflections, $R = 0.077$. The CuN₄N' chromophore involves a square pyramidal structure, distorted towards a trigonal bipyramidal stereochemistry, $\tau = 0.31$. The NCO⁻ anion is bonded to

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the copper(II) ion *via* the N atom. The two non-coordinated dpyam (dpyam = 2,2'-dipyridylamine) molecules are disordered about a centre and a two-fold axis of symmetry, respectively, and both are poorly defined. The [SO₄]²⁻ anion is also disordered about a centre of symmetry, SOF = 0.5, and the non-coordinated water molecule is also disordered, SOF = 0.5.

Introduction. The structure determination of the [Cu(dpyam)₂(NCO)]⁺ cation has been undertaken to establish (a) the mode of bonding of the NCO⁻ anion to the copper(II) cation, (b) the stereo-

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Table 1. Fractional atomic coordinates and thermal parameters (\AA^2) with e.s.d.'s in parentheses
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq} (\text{\AA}^2)$
Cu	0.26698 (8)	0.22426 (8)	0.46404 (9)	0.0553 (9)
N(1)	0.2241 (5)	0.1628 (5)	0.3806 (6)	0.052 (4)
C(1)	0.2314 (6)	0.1775 (6)	0.3071 (7)	0.056 (5)
C(2)	0.1912 (8)	0.1460 (7)	0.2456 (9)	0.078 (5)
C(3)	0.1385 (8)	0.0976 (7)	0.2606 (9)	0.073 (5)
C(4)	0.1306 (7)	0.0832 (6)	0.3349 (9)	0.068 (5)
C(5)	0.1754 (6)	0.1145 (6)	0.3943 (7)	0.051 (4)
N(3)	0.1707 (5)	0.0968 (5)	0.4683 (6)	0.065 (4)
C(6)	0.2256 (7)	0.0992 (6)	0.5285 (7)	0.058 (5)
C(7)	0.2276 (9)	0.0512 (8)	0.5840 (9)	0.097 (5)
C(8)	0.2894 (11)	0.0508 (10)	0.6443 (10)	0.122 (5)
C(9)	0.3486 (11)	0.0951 (8)	0.6431 (9)	0.116 (5)
C(10)	0.3441 (8)	0.1425 (7)	0.5870 (8)	0.077 (5)
N(2)	0.2811 (5)	0.1446 (5)	0.5310 (6)	0.060 (4)
N(4)	0.2992 (6)	0.2831 (5)	0.5549 (6)	0.056 (4)
C(11)	0.2617 (8)	0.2785 (8)	0.6196 (9)	0.112 (5)
C(12)	0.2688 (9)	0.3214 (8)	0.6812 (9)	0.089 (5)
C(13)	0.3185 (9)	0.3746 (8)	0.6727 (11)	0.097 (5)
C(14)	0.3552 (8)	0.3789 (8)	0.6109 (10)	0.083 (5)
C(15)	0.3450 (7)	0.3348 (7)	0.5527 (9)	0.070 (5)
N(6)	0.3828 (6)	0.3436 (6)	0.4870 (8)	0.084 (5)
C(16)	0.4118 (7)	0.2966 (8)	0.4411 (8)	0.070 (5)
C(17)	0.4719 (9)	0.3117 (9)	0.3973 (9)	0.089 (5)
C(18)	0.5031 (9)	0.2693 (11)	0.3548 (9)	0.110 (5)
C(19)	0.4753 (8)	0.2064 (10)	0.3534 (9)	0.099 (5)
C(20)	0.4168 (8)	0.1925 (9)	0.3937 (9)	0.084 (5)
N(5)	0.3814 (6)	0.2374 (6)	0.4349 (7)	0.074 (4)
N(7)	0.2102 (7)	0.2936 (7)	0.4134 (7)	0.081 (5)
C(21)	0.1853 (10)	0.3397 (11)	0.3991 (10)	0.103 (5)
O(1)	0.1524 (10)	0.3916 (8)	0.3787 (13)	0.224 (5)
S†	0.0000	0.0000	0.0000	0.0755 (31)
O(2)*	0.0516 (15)	0.0360 (13)	0.0712 (15)	0.037 (4)
O(3)*	0.0388 (13)	-0.0147 (11)	-0.0569 (14)	0.023 (4)
O(4)*	0.0724 (14)	0.0154 (12)	-0.0202 (14)	0.027 (4)
O(5)*	-0.0258 (13)	0.0719 (12)	-0.0331 (14)	0.027 (4)
O(6)*	0.0549 (8)	0.0551 (7)	0.6995 (8)	0.045 (3)
N(8)*	0.4670 (14)	-0.0248 (12)	-0.0743 (15)	0.071 (4)
C(31)*	0.4633 (20)	-0.0308 (16)	-0.1434 (19)	0.067 (5)
C(32)*	0.3877 (27)	-0.0445 (21)	-0.1924 (30)	0.133 (5)
C(33)*	0.3352 (19)	-0.0205 (14)	-0.1641 (17)	0.067 (5)
C(34)*	0.3400 (22)	0.0026 (19)	-0.0763 (23)	0.099 (5)
C(35)*	0.4096 (20)	-0.0055 (16)	-0.0347 (19)	0.084 (5)
N(9)*	0.4595 (18)	0.0263 (14)	0.0357 (18)	0.117 (5)
C(36)*	0.5102 (25)	-0.0017 (21)	0.0937 (26)	0.124 (5)
C(37)*	0.5639 (23)	-0.0164 (19)	0.0514 (24)	0.107 (5)
C(38)*	0.6384 (33)	-0.0225 (25)	0.0569 (31)	0.173 (6)
C(39)*	0.6704 (22)	0.0041 (18)	0.1274 (25)	0.100 (5)
C(40)*	0.6103 (26)	0.0217 (18)	0.1832 (26)	0.108 (5)
N(10)*	0.5388 (29)	0.0444 (25)	0.1662 (26)	0.170 (6)
N(11)*	0.0276 (13)	0.3190 (12)	0.6821 (14)	0.068 (5)
C(41)*	0.0453 (17)	0.3544 (18)	0.6223 (19)	0.091 (5)
C(42)*	0.0682 (17)	0.3346 (17)	0.5571 (20)	0.092 (5)
C(43)*	0.0670 (18)	0.2773 (18)	0.5545 (21)	0.085 (5)
C(44)*	0.0485 (16)	0.2305 (16)	0.6119 (17)	0.070 (5)
C(45)*	0.0272 (10)	0.2429 (11)	0.6841 (12)	0.022 (4)
N(12)†	0.0000	0.2194 (26)	0.7500	0.104 (6)
C(46)*	-0.0130 (11)	0.2183 (14)	0.7802 (12)	0.032 (4)
C(47)*	-0.0336 (14)	0.2854 (16)	0.8268 (16)	0.055 (5)
C(48)*	-0.0586 (19)	0.3059 (21)	0.8963 (22)	0.100 (5)
C(49)*	-0.0728 (13)	0.2437 (12)	0.9407 (15)	0.041 (4)
C(50)*	-0.0664 (16)	0.1913 (16)	0.9003 (17)	0.076 (5)
N(13)*	-0.0389 (12)	0.1797 (11)	0.8404 (13)	0.071 (4)

* SOF = 0.5.

† SOF = 0.25.

chemistry of the $\text{CuN}_4\text{N}'$ chromophore and (c) the possible existence of a series of cation distortion isomers of the $[\text{Cu}(\text{dpyam})_2(\text{NCO})]^+$ cation.

Experimental. (I) was prepared by adding a hot solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.25 g, 1 mmol) in 20 ml of water to a boiling solution of dpyam (0.342 g, 2 mmol) in 30 ml of absolute alcohol and 0.13 g of NaNCO (2 mmol) in 10 ml of water. An initial light-

green microcrystalline precipitate of $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{SO}_4]$ was filtered off and the filtrate deposited, on standing, dark green crystals of (I). Found: C, 53.33; H, 4.28; N, 20.60; Cu 9.56%. Calculated for $\text{C}_{62}\text{H}_{56}\text{N}_{20}\text{Cu}_2\text{O}_7\text{S}$: C, 54.34; H, 4.23; N, 20.45; Cu, 9.27%.

The unit-cell data (25 refined reflections, θ 3–25°) and intensities were collected on a Philips PW 1100 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Reflections with $3.0 < \theta < 25^\circ$ in one quadrant were examined in the ω - 2θ scan mode, with a constant scan speed of $0.05^\circ \text{ s}^{-1}$, and a variable scan width of $(0.7 + 0.1 \tan \theta)^\circ$. 2087 observed reflections were collected [$I > 2.5\sigma$; $-20 \leq h \leq 20$, $0 \leq k \leq 20$, $0 \leq l \leq 20$] of which 1893 were unique. Lorentz and polarization corrections were applied, but no correction was made for absorption. The structure was solved by *SHELX76* (Sheldrick, 1976), developed by difference Fourier techniques and 400 parameters refined by blocked-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$, with anisotropic temperature factors for S and for the non-H atoms of the cation. The sulfate anion, weighted at a half, was disordered about a centre of symmetry and the uncoordinated dpyam molecules were both disordered, one about a centre of symmetry and one about a twofold axis. The positions of the H atoms were calculated geometrically and 'floated' on the adjacent C, N or O atoms, assuming C—H, N—H and O—H distances of 1.08 Å, and a fixed temperature factor of 0.07 \AA^2 . Maximum shift/e.s.d. was < 0.004 , with a refined weighting scheme, $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$ with $k = 1.2417$ and $g = 0.0038$. $R = 0.077$ and $wR = 0.081$. The maximum and minimum residual electron density were 0.75 and -0.38 e \AA^{-3} , respectively. Complex neutral-atom scattering factors were employed and those for Cu were taken from Cromer & Waber (1974). All calculations were carried out with *SHELX76* (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1979). *CHEM-X* (Davies, 1980) and *PUBTAB* (Henrick, 1980) on the UCC mainframe IBM 4341 and VAX 11/780 computers. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.* Selected bond lengths and bond angles are given in Table 2. Fig. 1 shows the molecular structure of (I) and the atom-numbering scheme used.

Discussion. The asymmetric unit of (I) consists of a $[\text{Cu}(\text{dpyam})_2(\text{NCO})]^+$ cation, half a sulfate anion, one disordered non-coordinated dpyam molecule

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53364 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å) and angles (°) with *e.s.d.'s* in parentheses

Cu—N(1)	2.012 (10)	Cu—N(2)	2.014 (10)
Cu—N(4)	2.028 (10)	Cu—N(5)	2.162 (10)
Cu—N(7)	1.903 (13)	N(3)—C(5)	1.360 (15)
N(3)—C(6)	1.346 (15)	N(6)—C(15)	1.411 (18)
N(6)—C(16)	1.394 (18)	N(7)—C(21)	1.063 (19)
C(21)—O(1)	1.249 (21)	S—O(2)	1.630 (30)
S—O(3)	1.311 (25)	S—O(4)	1.405 (20)
S—O(5)	1.635 (24)		
N(2)—Cu—N(1)	85.5 (4)	N(4)—Cu—N(1)	173.0 (4)
N(4)—Cu—N(2)	91.5 (4)	N(5)—Cu—N(1)	100.9 (5)
N(5)—Cu—N(2)	100.7 (5)	N(5)—Cu—N(4)	85.9 (5)
N(7)—Cu—N(1)	90.1 (5)	N(7)—Cu—N(2)	154.7 (5)
N(7)—Cu—N(4)	90.0 (5)	N(7)—Cu—N(5)	104.6 (5)
C(6)—N(3)—C(5)	128.0 (10)	C(16)—N(6)—C(15)	129.0 (10)
C(21)—N(7)—Cu	164.0 (20)	O(1)—C(21)—N(7)	176.0 (20)

and half a water molecule. There are no interactions of less than 4.0 Å between the Cu atom and the sulfate anion, the uncoordinated dpyam molecule and the water molecule. The cation of (I) involves a five coordinate CuN₄N' chromophore, with an approximately trigonal bipyramidal stereochemistry, Fig. 1 (Hathaway, 1987). The out-of-plane bond lengths, Cu—N(1) and Cu—N(4), are not significantly different, with values of 2.012 (10) and 2.028 (10) Å, respectively. The in-plane bond lengths, Cu—N(2), Cu—N(5) and Cu—N(7), are significantly different, with values of 2.014 (10), 2.162 (10) and 1.903 (13) Å, respectively. The N(1,2) dpyam ligand is thus nearly symmetrically coordinated, but the N(4,5) dpyam ligand is very asymmetrically coordinated. The Cu—N(7) distance of 1.903 (13) Å then stands out as significantly shorter than all the Cu—N(dpyam) distances. The CuN₄N' chromophore stereochemistry is distorted from regular trigonal bipyramidal. The N(1)—Cu—N(4) (α_8) angle of 173.0 (4)° is nearly linear and distorted away from the Cu—N(7) direction [see Harrison, Kennedy, Power, Sheahan & Hathaway (1981) for angle notation]. The in-plane angles, N(2)—Cu—N(7) (α_1), N(5)—Cu—N(7) (α_2) and N(2)—Cu—N(5) (α_3), are all significantly different from 120°, namely, 154.7 (5), 104.6 (5) and 100.7 (5)°, respectively. The largest in-plane angle of 154.7° lies opposite the longest in-plane bond length, namely, the Cu—N(5) bond, and yields a τ -value of 0.31 ($\tau = \alpha_8 - \alpha_1$)/60 [see Addison, Nageswara Rao, Reedijk, van Rijn & Verschoor (1984) and Hathaway (1987, Table 23)]. These distortions together suggest the stereochemistry of the CuN₄N' chromophore of (I) is best described as trigonally distorted square-based pyramidal, rather than distorted trigonal bipyramidal (Harrison *et al.*, 1981). There are no unusual bond lengths or bond angles in the coordination of the dpyam ligands (Ray & Hathaway, 1978). The individual pyridine rings of the coordinated dpyam ligands are reasonably planar (Ray & Hathaway, 1978), with r.m.s. deviations < 0.025 Å. The dihedral angles between the pyridine rings within the same

dpyam ligand, are 34.6 and 27.2°, respectively. The N(1,2) and N(4,5) dpyam ligands involve bite angles at the Cu atom of 85.5 (4) and 85.9 (5)°, respectively, both significantly less than the 90–95° angles normally observed for the coordinated dpyam ligand (Ray & Hathaway, 1978). This difference is associated with the large dihedral angles within these ligands (Fuller & Jacobson, 1981). The mean planes of the separate dpyam ligands are inclined at 59.7° to each other.

Both of the non-coordinated dpyam molecules are disordered, one about a centre of symmetry and the other about the twofold axis (Fig. 2) with the central N(12) atom on a C₂ axis and common to both dpyams. In the former the close proximity of the pairs of pyridine rings, approximately 1.0 Å, affects the proper positioning of some of the H atoms. The structural results for the uncoordinated dpyam are

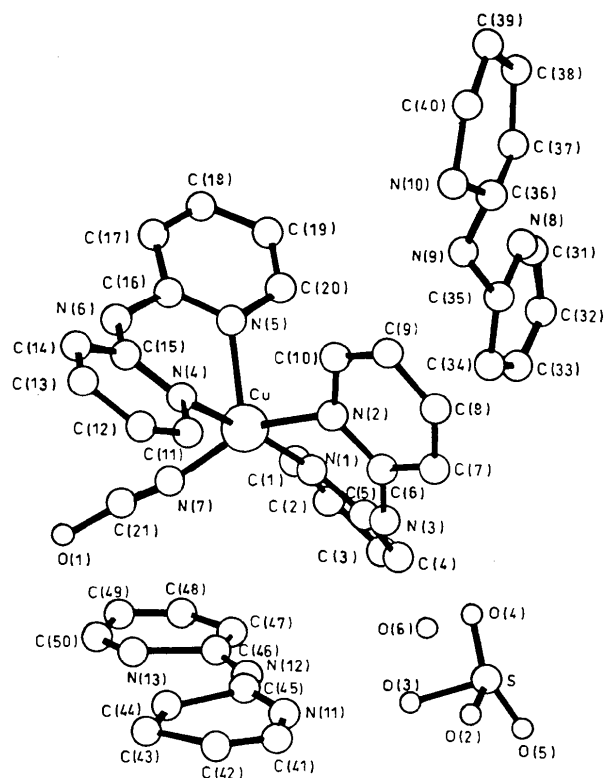


Fig. 1. The molecular structure of (I) and the atomic numbering scheme used.

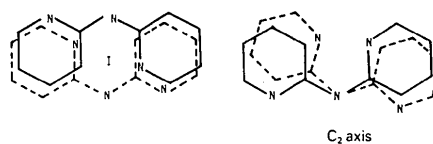


Fig. 2. The disordered dpyam molecules of (I) lying on (a) centres of symmetry and (b) twofold axes.

poorly defined, but consistent with the known *trans* configuration of the pyridine N atoms in the structure of dpyam (Johnson & Jacobson, 1973). The sulfate anion is also disordered about a centre of symmetry, with a SOF = 0.5. The O atoms can be separated into two poorly defined interpenetrating tetrahedra. The uncoordinated water molecule is also disordered, SOF = 0.5.

The square-based pyramidal distorted trigonal bipyramidal $\text{CuN}_4\text{N}'$ chromophore (I) has been observed previously in the cations of $[\text{Cu}(\text{bpy})_2(\text{NH}_3)][\text{BF}_4]_2$ (Stephens, 1972) ($\tau = 0.77$) and $[\text{Cu}(\text{bpy})_2(\text{NCS})][\text{BF}_4]$ (Tyagi & Hathaway, 1981) ($\tau = 0.60$) and in a series of cation distortion isomers of the $[\text{Cu}(\text{bpy})_2\text{Cl}]^+$ cation (Harrison *et al.*, 1981) ($\tau = 1.0-0.60$). These have been used to suggest a structural pathway from a regular trigonal bipyramidal ($\tau = 1.0$) to a distorted square-based pyramidal ($\tau = 0.0$) stereochemistry (Hathaway, 1984) and suggest that (I) forms a point in a more extensive ($\tau = 0.31$) structural pathway for the $\text{CuN}_4\text{N}'$ chromophore.

The ESR spectrum of (I) is isotropic, $g_i = 2.083$, and gives no information on the electronic ground state of the copper(II) ion, due to the misalignment of the local molecular axes (Hathaway, 1984) of the two differently orientated $\text{CuN}_4\text{N}'$ chromophores ($2\gamma = 90^\circ$) in (I). The electronic reflectance spectrum of (I) has two almost equally intense peaks at 10 630 and 14 230 cm^{-1} , $\Delta E = 3\ 600\ \text{cm}^{-1}$, consistent with its stereochemistry, and similar to the electronic spectra of the comparable structure in the series of cation distortion isomers of the $[\text{Cu}(\text{bpy})_2\text{Cl}]^{2+}$ cation (Harrison *et al.*, 1981).

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Structural Characterization of Two Hafnium(IV) Complexes, $\text{HfCl}_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2) \cdot 2\text{C}_7\text{H}_8$ and $\text{HfCl}_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)$

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Abstract. (1) [1,2-Bis(diphenylphosphino)ethane-*P,P'*)]tetrachlorohafnium(IV) bistoluene solvate,

$[\text{HfCl}_4(\text{C}_{26}\text{H}_{24}\text{P}_2)] \cdot 2\text{C}_7\text{H}_8$, $M_r = 903.01$, monoclinic, $C2/c$, $a = 11.340$ (3), $b = 18.243$ (6), $c = 19.661$ (3) Å, $\beta = 103.96$ (2)°, $V = 3947$ (3) Å³, $Z = 4$, $D_x = 1.519\ \text{g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu =$

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