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Structure of Bromobis[2,3-di(2-pyridyl)quinoxaline]copper(II) Hydrogensulfate–2,3-Di(2-pyridyl)quinoxaline (1/1)

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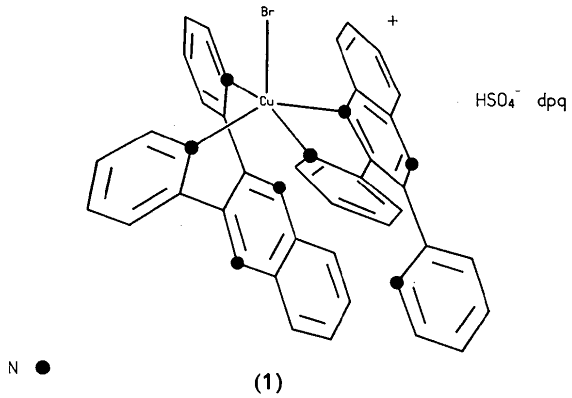
Abstract. $[CuBr(C_{18}H_{12}N_4)_2]HSO_4.C_{18}H_{12}N_4$, $C_{18}H_{12}N_4$ = dpq, $M_r = 1093{\cdot}54$, monoclinic, $C2/c$, $a = 26{\cdot}850\,(6)$, $b = 13{\cdot}487\,(4)$, $c = 27{\cdot}295\,(6)$ Å, $\beta = 107{\cdot}21\,(2)°$, $V = 9441\,(4)$ Å^3, $Z = 8$, $D_x = 1{\cdot}54$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 14{\cdot}04$ cm^{-1}, $F(000) = 4456$, $T = 294$ K, $R = 0{\cdot}0523$ for 3418 observed reflections. The title compound is the product of a side reaction in the bromo-induced oxidation of a copper/dpq system. Two dpq ligands are bonded to copper in a bidentate fashion; one is bonded only through pyridyl N atoms, while the other bonds through one pyridyl and one quinoxaline N atom. A third dpq molecule is not involved in bonding to copper nor in any other intermolecular or ionic interactions. The coordination sphere of the Cu atom has a distorted square pyramidal geometry, with the ligand N atoms forming the basal plane and the Br atom occupying the apical position.



(1)

Experimental. Green parallelepiped crystal of (1) obtained by slow evaporation of an ethanol solution, dimensions 0·20 × 0·25 × 0·38 mm. Data collected at room temperature, graphite-monochromated Mo $K\alpha$ radiation, Nicolet $R3mV$ diffractometer, ω scans of $2 - 15°\text{min}^{-1}$, $2\theta_{\max} = 45°$, $h = -29$ to 29, $k = 0$ to 15, $l = 0$ to 30, 6892 measurements, 6131 unique ($R_{\text{int}} = 0{\cdot}076$), 3418 observed [$I > 3\sigma(I)$]. Unit-cell dimensions determined by least-squares fit to settings for 29 reflections ($16 < 2\theta < 30°$). Empirical absorption correction ($\mu = 14{\cdot}04$ cm^{-1}), transmission factors 0·88–1·00; three standards monitored (± 2%), 66·9 h of X-ray exposure. Solved by the Patterson method; full-matrix least-squares refinement on F, $R = 0{\cdot}0523$, $wR = 0{\cdot}0568$, $S = 1{\cdot}24$, $(\Delta/\sigma)_{\max} = 0{\cdot}01$, 659 variables including positional parameters and anisotropic thermal parameters for all non-H atoms; H atoms located by standard techniques, included in the structure factor calculation in idealized positions (C—H = 0·96 Å) with group isotropic thermal parameter $U_{\text{H}} = 0{\cdot}057\,(5)$ Å^2. Function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + 0{\cdot}0005|F_o|^2]$. Final difference map peaks ranged from $-0{\cdot}46$ to $0{\cdot}56$ e Å^{-3}. Computer programs *SHELXTL* (Sheldrick, 1986), scattering factors (Cromer & Waber, 1974), real and imaginary anomalous-dispersion corrections (Cromer, 1974). Final atomic coordinates are given in Table 1,† selected distances and angles are reported in Table 2;

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52499 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Br(1)	7070 (1)	5380 (1)	1616 (1)	56 (1)
Cu(1)	6429 (1)	6542 (1)	1095 (1)	30 (1)
S(1)	3544 (1)	7558 (2)	−2171 (1)	51 (1)
O(1)	3436 (4)	7421 (7)	−2701 (4)	127 (6)
O(2)	3058 (3)	7803 (7)	−2113 (3)	89 (4)
O(3)	3744 (4)	6697 (6)	−1929 (4)	114 (5)
O(4)	3881 (3)	8354 (6)	−2028 (4)	116 (5)
N(1)	6636 (3)	7806 (5)	1498 (3)	30 (3)
N(2)	6002 (3)	9112 (5)	437 (3)	35 (3)
N(3)	5087 (3)	8046 (5)	354 (3)	40 (3)
N(4)	5791 (3)	6634 (5)	1360 (3)	35 (3)
N(5)	6043 (3)	5624 (5)	539 (3)	33 (3)
N(6)	6699 (3)	6990 (5)	481 (3)	32 (3)
N(7)	6634 (3)	8090 (6)	−391 (3)	44 (4)
N(8)	5416 (3)	6938 (6)	−853 (3)	48 (3)
N(9)	9020 (3)	3288 (6)	1762 (3)	56 (4)
N(10)	8390 (3)	3629 (5)	484 (3)	41 (3)
N(11)	8268 (3)	1560 (6)	460 (3)	40 (3)
N(12)	8745 (3)	657 (6)	1408 (3)	49 (4)
C(1)	7032 (3)	7864 (7)	1941 (3)	32 (3)
C(2)	7166 (4)	8744 (7)	2199 (3)	43 (4)
C(3)	6918 (4)	9583 (8)	1998 (4)	52 (4)
C(4)	6523 (3)	9539 (7)	1537 (3)	40 (4)
C(5)	6383 (3)	8626 (6)	1299 (3)	30 (3)
C(6)	5957 (3)	8560 (6)	813 (3)	31 (3)
C(7)	5599 (4)	9133 (7)	−2 (4)	43 (4)
C(8)	5654 (4)	9658 (7)	−429 (3)	46 (4)
C(9)	5250 (5)	9668 (8)	−869 (4)	59 (5)
C(10)	4791 (1)	9192 (8)	−901 (4)	56 (5)
C(11)	4721 (4)	8684 (8)	−496 (4)	57 (5)
C(12)	5137 (3)	8621 (7)	−41 (3)	40 (4)
C(13)	5495 (3)	7994 (6)	766 (3)	33 (4)
C(14)	5429 (3)	7342 (6)	1179 (3)	33 (3)
C(15)	5001 (4)	7413 (7)	1357 (4)	46 (4)
C(16)	4948 (4)	6758 (8)	1723 (4)	57 (5)
C(17)	5312 (4)	6039 (8)	1902 (4)	54 (5)
C(18)	5730 (4)	5996 (7)	1709 (3)	46 (4)
C(19)	5816 (4)	4786 (7)	614 (4)	51 (4)
C(20)	5597 (4)	4131 (8)	238 (4)	61 (5)
C(21)	5638 (4)	4312 (8)	−246 (4)	52 (4)
C(22)	5879 (3)	5172 (7)	−331 (3)	44 (4)
C(23)	6067 (3)	5826 (6)	65 (3)	30 (3)
C(24)	6353 (3)	6741 (6)	37 (3)	32 (3)
C(25)	7042 (3)	7719 (7)	493 (3)	32 (4)
C(26)	7455 (3)	7924 (7)	935 (4)	43 (4)
C(27)	7785 (4)	8690 (8)	934 (4)	52 (5)
C(28)	7734 (4)	9262 (8)	491 (5)	58 (5)
C(29)	7364 (4)	9058 (7)	53 (4)	49 (5)
C(30)	7014 (4)	8272 (7)	43 (4)	41 (4)
C(31)	6312 (3)	7363 (7)	−405 (3)	34 (4)
C(32)	5874 (4)	7251 (7)	−893 (3)	39 (4)
C(33)	5959 (4)	7544 (8)	−1346 (3)	51 (4)
C(34)	5543 (5)	7496 (9)	−1780 (4)	69 (5)
C(35)	5066 (5)	7162 (9)	−1753 (4)	70 (5)
C(36)	5028 (4)	6923 (8)	−1287 (4)	57 (5)
C(37)	9190 (5)	3809 (10)	2196 (5)	79 (6)
C(38)	8985 (5)	4694 (10)	2275 (5)	73 (6)
C(39)	8584 (5)	5068 (8)	1897 (5)	74 (6)
C(40)	8402 (5)	4557 (8)	1450 (4)	61 (5)
C(41)	8629 (4)	3684 (7)	1387 (4)	43 (4)
C(42)	8456 (4)	3105 (7)	900 (4)	41 (4)
C(43)	8262 (4)	3130 (7)	32 (4)	41 (4)
C(44)	8208 (4)	3627 (7)	−426 (4)	49 (4)
C(45)	8112 (4)	3132 (8)	−871 (4)	53 (5)
C(46)	8045 (4)	2112 (8)	−889 (4)	56 (5)
C(47)	8082 (3)	1586 (8)	−458 (3)	46 (4)
C(48)	8195 (4)	2067 (7)	13 (4)	41 (4)
C(49)	8387 (3)	2050 (7)	887 (3)	34 (4)
C(50)	8442 (4)	1435 (7)	1354 (3)	43 (4)
C(51)	8150 (4)	1644 (8)	1680 (4)	58 (4)
C(52)	8164 (5)	994 (9)	2080 (4)	66 (6)
C(53)	8467 (5)	190 (9)	2139 (4)	69 (6)
C(54)	8763 (5)	64 (8)	1806 (5)	71 (5)

illustrations and atomic numbering schemes of the cation and the uncomplexed ligand are shown in Figs. 1 and 2, respectively.

Table 2. *Selected bond distances* (Å) *and angles* (°)

Br(1)—Cu(1)	2·446 (2)	Cu(1)—N(1)	2·016 (7)
Cu(1)—N(4)	2·052 (8)	Cu(1)—N(5)	1·995 (7)
Cu(1)—N(6)	2·101 (8)	S(1)—O(1)	1·402 (11)
S(1)—O(2)	1·399 (9)	S(1)—O(3)	1·365 (9)
S(1)—O(4)	1·383 (9)	N(1)—C(1)	1·354 (9)
N(1)—C(5)	1·328 (10)	N(2)—C(6)	1·301 (12)
N(2)—C(7)	1·355 (11)	N(3)—C(12)	1·366 (13)
N(3)—C(13)	1·318 (10)	N(4)—C(14)	1·348 (11)
N(4)—C(18)	1·330 (13)	N(5)—C(19)	1·329 (12)
N(5)—C(23)	1·341 (12)	N(6)—C(24)	1·334 (10)
N(6)—C(25)	1·343 (11)	N(7)—C(30)	1·338 (11)
N(7)—C(31)	1·301 (12)	N(8)—C(32)	1·335 (14)
N(8)—C(36)	1·325 (11)	N(9)—C(37)	1·336 (14)
N(9)—C(41)	1·341 (12)	N(10)—C(42)	1·305 (12)
N(10)—C(43)	1·359 (12)	N(11)—C(48)	1·360 (13)
N(11)—C(49)	1·295 (12)	N(12)—C(50)	1·309 (13)
N(12)—C(54)	1·338 (15)	C(5)—C(6)	1·477 (10)
C(6)—C(13)	1·428 (12)	C(13)—C(14)	1·483 (13)
C(23)—C(24)	1·469 (12)	C(24)—C(31)	1·445 (13)
C(31)—C(32)	1·500 (11)	C(41)—C(42)	1·493 (13)
C(42)—C(49)	1·434 (13)	C(49)—C(50)	1·491 (13)
Br(1)—Cu(1)—N(1)	101·1 (2)	Br(1)—Cu(1)—N(4)	110·6 (2)
N(1)—Cu(1)—N(4)	83·1 (3)	Br(1)—Cu(1)—N(5)	99·3 (2)
N(1)—Cu(1)—N(5)	159·6 (3)	N(4)—Cu(1)—N(5)	90·3 (3)
Br(1)—Cu(1)—N(6)	107·3 (2)	N(1)—Cu(1)—N(6)	95·0 (3)
N(4)—Cu(1)—N(6)	141·7 (3)	N(5)—Cu(1)—N(6)	78·2 (3)
O(1)—S(1)—O(2)	103·5 (6)	O(1)—S(1)—O(3)	108·6 (6)
O(2)—S(1)—O(3)	113·1 (6)	O(1)—S(1)—O(4)	108·2 (7)
O(2)—S(1)—O(4)	109·8 (6)	O(3)—S(1)—O(4)	113·1 (5)
Cu(1)—N(1)—C(1)	123·6 (6)	Cu(1)—N(1)—C(5)	117·1 (5)
C(1)—N(1)—C(5)	119·2 (7)	C(6)—N(2)—C(7)	118·2 (8)
C(12)—N(3)—C(13)	116·9 (8)	Cu(1)—N(4)—C(14)	120·1 (6)
Cu(1)—N(4)—C(18)	120·4 (6)	C(14)—N(4)—C(18)	119·6 (8)
Cu(1)—N(5)—C(19)	124·6 (6)	Cu(1)—N(5)—C(23)	116·5 (6)
C(19)—N(5)—C(23)	118·5 (7)	Cu(1)—N(6)—C(24)	110·0 (6)
Cu(1)—N(6)—C(25)	126·1 (6)	C(24)—N(6)—C(25)	119·5 (8)
C(30)—N(7)—C(31)	119·3 (8)	C(32)—N(8)—C(36)	115·6 (9)
C(37)—N(9)—C(41)	116·9 (9)	C(42)—N(10)—C(43)	117·0 (8)
C(48)—N(11)—C(4)	118·8 (8)	C(50)—N(12)—C(54)	116·3 (10)
N(1)—C(5)—C(6)	119·0 (7)	C(4)—C(5)—C(6)	120·2 (7)
N(2)—C(6)—C(5)	116·5 (8)	N(2)—C(6)—C(13)	121·0 (7)
C(5)—C(6)—C(13)	122·3 (8)	N(3)—C(13)—C(6)	121·9 (8)
N(3)—C(13)—C(14)	115·0 (8)	C(6)—C(13)—C(14)	123·0 (7)
N(4)—C(14)—C(13)	117·6 (8)	C(13)—C(14)—C(15)	121·9 (8)
N(5)—C(23)—C(24)	113·4 (7)	C(22)—C(23)—C(24)	125·1 (9)
N(6)—C(24)—C(23)	113·4 (7)	N(6)—C(24)—C(31)	118·3 (8)
C(23)—C(24)—C(31)	128·3 (7)	N(7)—C(31)—C(24)	121·8 (7)
N(7)—C(31)—C(32)	116·2 (8)	C(24)—C(31)—C(32)	121·9 (8)
N(8)—C(32)—C(31)	117·4 (9)	C(31)—C(32)—C(33)	118·2 (9)
N(9)—C(41)—C(42)	116·0 (9)	C(40)—C(41)—C(42)	122·2 (8)
N(10)—C(42)—C(41)	114·7 (8)	N(10)—C(42)—C(49)	122·2 (8)
C(41)—C(42)—C(49)	123·0 (8)	N(11)—C(49)—C(42)	121·6 (9)
N(11)—C(49)—C(50)	115·0 (8)	C(42)—C(49)—C(50)	123·5 (8)
N(12)—C(50)—C(49)	116·4 (9)	C(49)—C(50)—C(51)	120·4 (9)

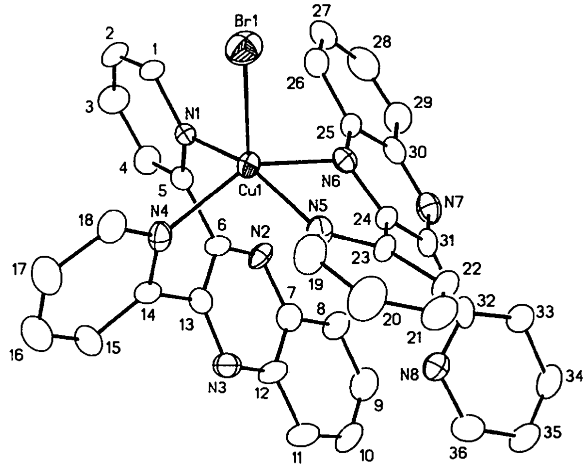

Fig. 1. Thermal ellipsoid plot (35% probability) and numbering scheme for the cation.

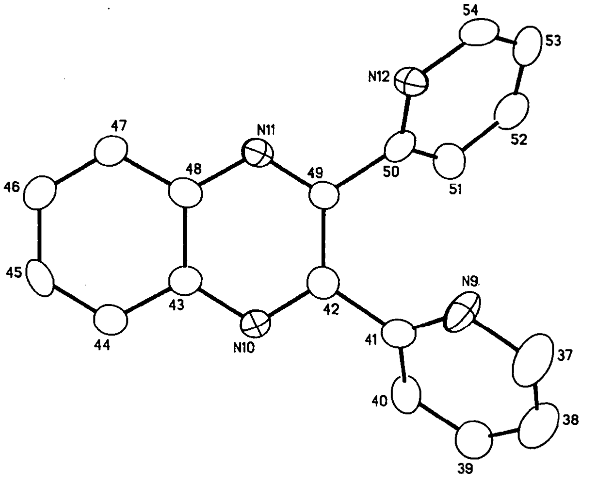

Fig. 2. Thermal ellipsoid plot (35% probability) and numbering scheme for the uncomplexed dpq molecule.

Related literature. The title compound represents the first example of copper coordinated to 2,3-di(2-pyridyl)quinoxaline. Related structures such as that of bis(2,2′-bipyridyl)monochlorocopper(II) perchlorate have been reported by Harrison, Kennedy, Power, Sheahan & Hathaway (1981, and references therein).

The Cu(1)—Br(1) distance is 2·446 (2) Å as compared to values of 2·394 (1) and 3·018 (1) Å observed for a system consisting of $CuBr_2$ units bridged by 2,2′-bipyrimidine (Julve, De Munno, Bruno & Verdaguer, 1988). In that compound, two short Cu–Br contacts lie *trans* to Cu—N bonds to the bridging ligand in a square-planar arrangement about the copper; two long Cu–Br contacts link the square-planar units into an extended array, and complete a distorted octahedral coordination about the Cu atom.

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Structure of 1,4-Diphenyl-2-tetrazenidobis(triethylphosphine)nickel

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Abstract. [$Ni(C_{12}H_{10}N_4)(C_6H_{15}P)_2$], $M_r = 505{\cdot}33$, orthorhombic, $Pbc2_1$, $a = 8{\cdot}670$ (3), $b = 17{\cdot}169$ (6), $c = 17{\cdot}923$ (7) Å, $V = 2668$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}26$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 8{\cdot}62$ cm^{-1}, $T = 298$ K, $F(000) = 1080$. $R = 0{\cdot}065$ for 1564 reflections with $I > 3{\cdot}0\sigma(I)$ (2019 independent observations). The coordination sphere of Ni is a tetrahedron distorted toward a square plane with a dihedral angle of 56·9° between NiN_4 and NiP_2 planes. Short Ni—N bonds [1·883 (8), 1·883 (10) Å] and three similar N—N bonds[1·28 (2)–1·36 (2) Å] indicate a delocalization of π-electron density in the metallacycle.

Experimental. X-ray data were collected with a Nicolet *R3m/V* automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Crystals of $Ni(1,4\text{-}Ph_2N_4)(PEt_3)_2$ were unexpectedly obtained from the reaction between $NiCl_2(PEt_3)_2$ and $[Li(THF)_x]_2(PhN_3NHCH_2CH_2NHN_3Ph)$ in tetrahydrofuran (THF) solvent. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit-cell parameters were determined from 25 machine-centered reflections with $15 < 2\theta < 30°$. The intensities of three check reflections ($3\bar{2}1$, 222, 320) were monitored after every 100 reflections and showed statistical variations within 3%. Data were corrected for Lorentz and polarization effects. No absorption correction was applied. The systematic absences $0kl(k = 2n + 1)$, $h0l(l = 2n + 1)$, $0k0(k = 2n + 1)$, and $00l(l = 2n + 1)$ indicated two possible space groups: $Pbc2_1$ and $Pbcm$. A statistical analysis of intensities suggested a non-centrosymmetric space group and the structure

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