

The Structures of Bis(2,2'-bipyridyl)monoiodocopper(II) Perchlorate and Bis(2,2'-bipyridyl)monobromocopper(II) Tetrafluoroborate

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Abstract

The crystal structures of bis(2,2'-bipyridyl)monoiodocopper(II) perchlorate, $[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{I}]\text{ClO}_4$, $\text{C}_{20}\text{H}_{16}\text{CuIN}_4^+\cdot\text{ClO}_4^-$ (I), and bis(2,2'-bipyridyl)monobromocopper(II) tetrafluoroborate, $[\text{CuBr}(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{BF}_4$, $\text{C}_{20}\text{H}_{16}\text{BrCuN}_4^+\cdot\text{BF}_4^-$ (II), have been established by X-ray analysis. (I) is triclinic, space group $P\bar{1}$ with $a = 7.420$ (2), $b = 10.944$ (2), $c = 14.270$ (2) Å, $\alpha = 108.41$ (2), $\beta = 95.09$ (2), $\gamma = 99.27$ (2)°, $Z = 2$; (II) is monoclinic, space group $P2_1/c$ with $a = 10.862$ (2), $b = 12.240$ (2), $c = 17.304$ (2) Å, $\beta = 113.87$ (5)°, $Z = 4$. Both structures involve a distorted five-coordinate $[\text{Cu}(\text{bpy})_2\text{X}]^+$ cation and ClO_4^- and BF_4^- anions for (I) and (II), respectively. (I) involves a symmetrical angular distortion of the trigonal-bipyramidal CuN_4X chromophore, while in (II) the distortion is unsymmetrical.

The crystal structure of bis(2,2'-bipyridyl)monoiodocopper(II) iodide (Barclay, Hoskins & Kennard, 1963) was the first crystal structure in which it was established that the $[\text{Cu}(\text{bpy})_2\text{X}]^+$ cation involved a five-coordinate trigonal-bipyramidal stereochemistry (bpy = 2,2'-bipyridyl). Owing to the presence of the heavy I atom and the use of visually estimated data the final R (0.09) was relatively high and the Cu–N distances, 1.96–2.10 Å, were not considered significantly different. As the electronic spectra of a series of $[\text{Cu}(\text{bpy})_2\text{X}]^+$ cations, where $\text{X} = \text{Cl}^-$, Br^- and I^- (Elliott, Hathaway & Slade, 1966), show splittings from 0.0– $3.8 \times 10^3 \text{ cm}^{-1}$ the crystal structures of $[\text{Cu}(\text{bpy})_2\text{I}]\text{ClO}_4$ (I) and $[\text{Cu}(\text{bpy})_2\text{Br}]\text{BF}_4$ (II) have been determined to establish a correlation between the electronic spectra and the structural distortions of the $[\text{Cu}(\text{bpy})_2\text{X}]^+$ cation.

Experimental

(I) was prepared as previously reported (Harris, Lockyer & Waterman, 1961; Elliott, Hathaway & Slade, 1966); (II) was prepared by an analogous

method; composition found: C 44.21, H 2.97, N 10.41, Br 14.72, Cu 11.26%; calculated for $\text{C}_{20}\text{H}_{16}\text{BBrcuF}_4\text{N}_4$: C 44.25, H 2.95, N 10.32, Br 14.74, Cu 11.72%.

Crystal data

The crystal and refinement data for (I) and (II) are summarized in Table 1. For both complexes the preliminary cell dimensions and space group were determined from precession photographs and refined on a Philips PW 1100 four-circle diffractometer. The intensities were collected on the diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. A θ – 2θ scan mode was used and reflections with $3.0 < \theta < 32^\circ$ in one quadrant were examined. A constant scan speed of $0.05^\circ \text{ s}^{-1}$ was used with a variable scan width of $(0.7 + 0.1 \tan \theta)^\circ$. With an acceptance criterion $I > 2.5\sigma(I)$, 4065 reflections for (I) and 2123 for (II) were retained. Lorentz and polarization corrections were

Table 1. Crystal and refinement data

	(I)	(II)
Compound	$[\text{Cu}(\text{bpy})_2\text{I}]\text{ClO}_4$	$[\text{Cu}(\text{bpy})_2\text{Br}]\text{BF}_4$
M_r	601.93	542.29
Stoichiometry	$\text{C}_{20}\text{H}_{16}\text{ClCuIN}_4\text{O}_4$	$\text{C}_{20}\text{H}_{16}\text{BBrcuF}_4\text{N}_4$
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	7.420 (2)	10.862 (2)
b (Å)	10.944 (2)	12.240 (2)
c (Å)	14.270 (2)	17.304 (2)
α (°)	108.41 (2)	
β (°)	95.09 (2)	113.87 (5)
γ (°)	99.27 (2)	
Z	2	4
U (Å ³)	1073.01	2103.80
D_m (floatation) (Mg m^{-3})	1.914	1.78
D_c (Mg m^{-3})	1.863	1.706
$F(000)$	589.98	1075.96
μ (mm^{-1})	0.2480	0.2911
Radiation ($\lambda = 0.7107$ Å)	Mo $K\alpha$	Mo $K\alpha$
Number of unique reflections (N)	4065	2123
Number of anisotropic atoms	33	29
Number of parameters (NP)	298	262
N/NP	13.64	8.13
$R = (\sum \Delta / \sum F_o)$	0.0475	0.0563
$R_w = (\sum \Delta w^{1/2} / \sum F_o w^{1/2})$	0.0573	0.0643
k	0.7402	1.2119
g	0.002901	0.001573
Maximum final shift/e.s.d.	0.02	0.01
Residual electron density (e Å^{-3})	0.99	0.75

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applied, but no correction was made for absorption. The structures were solved by Patterson and Fourier techniques and refined by blocked-matrix least squares, with anisotropic temperature factors for all non-hydrogen atoms. The positions of the H atoms were calculated geometrically with $\text{C}-\text{H} = 1.08 \text{ \AA}$ and a fixed temperature factor of 0.07 \AA^2 , and floated on the adjacent C atoms. The refinement converged when the maximum shift/e.s.d. was <0.02 with a weighting scheme $w = k/[\sigma^2(F_o) + g(F_o)^2]$ (Table 1).^{*} Complex neutral-atom scattering factors were used for the non-

^{*} Lists of structure factors, calculated H atom positions and anisotropic temperature factors for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34819 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

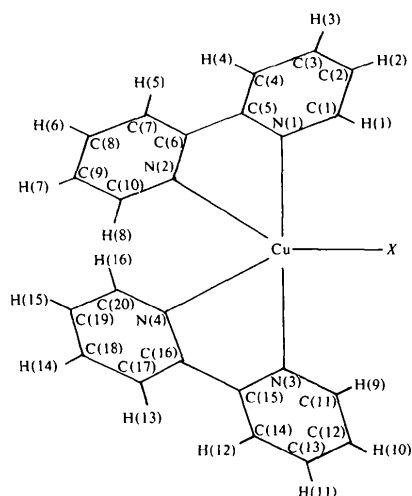


Fig. 1. The molecular structure of the $[\text{Cu}(\text{bpy})_2\text{X}]^+$ cation with the atom numbering.

Table 2. Fractional coordinates ($\times 10^4$) for the non-hydrogen atoms

	* (I) $[\text{Cu}(\text{bpy})_2]\text{ClO}_4$			(II) $[\text{Cu}(\text{bpy})_2\text{Br}]\text{BF}_4$		
	x	y	z	x	y	z
Cu	5645 (1)	1441 (1)	7743 (1)	1281 (1)	475 (1)	3639 (1)
X*	9208 (1)	1323 (1)	7686 (1)	1304 (1)	-1501 (1)	3641 (1)
N(1)	4752 (7)	-272 (4)	6650 (4)	2816 (6)	570 (5)	4770 (4)
C(1)	5181 (9)	-1395 (6)	6673 (5)	2933 (8)	-55 (7)	5436 (4)
C(2)	4376 (10)	-2584 (7)	5940 (6)	4067 (9)	1 (7)	6185 (4)
C(3)	3190 (10)	-2595 (7)	5141 (6)	5075 (9)	702 (7)	6254 (5)
C(4)	2783 (8)	-1419 (7)	5095 (5)	4977 (8)	1341 (6)	5587 (5)
C(5)	3572 (7)	-257 (6)	5872 (4)	3800 (7)	1270 (6)	4836 (5)
C(6)	3229 (7)	1064 (6)	5926 (4)	3554 (7)	1933 (6)	4056 (5)
C(7)	2115 (8)	1252 (7)	5173 (5)	4402 (8)	2748 (6)	4018 (6)
C(8)	1879 (9)	2534 (9)	5299 (6)	4055 (11)	3316 (7)	3269 (7)
C(9)	2712 (10)	3553 (8)	6132 (6)	2905 (10)	3079 (7)	2591 (6)
C(10)	3857 (9)	3266 (6)	6846 (5)	2098 (8)	2223 (6)	2665 (5)
N(2)	4093 (7)	2053 (5)	6744 (3)	2421 (5)	1670 (5)	3394 (4)
N(3)	6316 (6)	3115 (4)	8890 (3)	-281 (6)	501 (5)	2518 (3)
C(11)	7404 (8)	4220 (6)	8884 (5)	-280 (9)	-49 (7)	1839 (5)
C(12)	8002 (9)	5303 (6)	9727 (6)	-1440 (9)	-115 (8)	1092 (5)
C(13)	7540 (9)	5243 (7)	10625 (5)	-2585 (9)	373 (7)	1054 (5)
C(14)	6438 (9)	4104 (7)	10643 (5)	-2566 (8)	944 (7)	1742 (5)
C(15)	5770 (7)	3068 (6)	9758 (4)	-1390 (7)	1013 (5)	2470 (4)
C(16)	4503 (7)	1858 (6)	9690 (4)	-1245 (7)	1644 (5)	3228 (4)
C(17)	3643 (9)	1692 (7)	10486 (5)	-2203 (8)	2366 (7)	3246 (5)
C(18)	2484 (9)	533 (8)	10344 (6)	-1953 (10)	2969 (7)	3969 (6)
C(19)	2114 (9)	-453 (8)	9421 (6)	-728 (9)	2821 (7)	4668 (5)
C(20)	2988 (8)	-224 (6)	8652 (5)	162 (8)	2078 (6)	4600 (5)
N(4)	4160 (6)	904 (5)	8786 (4)	-66 (6)	1481 (5)	3920 (4)
Cl	950 (3)	3707 (2)	2835 (2)	B(1)	-3615 (4)	5994 (3)
O(1)	668 (25)	4334 (13)	3807 (9)	F(1)	-2524 (4)	6631 (3)
O(2)	826 (18)	2343 (9)	2755 (9)	F(2)	-3257 (4)	5238 (3)
O(3)	-234 (17)	3778 (14)	2061 (10)	F(3)	-4627 (14)	6640 (3)
O(4)	2874 (19)	4009 (16)	2678 (12)	F(4)	-4054 (4)	5469 (3)
O(1')	696 (44)	5023 (29)	2930 (20)			
O(2')	-333 (52)	3020 (32)	3159 (25)			
O(3')	1397 (63)	3085 (34)	2071 (36)			
O(4')	2476 (58)	4410 (41)	3334 (34)			

* X = I in (I) and Br in (II).

Table 3. Bond lengths (Å) with e.s.d.'s in parentheses

	(I) [Cu(bpy) ₂]ClO ₄	(II) [Cu(bpy) ₂]BrBF ₄
X—Cu*	2.675 (4)	2.419 (3)
N(1)—Cu	1.989 (6)	1.996 (6)
N(2)—Cu	2.090 (8)	2.068 (8)
N(3)—Cu	1.987 (6)	1.995 (7)
N(4)—Cu	2.100 (7)	2.114 (9)
C(1)—N(1)	1.328 (10)	1.346 (11)
C(5)—N(1)	1.357 (9)	1.338 (11)
C(2)—C(1)	1.386 (9)	1.381 (10)
C(3)—C(2)	1.372 (12)	1.357 (14)
C(4)—C(3)	1.389 (12)	1.363 (14)
C(5)—C(4)	1.394 (8)	1.409 (10)
C(6)—C(5)	1.487 (10)	1.503 (13)
C(7)—C(6)	1.385 (10)	1.377 (13)
N(2)—C(6)	1.338 (7)	1.337 (9)
C(8)—C(7)	1.398 (14)	1.382 (15)
C(9)—C(8)	1.360 (11)	1.355 (13)
C(10)—C(9)	1.411 (13)	1.404 (14)
N(2)—C(10)	1.331 (10)	1.347 (11)
C(11)—N(3)	1.345 (9)	1.355 (12)
C(15)—N(3)	1.349 (9)	1.331 (11)
C(12)—C(11)	1.373 (9)	1.395 (11)
C(13)—C(12)	1.374 (12)	1.358 (15)
C(14)—C(13)	1.386 (11)	1.373 (13)
C(15)—C(14)	1.389 (8)	1.387 (10)
C(16)—C(15)	1.466 (9)	1.474 (11)
C(17)—C(16)	1.398 (11)	1.376 (12)
N(4)—C(16)	1.350 (7)	1.368 (8)
C(18)—C(17)	1.358 (12)	1.381 (14)
C(19)—C(18)	1.384 (11)	1.401 (12)
C(20)—C(19)	1.391 (12)	1.368 (14)
N(4)—C(20)	1.339 (9)	1.320 (11)
O(1)—Cl	1.391 (14)	F—B 1.37
O(2)—Cl	1.447 (11)	
O(3)—Cl	1.379 (16)	
O(4)—Cl	1.465 (15)	
O(1')—Cl	1.448 (35)	
O(2')—Cl	1.324 (39)	
O(3')—Cl	1.196 (47)	
O(4')—Cl	1.270 (38)	

* X = I in (I) and Br in (II).

hydrogen atoms and those for the heavy atoms were corrected for anomalous dispersion (Cromer & Waber, 1965; Cromer & Liberman, 1970). All calculations were carried out with *SHELX 76* (Sheldrick, 1976), *PLUTO* (W. D. S. Motherwell), and *XPUB* (R. Taylor) on an IBM 370/138 computer. The final non-hydrogen atom coordinates are given in Table 2, bond lengths in Table 3, bond angles in Table 4, and some mean planes in Table 5. Fig. 1 illustrates the structures and the atom numbering.

Discussion

Both complexes consist of independent five-coordinate cations and tetrahedral anions, [Cu(bpy)₂I]⁺ and ClO₄⁻ in (I), [Cu(bpy)₂Br]⁺ and BF₄⁻ in (II). In neither structure is there any unusual feature in either the bond lengths or angles of the organic ligands (Stephens, 1969, 1972; Ray & Hathaway, 1978). Both anions yielded clear evidence for disorder; in the perchlorate anion of (I) this was best represented by two interpenetrating anions with a 66% occupation factor (Kilbourne, Ryan & Dunitz, 1969) and in the tetrafluoroborate anion by a rigid tetrahedron with fixed B—F distances of 1.37 Å (Stynes & Ibers, 1971). In neither complex was there any evidence for even semicoordination of the perchlorate or tetrafluoroborate anions to the [Cu(bpy)₂X]⁺ cations (Tomlinson, Hathaway, Billing & Nichols, 1969). Both Cu^{II} cations involve a distorted trigonal-bipyramidal five-coordinate CuN₄X geometry; the Cu—N(1) and Cu—N(3) distances are not significantly different (av. 1.99 Å) and the N(1)—Cu—N(3) angles are almost 180° (av. 175°). In (I) the in-plane Cu—N distances are not significantly different (av. 2.095 Å) and ca 0.1 Å longer than the axial Cu—N distance as observed previously in trigonal-bipyramidal Cu^{II} complexes (Huq & Skapski, 1971). In

Table 4. Bond angles (°) with e.s.d.'s in parentheses

	(I) [Cu(bpy) ₂]I· ClO ₄	(II) [Cu(bpy) ₂]Br· BF ₄	(I) [Cu(bpy) ₂]I· ClO ₄	(II) [Cu(bpy) ₂]Br· BF ₄	(I) [Cu(bpy) ₂]I· ClO ₄	(II) [Cu(bpy) ₂]Br· BF ₄		
N(1)—Cu—X*	93.8 (2)	93.0 (3)	N(2)—C(6)—C(5)	115.3 (6)	113.9 (7)	N(4)—C(16)—C(17)	121.1 (6)	121.5 (8)
N(2)—Cu—X*	122.9 (2)	134.5 (2)	N(2)—C(6)—C(7)	122.6 (7)	122.4 (8)	C(18)—C(17)—C(16)	118.7 (7)	119.3 (8)
N(2)—Cu—N(1)	80.3 (3)	80.1 (3)	C(8)—C(7)—C(6)	117.5 (6)	118.4 (8)	C(19)—C(18)—C(17)	120.9 (9)	118.9 (10)
N(3)—Cu—X*	91.0 (2)	91.2 (3)	C(9)—C(8)—C(7)	121.1 (9)	120.7 (10)	C(20)—C(19)—C(18)	117.9 (8)	117.9 (9)
N(3)—Cu—N(1)	174.4 (2)	175.6 (2)	C(10)—C(9)—C(8)	117.2 (9)	118.2 (10)	N(4)—C(20)—C(19)	122.0 (6)	124.1 (7)
N(3)—Cu—N(2)	99.5 (3)	97.7 (3)	N(2)—C(10)—C(9)	122.7 (6)	121.7 (7)	C(16)—N(4)—Cu	112.3 (5)	111.9 (6)
N(4)—Cu—X*	122.8 (2)	126.2 (3)	C(6)—N(2)—Cu	113.2 (5)	114.5 (6)	C(20)—N(4)—Cu	128.2 (5)	129.0 (6)
N(4)—Cu—N(1)	94.9 (3)	97.0 (3)	C(10) N(2) Cu	127.9 (5)	126.6 (5)	C(20)—N(4) C(16)	119.5 (7)	118.1 (7)
N(4)—Cu—N(2)	114.3 (3)	99.4 (3)	C(10)—N(2)—C(6)	118.9 (7)	118.7 (8)	O(2)—Cl—O(1)	104.8 (9)	F—B—F 109.5
N(4)—Cu—N(3)	80.1 (3)	79.6 (3)	C(11)—N(3)—Cu	124.9 (5)	122.5 (6)	O(3)—Cl—O(1)	118.0 (10)	
C(1)—N(1)—Cu	123.7 (5)	123.9 (6)	C(15)—N(3)—Cu	115.9 (5)	117.4 (6)	O(3)—Cl—O(2)	109.2 (8)	
C(5)—N(1)—Cu	116.0 (5)	116.3 (6)	C(15)—N(3)—C(11)	118.9 (5)	120.0 (7)	O(4)—Cl—O(1)	113.3 (10)	
C(5)—N(1)—C(1)	120.2 (6)	119.7 (6)	C(12)—C(11)—N(3)	122.7 (8)	121.0 (10)	O(4)—Cl—O(2)	99.0 (10)	
C(2)—C(1)—N(1)	121.5 (7)	120.9 (9)	C(13)—C(12)—C(11)	118.9 (7)	119.0 (10)	O(4)—Cl—O(3)	110.5 (10)	
C(3)—C(2)—C(1)	119.4 (8)	119.7 (9)	C(14)—C(13)—C(12)	118.8 (6)	119.3 (8)	O(2')—Cl—O(1')	114.7 (22)	
C(4)—C(3)—C(2)	119.4 (7)	120.3 (8)	C(15)—C(14)—C(13)	119.8 (7)	120.3 (9)	O(3')—Cl—O(1')	117.0 (27)	
C(5)—C(4)—C(3)	118.9 (7)	118.4 (8)	C(14)—C(15)—N(3)	120.6 (6)	120.3 (8)	O(3')—Cl—O(2')	113.7 (24)	
C(4)—C(5)—N(1)	120.5 (7)	120.9 (8)	C(16)—C(15)—N(3)	115.5 (5)	115.1 (6)	O(4')—Cl—O(1')	77.6 (26)	
C(6)—C(5)—N(1)	115.0 (5)	115.1 (6)	C(16)—C(15)—C(14)	124.0 (7)	124.6 (8)	O(4')—Cl—O(2')	126.6 (29)	
C(6)—C(5)—C(4)	124.5 (7)	124.0 (8)	C(17)—C(16)—C(15)	123.4 (6)	123.1 (7)	O(4')—Cl—O(3')	102.8 (30)	
C(7)—C(6)—C(5)	122.1 (6)	123.7 (7)	N(4)—C(16)—C(15)	115.5 (6)	115.3 (7)			

* X = I in (I) and Br in (II).

Table 5. Equations of the planes of best fit given in the form $lX + mY + nZ - p = 0$ with reference to the cell axes and with p in Å

The deviations (Å) of the most relevant atoms from the planes are given in square brackets; the r.m.s. deviation of the planes and the angles between them are given where relevant.

(I) $[\text{Cu}(\text{bpy})_2\text{I}]\text{ClO}_4$; e.s.d.'s are in the range 0.0010–0.0022 Å

	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
Plane (1): N(1), C(1)–C(5) (r.m.s.d. = 0.0125)	0.7672	–0.0353	–0.6404	3.2524
[C(1) 0.0205, C(2) –0.0145, C(4) 0.0128]				
Plane (2): C(6)–C(10), N(2) (r.m.s.d. = 0.0075)	0.7890	–0.0128	–0.6143	2.9922
[C(9) –0.0116, C(10) 0.0089, C(6) –0.0084]				
Plane (3): N(1), C(1)–C(10), N(2) (r.m.s.d. = 0.0223)	0.7780	–0.0231	–0.6278	3.1386
[C(1) 0.0415, C(7) 0.0319, C(3) –0.0286]				
Plane (4): N(3), C(11)–C(15) (r.m.s.d. = 0.0201)	0.8092	–0.5428	0.2248	–4.9537
[C(15) –0.0324, C(14) 0.0225, C(12) –0.0218]				
Plane (5): C(16)–C(20), N(4) (r.m.s.d. = 0.0060)	0.7628	–0.5451	0.3477	–6.2754
[C(17) –0.0100, C(18) 0.0072]				
Plane (6): N(3), C(11)–C(20), N(4) (r.m.s.d. = 0.066)	0.7813	–0.5523	0.2907	–5.5702
[C(14) 0.1235, C(12) –0.0822, C(18) –0.0779]				
Plane (7): Cu, I, N(1), N(3) (r.m.s.d. = 0.0201)	–0.0202	–0.5000	0.8658	–8.4325
[Cu –0.0331]				
Plane (8): Cu, I, N(2), N(4) (r.m.s.d. = 0.0036)	0.2605	0.9085	0.3268	–4.9866
[Cu 0.0063]				

Angles between planes (1) and (2) = 2.34° ; (3) and (6) = 64.02° ; (4) and (5) = 7.53° ; (7) and (8) = 100.17° . [E.s.d.'s are in the range 0.4–1.2°.]

(II) $[\text{Cu}(\text{bpy})_2\text{Br}]\text{BF}_4$; e.s.d.'s are in the range 0.0011–0.0024 Å

	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
Plane (1): N(1), C(1)–C(5) (r.m.s.d. = 0.005)	–0.4333	0.7151	0.5485	–3.1426
[C(5) 0.0082, C(4) –0.0063, N(1) –0.0059]				
Plane (2): C(6)–C(10), N(2) (r.m.s.d. = 0.0066)	–0.5052	0.6613	0.5545	–2.8037
[C(9) 0.0106, C(10) –0.0095, C(6) 0.0052]				
Plane (3): N(1), C(1)–C(10), N(2) (r.m.s.d. = 0.0441)	–0.4703	0.6905	0.5495	–2.9852
[C(4) –0.0640, N(2) –0.0603, C(1) 0.0617]				
Plane (4): N(3), C(11)–C(15) (r.m.s.d. = 0.0107)	0.2662	0.8306	–0.4891	1.7423
[C(15) 0.0153, N(3) –0.0147, C(12) 0.0109]				
Plane (5): C(16)–C(20), N(4) (r.m.s.d. = 0.0089)	0.4203	0.7172	–0.5559	2.5007
[N(4) –0.0146, C(16) 0.0135]				
Plane (6): N(3), C(11)–C(20), N(4) (r.m.s.d. = 0.0984)	0.3470	0.7793	0.5218	2.0084
[N(4) –0.1572, C(11) 0.1400, C(14) –0.1374]				
Plane (7): Cu, Br, N(1), N(3) (r.m.s.d. = 0.0072)	–0.6361	–0.0135	0.7715	–3.6209
[Cu –0.0119]				
Plane (8): Cu, Br, N(2), N(4) (r.m.s.d. = 0.0000)	0.6295	0.0039	0.7770	–5.2603

Angles between planes (1) and (2) = 5.16° ; (4) and (5) = 11.63° ; (3) and (6) = 84.94° ; (7) and (8) = 78.52° . [E.s.d.'s are in the range 0.5–1.4°.]

(II), the Cu–N(4) distance, 2.114 Å, is significantly longer than the Cu–N(2) distance, 2.068 Å. The Cu–I distance of 2.675 Å in (I) and the Cu–Br distance of 2.419 Å in (II) are consistent with those previously observed for the Cu–halide distances of 2.70 and 2.423 Å respectively (Barclay, Hoskins & Kennard, 1963; Hoskins & Whillans, 1970). In both (I) and (II) the out-of-plane angular distortions are comparable, Table 4, but there are significant differences in the in-plane angular distortions from the 120° of a regular trigonal-bipyramidal stereochemistry. In (I) the in-plane distortion is symmetrical with the N(2)–Cu–N(4) angle less than 120° at 114° , while in (II) this angle is even smaller (99.4°), and accompanied by an unsymmetrical angular distortion of the I–Cu–N(2) and I–Cu–N(4) angles of 134.5 and 126.2° , respectively. The bond lengths and angular distortion of (II) together represent a distortion from a regular trigonal-bipyramidal stereochemistry towards a square-pyramidal

stereochemistry with the Cu–N(4) elongation opposite the larger in-plane I–Cu–N(2) angle as previously observed for the CuN_4Cl chromophore in $[\text{Cu}(\text{bpy})_2\text{Cl}]_2\text{S}_5\text{O}_6 \cdot 6\text{H}_2\text{O}$ (IV) (Table 6) (Harrison, Hathaway & Kennedy, 1979). The stereochemistry of the CuN_4I chromophore of (I) is closely comparable to that for this chromophore in $[\text{Cu}(\text{bpy})_2\text{I}]$ (III) (Table 6) (re-evaluated with the published atom positions and the program *XANADU*). Owing to the relatively low accuracy of this structure the apparent differences in bond lengths and angles are not significant (Barclay, Hoskins & Kennard, 1963). Consequently the CuN_4I cations of (I) and $[\text{Cu}(\text{bpy})_2\text{I}]$ cannot be considered as cation distortion isomers (Ray, Hulett, Sheahan & Hathaway, 1978) but as essentially isostructural with a stereochemistry that is not as regular a trigonal bipyramid as that of the CuN_4Cl chromophore of $[\text{Cu}(\text{bpy})_2\text{Cl}]\text{Cl} \cdot 6\text{H}_2\text{O}$ (V) (Stephens & Tucker, 1973) but comparable to the distorted trigonal-bipyramidal

Table 6. *The local molecular stereochemistry of (I) [Cu(bpy)₂]ClO₄; (II) [Cu(bpy)₂Br]BF₄; (III) [Cu(bpy)₂]I; (IV) [Cu(bpy)₂Cl]₂S₅O₆·6H₂O; (V) [Cu(bpy)₂Cl]Cl·6H₂O and (VI) [Cu(bpy)₂][CuCl₂]₂ (notation of Fig. 1)*

	(I)	(II)	(III)	(IV)	(V)	(VI)
Cu—X	2.675 (4)	2.419 (3)	2.697	2.292 (4)	2.361 (4)	2.356 (2)
Cu—N(1)	1.989 (6)	1.996 (7)	1.988	1.992 (6)	1.989 (10)	1.986 (5)
Cu—N(2)	2.090 (8)	2.068 (8)	1.961	2.092 (6)	2.077 (10)	2.063 (5)
Cu—N(3)	1.987 (6)	1.995 (7)	2.021	1.988 (6)	1.970 (10)	1.995 (5)
Cu—N(4)	2.100 (7)	2.114 (9)	2.106	2.106 (5)	2.087 (11)	2.086 (5)
N(2)—Cu—X	122.9 (2)	134.5 (2)	121.9	130.7 (1)	118.7 (3)	133.4
N(4)—Cu—X	122.8 (2)	126.2 (3)	124.4	122.0 (2)	118.7 (3)	111.1
N(2)—Cu—N(4)	114.3 (3)	99.4 (3)	113.8	107.3 (2)	122.8 (4)	115.5

stereochemistry of [Cu(bpy)₂][CuCl₂]₂ (VI) (Table 6) (Kaiser, Brauer, Schröder, Taylor & Rasmussen, 1974).

The pyridine rings of (I) and (II) are reasonably planar, Table 5, and the angles of twist between the pyridine rings of the individual bpy ligands, 2.34–11.63°, are in the range previously reported for the bpy ligand (0–11°) (Barclay, Hoskins & Kennard, 1963; Procter & Stephens, 1969). The angles for (I), 2.34 and 7.53°, are in reasonable agreement with the values of 1.65 and 6.14° recalculated for [Cu(bpy)₂]I but not with the values previously reported for this complex (Barclay, Hoskins & Kennard, 1963). The angles for (II), 5.16 and 11.63°, include the largest angle observed in [Cu(bpy)₂X]Y systems, and is comparable to the values of 10.8 and 11.6° in [Cu(bpy)₂(ONO)]NO₃ (Procter & Stephens, 1969). It is not as large as that of 31.3° in [Cu(bpy)₃](ClO₄)₂ (Anderson, 1972) in which the bpy ligand is unsymmetrically coordinated with Cu—N distances of 2.026 and 2.45 Å respectively, which suggests that the larger angles of twist of the bpy ligand are associated with marked differences in the Cu—N distances involved when the bpy functions as a bidentate ligand.

The differences in the angular distortions of the CuN₄X chromophores of (I) and (II) are reflected in the electronic spectra of the complex. While (I) involves a single peak at 12.12 × 10³ cm⁻¹, (II) involves two clear bands at 10.10 and 13.25 × 10³ cm⁻¹ which parallels the differences previously noted for [Cu(bpy)₂H₂O]S₅O₆ and [Cu(bpy)₂Cl]₂S₅O₆·6H₂O, respectively (Harrison, Hathaway & Kennedy, 1979).

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