

the $P2_1$ structure. That two related phases were obtained by using acetone or CCl_4 as a solvent is an interesting phenomenon.

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The Structures of Acetatobis(2,2'-bipyridyl)copper(II) Perchlorate Monohydrate and Tetrafluoroborate – Cation Distortion Isomers

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Abstract

The structures of acetatobis(2,2'-bipyridyl)copper(II) perchlorate monohydrate, $[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{C}_2\text{H}_3\text{O}_2)]\text{ClO}_4 \cdot \text{H}_2\text{O}$, $\text{C}_{22}\text{H}_{19}\text{CuN}_4\text{O}_2^+\text{ClO}_4^- \cdot \text{H}_2\text{O}$ (I), and tetrafluoroborate (II) have been determined by X-ray analysis. (I) crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.338$ (2), $b = 9.660$ (2), $c = 14.912$ (3) Å, $\alpha = 100.35$ (5), $\beta = 95.99$ (5), $\gamma = 84.90$ (5)°, $Z = 2$. (II) crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.333$ (2), $b = 28.078$ (4), $c = 11.601$ (3) Å, $\beta = 111.42$ (5)°, $Z = 4$. Both structures involve a $[\text{Cu}(\text{bpy})_2(\text{CH}_3\text{CO}_2)]^+$ cation with a stereochemistry intermediate between five- and six-coordinate, with the second acetate O atom involved in semi-coordinate off-the-z-axis bonding to the Cu^{II} ion. The local $\text{CuN}_4\text{OO}'$ chromophore is best considered as having a distorted square-pyramidal stereochemistry rather than

the more usual trigonal-bipyramidal stereochemistry of the $[\text{Cu}(\text{bpy})_2\text{X}]^+$ cation. The cations of (I) and (II) involve significantly different Cu–ligand bond lengths and angles and represent a pair of cation distortion isomers which may be distinguished by their electronic reflectance spectra.

Introduction

The nitrite ion is unique in the stereochemistry of the $[\text{Cu}(\text{bpy})_2\text{X}]Y$ complexes, $\text{bpy} = 2,2'$ -bipyridyl, in forming a *cis*-distorted octahedral $\text{CuN}_4\text{OO}'$ chromophore in bis(2,2'-bipyridyl)nitrocopper(II) nitrate (Procter & Stephens, 1969; Procter, Hathaway, Billing, Dudley & Nicholls, 1969). As the nitrite and acetate anions have comparable bonding roles with the Cu^{II} ion, frequently bonding as bidentate chelate ligands but with non-equivalent Cu–O distances (Hathaway, 1973), a series of $[\text{Cu}(\text{bpy})_2(\text{CH}_3\text{CO}_2)_2]Y$ complexes

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Table 1. *Crystal and refinement data*

Compound	(I)	(II)
	[Cu(bpy) ₂ (CH ₃ CO ₂)] ClO ₄ ·H ₂ O	[Cu(bpy) ₂ (CH ₃ CO ₂)]BF ₄
<i>M_r</i>	552.00	521.57
Stoichiometry	C ₂₂ H ₂₁ ClCuN ₄ O ₇	C ₂₂ H ₁₉ BCuF ₄ N ₄ O ₂
Space group	<i>P</i> 1 (triclinic)	<i>P</i> 2 ₁ / <i>c</i> (monoclinic)
<i>a</i> (Å)	8.338 (2)	7.333 (2)
<i>b</i> (Å)	9.660 (2)	28.078 (4)
<i>c</i> (Å)	14.912 (3)	11.601 (3)
α (°)	100.35 (5)	—
β (°)	95.99 (5)	111.42 (5)
γ (°)	84.90 (5)	—
<i>Z</i>	2	4
<i>D_s</i> (floatation) (Mg m ⁻³)	1.55	1.59
<i>D_c</i> (Mg m ⁻³)	1.564	1.558
Radiation (wavelength, Å)	Mo <i>K</i> α (0.7107)	Mo <i>K</i> α (0.7107)
<i>F</i> (000)	566.0	1060.0
μ (mm ⁻¹)	1.048	0.999
Number of unique reflections	3605	2832
Number varied parameters	317	308
<i>R</i> = ($\sum \Delta / \sum F_o $)	0.0485	0.0468
<i>R_w</i> = ($\sum \Delta^2 w / \sum F_o^2 w$)	0.0535	0.0495
<i>k</i>	1.3054	1.5491
<i>q</i>	0.000604	0.000036
Maximum final shift/e.s.d.	0.01	0.03
Residual electron density (e Å ⁻³)	0.303	0.415
Number of atoms anisotropic	35	34

has been prepared and the crystal structures of [Cu(bpy)₂(CH₃CO₂)]ClO₄·H₂O (I) and [Cu(bpy)₂(CH₃CO₂)]BF₄ (II) have been determined.

Experimental

(I) was prepared by mixing 0.01 mol of [Cu(CH₃CO₂)₂].H₂O and 0.01 mol of [Cu(H₂O)₆](ClO₄)₂, both in 60 ml of (1:2) aqueous ethanol, and adding 0.022 mol of bpy in 60 ml of (1:2) aqueous ethanol. The solution was boiled, filtered and allowed to stand. Turquoise-green crystals of (I) were deposited overnight. (II) was prepared similarly, from [Cu(H₂O)₆](BF₄)₂, as purple-blue crystals. (I), found: C, 48.86; H, 3.58; N, 10.13; Cl, 6.53; Cu, 11.52%; calculated for C₂₂H₂₁ClCuN₄O₇: C, 47.8; H, 3.80; N, 10.2; Cl, 6.42; Cu, 11.5%. (II), found: C, 49.71; H, 3.74; N, 10.56; Cu, 12.39%; calculated for C₂₂H₁₉BCuF₄N₄O₂: C, 50.6; H, 3.64; N, 10.7; Cu, 12.2%.

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

	[Cu(bpy) ₂ (CH ₃ CO ₂)]ClO ₄ ·H ₂ O			[Cu(bpy) ₂ (CH ₃ CO ₂)]BF ₄		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Cu	-419 (1)	213 (1)	-2547	5023 (1)	1286	134
N(1)	-418 (4)	-1227 (3)	-1763 (2)	4118 (4)	761 (1)	954 (3)
C(1)	302 (5)	-2534 (4)	-1942 (3)	4458 (6)	741 (2)	2176 (4)
C(2)	148 (6)	-3551 (4)	-1425 (3)	3855 (6)	358 (2)	2697 (4)
C(3)	-800 (6)	-3201 (5)	-695 (3)	2880 (6)	-18 (2)	1929 (5)
C(4)	-1521 (5)	-1867 (5)	-497 (3)	2531 (6)	3 (2)	674 (4)
C(5)	-1308 (4)	-889 (4)	-1045 (3)	3163 (5)	402 (1)	213 (4)
C(6)	-2016 (4)	583 (4)	-891 (2)	2878 (5)	466 (1)	-1099 (4)
C(7)	-2857 (5)	1178 (5)	-149 (3)	1941 (6)	131 (2)	-2011 (4)
C(8)	-3484 (6)	2546 (5)	-84 (3)	1789 (7)	222 (2)	-3223 (4)
C(9)	-3254 (6)	3313 (5)	-739 (3)	2518 (7)	642 (2)	-3486 (4)
C(10)	-2399 (5)	2670 (4)	-1471 (3)	3403 (7)	955 (2)	-2549 (4)
N(2)	-1784 (4)	1324 (3)	-1548 (2)	3601 (5)	877 (1)	-1374 (3)
N(3)	-628 (4)	1615 (3)	-3391 (2)	5880 (5)	1811 (1)	-742 (3)
C(11)	74 (5)	2852 (4)	-3191 (3)	7111 (7)	1735 (2)	-1333 (4)
C(12)	-68 (6)	3802 (5)	-3788 (3)	7699 (8)	2107 (2)	-1906 (5)
C(13)	-966 (6)	3466 (5)	-4624 (2)	7064 (8)	2557 (2)	-1821 (5)
C(14)	-1651 (5)	2181 (5)	-4843 (3)	5821 (7)	2639 (2)	-1198 (5)
C(15)	-1460 (4)	1273 (4)	-4209 (2)	5205 (6)	2258 (2)	-668 (4)
C(16)	-2139 (4)	-135 (4)	-4389 (2)	3804 (6)	2301 (2)	-22 (4)
C(17)	-2952 (6)	-666 (5)	-5220 (3)	3134 (7)	2740 (2)	245 (5)
C(18)	-3583 (6)	-1964 (5)	-5325 (3)	1767 (8)	2739 (2)	804 (5)
C(19)	-3391 (6)	-2704 (5)	-4606 (3)	1127 (7)	2314 (2)	1102 (5)
C(20)	-2533 (5)	-2116 (4)	-3804 (3)	1870 (7)	1894 (2)	838 (5)
N(4)	-1925 (4)	-847 (3)	-3693 (2)	3166 (5)	1885 (1)	279 (3)
O(1)	1819 (3)	-476 (3)	-2936 (2)	7142 (2)	1460 (1)	1709 (3)
O(2)	2377 (5)	863 (4)	-1622 (2)	8867 (5)	955 (1)	1060 (3)
C(21)	2798 (5)	64 (4)	-2319 (3)	8681 (6)	1218 (1)	1882 (4)
C(22)	4551 (6)	-248 (8)	-2439 (4)	10269 (7)	1253 (2)	3115 (5)
Cl	5341 (2)	4711 (1)	2812 (1)			
O(3)	6332 (7)	4153 (6)	3493 (4)			
O(4)	5906 (11)	5886 (9)	2614 (4)			
O(5)	3916 (8)	5071 (10)	3125 (6)			
O(6)	5072 (13)	3803 (7)	2038 (4)			
OH(2)	2617 (5)	3701 (4)	8963 (3)			
B(1)				-2707 (10)	1090 (2)	-4357 (6)
F(1)				-4635 (5)	1224 (1)	-4821 (5)
F(2)				-2027 (7)	1031 (1)	-3119 (3)
F(3)				-1631 (7)	1445 (2)	-4560 (5)
F(4)				-2410 (6)	688 (2)	-4863 (4)

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

	(I)	(II)		(I)	(II)		(I)	(II)
N(1)—Cu	1.971 (5)	1.995 (5)	C(9)—C(8)	1.366 (9)	1.373 (9)	C(19)—C(18)	1.380 (8)	1.372 (9)
N(2)—Cu	2.056 (5)	2.033 (6)	C(10)—C(9)	1.387 (7)	1.365 (7)	C(20)—C(19)	1.384 (7)	1.379 (9)
N(3)—Cu	1.994 (5)	2.016 (6)	N(2)—C(10)	1.344 (6)	1.335 (7)	N(4)—C(20)	1.345 (6)	1.332 (8)
N(4)—Cu	2.168 (5)	2.209 (6)	N(2)—C(6)	1.351 (6)	1.357 (6)	C(21)—O(1)	1.238 (5)	1.270 (6)
O(1)—Cu	2.031 (5)	1.980 (4)	C(11)—N(3)	1.349 (6)	1.335 (8)	C(21)—O(2)	1.241 (6)	1.252 (7)
O(2)—Cu	2.648 (5)	2.785 (5)	C(15)—N(3)	1.340 (5)	1.363 (7)	C(22)—C(21)	1.489 (7)	1.481 (7)
C(1)—N(1)	1.343 (6)	1.347 (7)	C(12)—C(11)	1.378 (8)	1.388 (9)	O(3)—Cl	1.395 (7)	
C(5)—N(1)	1.343 (6)	1.343 (6)	C(13)—C(12)	1.387 (7)	1.363 (9)	O(4)—Cl	1.358 (10)	
C(2)—C(1)	1.375 (8)	1.384 (8)	C(14)—C(13)	1.383 (7)	1.374 (10)	O(5)—Cl	1.317 (8)	
C(3)—C(2)	1.386 (8)	1.397 (7)	C(15)—C(14)	1.389 (7)	1.391 (8)	O(6)—Cl	1.331 (7)	
C(4)—C(3)	1.368 (7)	1.385 (8)	C(16)—C(15)	1.489 (6)	1.481 (8)	F(1)—B(1)		1.369 (8)
C(5)—C(4)	1.389 (7)	1.394 (7)	C(17)—C(16)	1.384 (6)	1.402 (8)	F(2)—B(1)		1.347 (8)
C(6)—C(5)	1.478 (6)	1.469 (7)	N(4)—C(16)	1.333 (6)	1.352 (7)	F(3)—B(1)		1.345 (10)
C(7)—C(6)	1.382 (6)	1.394 (7)	C(18)—C(17)	1.379 (8)	1.378 (10)	F(4)—B(1)		1.327 (9)
C(8)—C(7)	1.368 (7)	1.393 (8)						

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

	(I)	(II)		(I)	(II)		(I)	(II)
N(2)—Cu—N(1)	80.4 (2)	80.6 (2)	N(2)—C(6)—C(7)	121.6 (4)	121.4 (5)	C(19)—C(18)—C(17)	119.7 (5)	119.7 (6)
N(3)—Cu—N(1)	174.5 (1)	178.3 (1)	C(8)—C(7)—C(6)	119.0 (5)	118.6 (5)	C(20)—C(19)—C(18)	118.0 (5)	119.2 (7)
N(3)—Cu—N(2)	98.7 (2)	97.8 (2)	C(9)—C(8)—C(7)	120.1 (5)	119.2 (5)	N(1)—C(20)—C(19)	122.6 (5)	122.3 (6)
N(4)—Cu—N(1)	96.4 (2)	101.8 (2)	C(10)—C(9)—C(8)	118.7 (5)	119.1 (6)	C(16)—N(4)—Cu	112.1 (3)	110.9 (4)
N(4)—Cu—N(2)	111.6 (2)	111.0 (2)	N(2)—C(10)—C(9)	122.0 (5)	123.4 (5)	C(20)—N(4)—Cu	129.1 (4)	128.4 (4)
N(4)—Cu—N(3)	78.8 (2)	78.3 (3)	C(6)—N(2)—Cu	113.6 (3)	113.6 (4)	C(20)—N(4)—C(16)	118.7 (4)	119.1 (5)
O(1)—Cu—N(1)	93.1 (2)	91.6 (2)	C(10)—N(2)—Cu	127.8 (4)	128.0 (4)	C(21)—O(1)—Cu	106.5 (3)	111.5 (4)
O(1)—Cu—N(2)	147.6 (1)	156.5 (1)	C(10)—N(2)—C(6)	118.6 (4)	118.3 (4)	O(2)—C(21)—O(1)	122.8 (5)	122.2 (4)
O(1)—Cu—N(3)	90.5 (2)	90.0 (2)	C(11)—N(3)—Cu	123.2 (4)	122.5 (4)	C(22)—C(21)—O(1)	117.8 (5)	117.2 (5)
O(1)—Cu—N(4)	100.7 (2)	92.3 (2)	C(15)—N(3)—Cu	117.6 (4)	117.0 (4)	C(22)—C(21)—O(2)	119.4 (5)	120.6 (5)
C(1)—N(1)—Cu	124.4 (4)	124.4 (4)	C(15)—N(3)—C(11)	119.1 (4)	120.5 (5)	O(4)—Cl—O(3)	112.4 (5)	
C(5)—N(1)—Cu	116.4 (3)	115.8 (4)	C(12)—C(11)—N(3)	122.4 (5)	120.9 (6)	O(5)—Cl—O(3)	107.3 (6)	
C(5)—N(1)—C(1)	118.9 (5)	119.7 (5)	C(13)—C(12)—C(11)	118.4 (5)	119.2 (7)	O(5)—Cl—O(4)	107.7 (7)	
C(2)—C(1)—N(1)	122.6 (5)	121.7 (5)	C(14)—C(13)—C(12)	119.4 (5)	120.3 (7)	O(6)—Cl—O(3)	114.4 (4)	
C(3)—C(2)—C(1)	118.1 (5)	118.6 (5)	C(15)—C(14)—C(13)	119.2 (5)	119.2 (6)	O(6)—Cl—O(4)	108.7 (4)	
C(4)—C(3)—C(2)	119.9 (6)	119.6 (6)	C(14)—C(15)—N(3)	121.4 (4)	119.8 (6)	O(6)—Cl—O(5)	105.9 (6)	
C(5)—C(4)—C(3)	119.0 (5)	118.5 (5)	C(16)—C(15)—N(3)	115.7 (4)	116.3 (5)	F(2)—B(1)—F(1)		112.4 (8)
C(4)—C(5)—N(1)	121.4 (4)	121.8 (5)	C(16)—C(15)—C(14)	122.9 (4)	123.9 (5)	F(3)—B(1)—F(1)		108.4 (6)
C(6)—C(5)—N(1)	114.9 (4)	114.6 (5)	C(17)—C(16)—C(15)	122.3 (5)	123.3 (5)	F(3)—B(1)—F(2)		105.4 (6)
C(6)—C(5)—C(4)	123.7 (4)	123.6 (4)	N(4)—C(16)—C(15)	115.5 (4)	115.4 (5)	F(4)—B(1)—F(1)		111.8 (6)
C(7)—C(6)—C(5)	124.1 (5)	123.3 (5)	N(4)—C(16)—C(17)	122.1 (5)	121.3 (6)	F(4)—B(1)—F(2)		108.0 (6)
N(2)—C(6)—C(5)	114.3 (4)	115.3 (4)	C(18)—C(17)—C(16)	118.8 (5)	118.5 (6)	F(4)—B(1)—F(3)		110.6 (8)

Crystal data

The crystal and refinement data for (I) and (II) are summarized in Table 1. For both complexes preliminary cell dimensions and space group were determined from precession photographs and refined on a Phillips 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 $0.05^\circ \text{ s}^{-1}$ and a variable scan width of $(0.7 + 0.1 \times \tan \theta)^\circ$ were used. With an acceptance criterion of $I > 2.5\sigma(I)$, 3605 reflections for (I) and 2837 for (II) were retained. Lorentz and polarization corrections were applied, but none for absorption; the Cu atom was corrected for anomalous dispersion. 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 geometri-

cally, except for the water molecule, and floated on the adjacent C or O atoms assuming C—H or O—H = 1.08 Å and a fixed temperature factor of 0.07 \AA^2 . The refinement converged when the maximum shift/e.s.d. was < 0.05 , with a weighting scheme $w = k/[\sigma^2(F_o) + g(F_o)^2]$ (Table 1). Complex atomic scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). All calculations were carried out with *SHELX 76* and *XANADU* (G. M. Sheldrick), *PLUTO* (S. Motherwell) and *XPUB* (R. Taylor) on an IBM 370/138 computer. Table 2 gives the non-hydrogen atomic coordinates, Table 3 the bond lengths, Table 4 the bond angles and Table 5 some mean planes.* Fig. 1 illustrates the structures and atom numbering.

* Lists of structure factors, anisotropic thermal parameters and calculated H atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35084 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. Equations of least-squares planes in the form $lX + mY + nZ - p = 0$, where X , Y , and Z are orthogonal axes, with deviations (Å) of relevant atoms from the planes

(a) [Cu(bpy) ₂ (CH ₃ CO ₂)]ClO ₄ ·H ₂ O (e.s.d.'s 0.0009–0.0020 Å)	l	m	n	p
Plane (1): N(1), C(1)–C(5) (r.m.s.d. = 0.0056 Å) [N(1)–0.0071, C(2)–0.0061, C(3)–0.0081]	0.8084	0.3536	0.4706	1.8132
Plane (2): C(6)–C(10), N(2) (r.m.s.d. = 0.0028 Å) [C(7)–0.0038, C(8)–0.0047, C(9)–0.0031]	0.8496	0.3679	0.3779	1.7297
Plane (3): N(1), C(1)–C(10), N(2) (r.m.s.d. = 0.0499 Å) [C(1)–0.0664, C(4)–0.0658, C(7)–0.0688]	0.8315	0.3582	0.4247	1.7693
Plane (4): N(3), C(11)–C(15) (r.m.s.d. = 0.0089 Å) [N(3)–0.0127, C(13)–0.0125, C(14)–0.0066]	0.8304	–0.3732	–0.4138	–1.2081
Plane (5): C(16)–C(20), N(4) (r.m.s.d. = 0.0061 Å) [C(16)–0.0069, C(19)–0.0091, C(20)–0.0079]	0.8552	–0.3834	–0.3489	–0.8028
Plane (6): N(3), C(11)–C(20), N(4) (r.m.s.d. = 0.0359 Å) [C(11)–0.0501, C(13)–0.0501, C(17)–0.0577]	0.8467	–0.3705	–0.3819	–1.0052
Plane (7): O(1), O(2), C(21), C(22) (r.m.s.d. = 0.0032 Å) [C(21)–0.0056]	–0.0071	0.7904	–0.6126	–2.4435
Plane (8): Cu, N(2), N(4), O(1), O(2), C(21), C(22) (r.m.s.d. = 0.0184 Å) [Cu–0.0309, N(2)–0.0245, O(2)–0.0229]	–0.0100	0.8009	–0.5987	–2.3885
Plane (9): N(1), N(2), N(3), O(1) (r.m.s.d. = 0.3189 Å) [N(1)–0.2332, N(2)–0.3254, N(3)–0.2918, O(1)–0.3112, Cu–0.2332]	0.6361	0.5934	0.4932	1.7553
Angles between planes: (1) and (2) = 5.87; (4) and (5) = 4.02; (3) and (6) = 65.85; (7) and (8) = 1.02°. (E.s.d.'s 0.5–1.3°.)				
(b) [Cu(bpy) ₂ (CH ₃ CO ₂)]BF ₄ (e.s.d.'s 0.0011–0.0021 Å)				
Plane (1): N(1), C(1)–C(5) (r.m.s.d. = 0.0036 Å) [C(2)–0.0038, C(5)–0.0059]	0.8744	–0.4531	–0.1736	–1.4860
Plane (2): C(6)–C(10), N(2) (r.m.s.d. = 0.0048 Å) [C(7)–0.0077, C(8)–0.0074]	0.8792	–0.4482	–0.1617	–1.4684
Plane (3): N(1), C(1)–C(10), N(2) (r.m.s.d. = 0.0088 Å) [C(6)–0.0112, C(8)–0.0173, N(2)–0.0107, C(7)–0.0105]	0.8764	–0.4502	–0.1712	–1.4939
Plane (4): N(3), C(11)–C(15) (r.m.s.d. = 0.0094 Å) [C(11)–0.0124, C(12)–0.0126]	0.7827	0.1511	0.6038	–2.4399
Plane (5): C(16)–C(20), N(4) (r.m.s.d. = 0.0062 Å) [C(17)–0.0088, C(20)–0.0087]	0.7417	0.0203	0.6704	–1.3622
Plane (6): N(3), C(11)–C(20), N(4) (r.m.s.d. = 0.0744 Å) [N(3)–0.1066, C(13)–0.1024, C(17)–0.1104]	0.7622	0.0862	0.6415	–1.8298
Plane (7): O(1), O(2), C(21), C(22) (r.m.s.d. = 0.0013 Å) [C(21)–0.0022]	0.3972	0.7642	–0.5081	–5.0357
Plane (8): Cu, N(2), N(4), O(1), O(2), C(21), C(22) (r.m.s.d. = 0.159 Å) [O(2)–0.2974, C(22)–0.2004, N(2)–0.1691]	0.3604	0.6340	–0.6842	–4.3671
Plane (9): N(1), N(2), N(3), O(1) (r.m.s.d. = 0.1941 Å) [N(1)–0.2085, N(2)–0.1952, N(3)–0.1792, O(1)–0.1925, Cu–0.1913]	–0.7492	0.5721	0.3338	1.0912
Angles between planes: (1) and (2) = 0.78; (4) and (5) = 8.74; (3) and (6) = 58.72; (7) and (8) = 12.75°. (E.s.d.'s 0.4–1.3°.)				

Discussion

Both complexes involve [Cu(bpy)₂(CH₃CO₂)]⁺ cations, and discrete ClO₄[–] and BF₄[–] anions for (I) and (II) respectively; (I) also contains a molecule of uncoordinated water. In neither structure is there any unusual feature in the bond lengths or angles of the organic ligands (Stephens, 1969, 1972; Ray & Hathaway, 1978). Both anions show disorder (Kilbourne, Ryan & Dunitz, 1969; Stynes & Ibers, 1971), which was best approximated by the use of high anisotropic tempera-

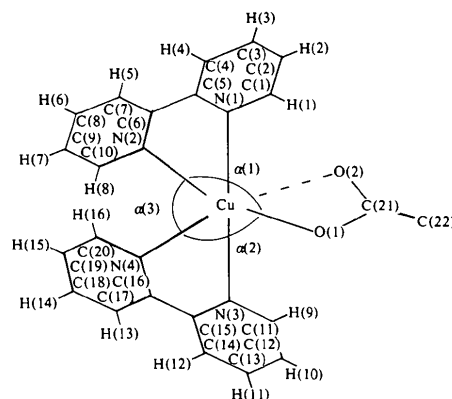


Fig. 1. The structure of the [Cu(bpy)₂(CH₃CO₂)]⁺ cation and the atom numbering.

ture factors which reduced the residual electron density to $<0.5 \text{ e } \text{Å}^{-3}$. For this reason the Cl–O and B–F lengths are subject to significant error due to the presence of high thermal motion. *XANADU* was used to simulate the anisotropic thermal motion and the Cl–O and B–F distances were corrected for librational effects (Table 6). This increased the bond distances for both anions by up to 0.21 Å compared with the values normally observed of 1.44 and 1.41 Å respectively (Wells, 1975). There is no evidence for semi-coordination of the ClO₄[–] anion or water molecule in (I) or the BF₄[–] anion in (II) to the Cu^{II} ion (Procter, Hathaway & Nicholls, 1968).

The stereochemistries of the [Cu(bpy)₂(CH₃CO₂)]⁺ cations are basically five-coordinate with a CuN₄O chromophore, but with the second O atom of the acetate group occupying the sixth coordination position at a distance $>2.6 \text{ Å}$ to give a 4 + 1 + 1' type coordination (Hathaway, 1973). The CuN₄O chromophore involves a very distorted stereochemistry intermediate between trigonal bipyramidal and square-based pyramidal, but still related to the more usual distorted trigonal-bipyramidal stereochemistry of the [Cu(bpy)₂X]Y complexes (Barclay, Hoskins & Kennard, 1963; Stephens & Tucker, 1973; Harrison, Hathaway & Kennedy, 1979), with the mean planes of the bpy ligands inclined at *ca* 120° to each other and not approximately coplanar (44.37°) as in the distorted square-pyramidal stereochemistry of [Cu(bpy)₂(ONO₂)]NO₃ (Nakai, Ooi & Kuroya, 1970). The axial Cu–N(1) and Cu–N(3) distances are not significantly different with an average Cu–N distance of 2.00 Å. The N(1)–Cu–N(3) angle is virtually 180° in (II), 178.3°, and only slightly less in (I), 174.5°. The mean in-plane Cu–N distances of 2.112 in (I) and 2.116 Å in (II) are not significantly different and are 0.1 Å longer than the axial Cu–N distances previously reported for the trigonal-bipyramidal Cu^{II} stereochemistry (Huq & Skapski, 1971). Nevertheless, the in-plane Cu–N distances are significantly different,

Table 6. Observed and calculated U_{ij} (\AA^2) for ClO_4^- and BF_4^- , and observed and corrected Cl—O and B—F bond distances (\AA)

ClO_4^-							BF_4^-						
	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}		U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
Cl	U_o 0.0727	-0.0088	0.0065	0.0636	-0.0009	0.0475	B(1)	U_o 0.0689	0.0030	0.0117	0.0539	0.0007	0.0443
	U_c 0.0755	-0.0072	0.0086	0.0690	0.0007	0.0530		U_c 0.0677	0.0061	0.0120	0.0600	0.0023	0.0504
O(3)	0.1735	-0.0109	-0.0659	0.1610	0.0364	0.1143	F(1)	0.0680	0.0189	0.0232	0.0963	-0.0029	0.1799
	0.1661	-0.0048	-0.0647	0.1649	0.0318	0.1223		0.0722	0.0200	0.0257	0.0954	-0.0049	0.1804
O(4)	0.3177	-0.1663	-0.0466	0.2106	0.0675	0.1025	F(2)	0.2003	0.0224	-0.0077	0.1056	0.0027	0.0552
	0.3132	-0.1643	-0.0394	0.2124	0.0881	0.0955		0.1985	0.0238	-0.0112	0.1057	0.0094	0.0525
O(5)	0.1364	0.0895	0.0955	0.3041	0.1174	0.2279	F(3)	0.1159	-0.0058	0.0452	0.1629	0.0886	0.1623
	0.1447	0.0985	0.1055	0.3013	0.0980	0.2211		0.1129	-0.0143	0.0468	0.1516	0.0880	0.1629
O(6)	0.4070	0.0515	-0.0792	0.1458	-0.0627	0.1236	F(4)	0.1050	0.0533	-0.0597	0.1398	-0.0976	0.1707
	0.4079	0.0327	-0.0996	0.1375	-0.0609	0.1240		0.1068	0.0563	-0.0606	0.1458	-0.1034	0.1662
		Observed	Correction	Corrected				Observed	Correction	Corrected			
Cl—O(3)		1.395 (7)	0.097	1.491			B—F(1)	1.369 (8)	0.055	1.424			
Cl—O(4)		1.358 (10)	0.141	1.499			B—F(2)	1.347 (8)	0.088	1.435			
Cl—O(5)		1.317 (8)	0.209	1.526			B—F(3)	1.345 (10)	0.097	1.442			
Cl—O(6)		1.331 (7)	0.162	1.493			B—F(4)	1.327 (9)	0.073	1.401			

with $\Delta\text{Cu—N}$ values of 0.112 and 0.176 \AA in (I) and (II) respectively. The short Cu—O distances in (I) and (II) are not significantly different and are equivalent to a normal short Cu—O distance, *ca* 2.00 \AA (Hathaway & Hodgson, 1972; Hathaway, 1973).

Both complexes show comparable out-of-the-trigonal-plane angular distortions, but the in-plane angular distortions show substantial deviations from the 120° of a regular trigonal bipyramid: the O(1)—Cu—N(2) angles of (I) and (II) are very much greater, 147.6 and 156.5° respectively, while the O(1)—Cu—N(4) and N(2)—Cu—N(4) angles are significantly smaller, 100.7 and 92.3, and 111.6 and 111.0°, respectively. As the large O(1)—Cu—N(2) angle is opposite the elongated Cu—N(4) direction it represents the basal angle of the square-pyramidal stereochemistry and further justifies this description of the CuN_4O chromophore distortion. Nevertheless, the square-pyramidal stereochemistry is not regular {as in $\text{K}[\text{Cu}(\text{NH}_3)_5](\text{PF}_6)_3$, which has almost equal basal angles of $166 \pm 1^\circ$ (Duggan, Ray, Hathaway, Tomlinson, Brint & Pelin, 1980)} but has a clear trigonal distortion of the N(1), N(2), N(3), O(1) plane, Table 5, with a large r.m.s.d. of *ca* 0.3 \AA , compared with the 0.0105 \AA in the corresponding basal plane of $\text{K}[\text{Cu}(\text{NH}_3)_5](\text{PF}_6)_2$. The senses of the distortions of the N(1), N(2), N(3), O(1) planes of both (I) and (II) are related to the mechanistic pathway of the Berry (1960) twist, correlating the trigonal and square-pyramidal stereochemistries of the Cu^{II} ion (Ray, Hulett, Sheahan & Hathaway, 1978; Ray & Hathaway, 1978; Druhan & Hathaway, 1979).

The acetate groups are planar and reasonably coplanar with the Cu, N(2), N(4) plane (Table 5) and, due to the O(1)—Cu—O(2) bite angle of 52°, O(2) lies well off the *z* axis of the square pyramid [Fig. 2(a)] at a distance >2.6 \AA , but close enough to be involved in off-the-*z*-axis weak coordination to the Cu^{II} ion

(Hathaway, 1973). The mean C—O distance, 1.25 ± 0.02 \AA , agrees with the reported value (1.26 \AA ; Wells, 1975); the separate C—O distances in (I) and (II) are not significantly different and do *not* reflect the unsymmetrical bonding role of these bidentate acetate ions. The local molecular structures of the title compounds, especially (II), are then comparable to that found in $[\text{Cu}(\text{bea})(\text{HCO}_2)]\text{HCO}_2$ [bea = bis(2-aminoethylamine)] (Davey & Stephens, 1971), Fig. 2(b). Thus the structures of (I) and (II) are clearly established as having distorted square-pyramidal stereochemistries with an additional long distance to an off-the-*z*-axis O ligand justifying a 4 + 1 + 1' type coordination, clearly different from the symmetrical elongated rhombic-octahedral coordination (4 + 2) of $[\text{Cu}(\text{bpy})_2(\text{S}_3\text{O}_6)]$ and $[\text{Cu}(\text{bpy})_2(\text{S}_4\text{O}_6)]$ (Ferrari, Fava & Pelizzi, 1977; Harrison & Hathaway, 1978) and the unsymmetrical rhombic-octahedral coordination (4 + 1 + 1') of $[\text{Cu}(\text{bpy})_2(\text{ClO}_4)_2]$ (Nakai, 1971). There is some similarity to the *cis*-distorted rhombic-octahedral stereochemistry of $[\text{Cu}(\text{bpy})_2(\text{ONO})]\text{NO}_3$ (Procter & Stephens, 1969), Fig. 2(c), in which the nitrito ligand is acting as an almost symmetrical chelate ligand with Cu—O distances of 2.238 (10) and 2.329 \AA , both of which are clearly elongated compared to the short Cu—O distances of 1.99 \AA in (I) and (II). There is a closer similarity in structure to the $\text{CuN}_4\text{OO}'$ chromophore of $[\text{Cu}(\text{bpy})_2(\text{ONO})]\text{BF}_4$ (Hathaway, Walsh & Walsh, 1980), Fig. 2(d), but even here the significantly longer Cu—O(1) distance, 2.117 (4) \AA , and the shorter Cu—O(2) distance, 2.463 (4) \AA , compared with those for (I) and (II), suggests that the comparison of the Cu—O distances for nitrite and acetate ligands may not be justified.

While the geometries of the $\text{CuN}_4\text{OO}'$ chromophores of (I) and (II) are clearly comparable, there are several small, but significant, differences. Thus, while in

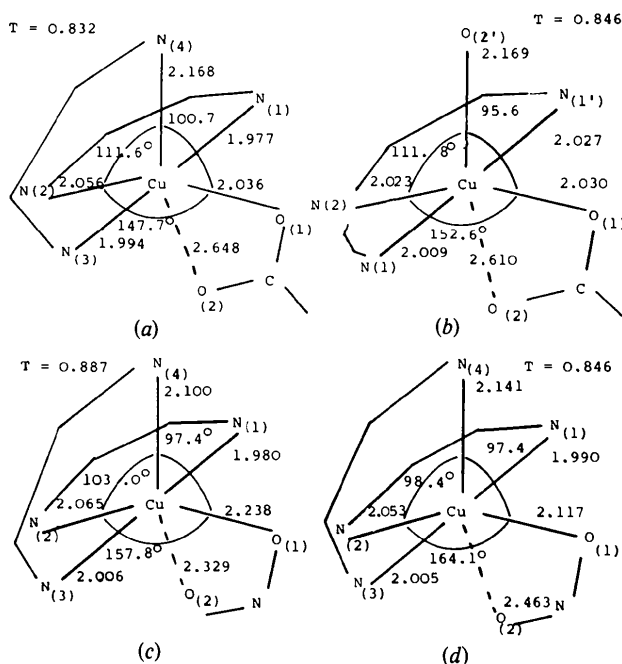


Fig. 2. The local molecular stereochemistries of (a) [Cu(bpy)₂(CH₃CO₂)]ClO₄; (b) [Cu(bee)(HCO₂)]HCO₂; (c) [Cu(bpy)₂(ONO)]NO₃; and (d) [Cu(bpy)₂(ONO)]BF₄.

(I) the Cu—N(2) and Cu—O(1) distances are shorter than in (II), the Cu—N(4) and Cu—O(2) distances are longer; in addition, the O(1)—Cu—N(2) angle is smaller in (I) than in (II). Fig. 3 shows a plot of the differences between the Cu—N(4) and Cu—N(2) distances, ΔN , and the differences between the Cu—O(2) and Cu—O(1) distances, ΔO , for (I), (II) and the [Cu(bpy)₂(ONO)]NO₃ and BF₄ complexes. The plot suggests that there may be a correlation between ΔN and ΔO in the sense that the shorter the Cu—N(4) distance, the shorter the Cu—O(2) distance, and the more symmetrically are the acetate or nitrite groups coordinated. The differences are reflected in the tetragonalities (*T*) of (I)

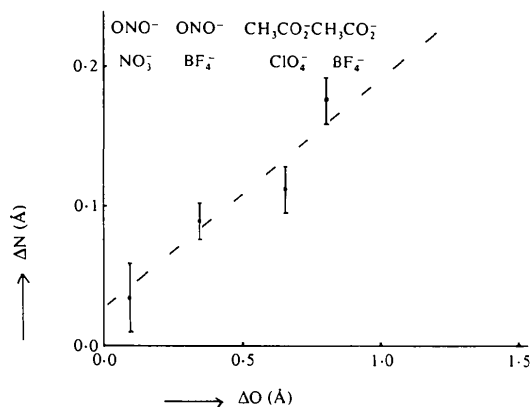


Fig. 3. Correlation between ΔN {[Cu—N(4)] — [Cu—N(2)]} and ΔO {[Cu—O(2)] — [Cu—O(1)]}.

and (II), 0.832 and 0.803 respectively, where *T* = mean out-of-plane bond distance/mean in-plane bond distance (Hathaway, 1973).

In (I) and (II) the Cu—N(4) elongation is restricted by the out-of-plane bite of the N(3), N(4) bpy ligand to angles of $80 \pm 1^\circ$ in symmetrically coordinated bpy ligands. It has been suggested (Anderson, 1972) that when the bpy ligand is coordinated to a Cu^{II} atom involved in a significant elongation of one of its Cu—N distances, the bite angle decreases to *ca* 74° and the dihedral angle between the pyridine rings can increase up to 31.3° . In both (I) and (II) the elongation of the Cu—N(4) length is not sufficient to decrease the bite angle to $< 78.0^\circ$, but the bite angles for the N(1), N(2) bpy ligands, 80.4 and 80.7° for (I) and (II) respectively, are significantly larger than the corresponding angles of 78.8 and 78.1° for the N(3), N(4) bpy ligands which involve the elongated Cu—N(4) distance, which is significantly longer in (II), 2.207 (5), than in (I), 2.168 (5) Å, and yields the slightly lower bite angle of 78.1 (2) $^\circ$, although this may not be significantly different from the value of 78.8 (2) $^\circ$ in (I). While the pyridine rings in (I) and (II) are reasonably planar (Table 5), the angles between these planes do show significant differences; in (I) the angles are comparable, 5.87 and 4.02° , while in (II) they are 0.98 and 9.60° , with the latter associated with the more elongated Cu—N(4) distance of 2.207 Å. This suggests that the Cu—N(4) elongation of 2.168 Å in (I) can occur without any undue strain of the bpy ligand, while the increase to 2.207 Å in (II) is sufficient to produce a significant increase in the dihedral angle between the pyridine rings of the bpy ligand involved in the elongation. This suggests that elongation of the Cu—N(4) distance is not restricted by the geometry of the bpy ligand, as even greater elongations have been observed for the bpy ligand in [Cu(bpy)₃](ClO₄)₂ of 2.45 and 2.22 Å for which the bite angles decreased to 73.9 and 78.1° and the dihedral angles increased to 31.5 and 13.6° respectively (Anderson, 1972).

The distortion of the CuN₄O chromophore from trigonal bipyramidal to distorted square pyramidal is associated with a change in the electronic reflectance spectra from a single broad peak to two clearly resolved peaks (Harrison, Hathaway & Kennedy, 1979), and the electronic spectra of both (I) and (II) involve two peaks separated by *ca* 4000 cm⁻¹, Table 7. The spectra differ in the relative energies involved, with

Table 7. The electronic reflectance spectra (cm⁻¹) of (I) [Cu(bpy)₂(CH₃CO₂)]ClO₄·H₂O and (II) [Cu(bpy)₂(CH₃CO₂)]BF₄ and a suggested assignment of the spectra

Assignment	(I)	(II)
$d_z^2 \rightarrow d_{x^2-y^2}$	9990	10860
$d_{xz}, d_{yz}, d_{xy} \rightarrow d_{x^2-y^2}$	13880	15150

the bands of (II) *ca* 1000 cm⁻¹ higher in energy than those in (I), consistent with the lower tetragonality of (II), 0.803, suggesting the tentative assignment of the electronic spectra with a $d_{x^2-y^2}$ ground state by analogy with the assignment of [Cu(beat)(HCO₂)]HCO₂, Table 7 (Bew, Dudley, Fereday, Hathaway & Slade, 1971).

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The Structure of Diaquasuccinatocalcium(II) Monohydrate

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Abstract

The crystal structure of the title compound, [Ca(C₄H₄O₄)(H₂O)₂].H₂O, C₄H₈CaO₆.H₂O, was determined from three-dimensional single-crystal X-ray diffraction data collected on an automated diffractometer.

The crystals are triclinic, space group $P\bar{1}$, with $a = 7.937$ (7), $b = 9.450$ (11), $c = 6.688$ (7) Å, $\alpha = 91.47$ (5), $\beta = 111.80$ (6), $\gamma = 71.60$ (6)°, $Z = 2$, $d_m = 1.61$ and $d_c = 1.59$ Mg m⁻³. The structure was refined by full-matrix least squares to a conventional R index of 0.030. There are two different succinate ions in the