Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

	x	y	z	$B_{eq}(\text{Å}^2)$
Pt	0·0	0·54255 (9)	0·35	2·76 (4)
N(1)	0·0713 (8)	0·414 (1)	0·360 (7)	2·4 (2)
C(1)	0·140 (1)	0·424 (2)	0·375 (7)	3·6 (5)
C(2)	0·185 (1)	0·329 (2)	0·384 (5)	3·9 (5)
C(3)	0·156 (1)	0·222 (2)	0·365 (9)	4·0 (5)
C(4)	0·080 (1)	0·212 (2)	0·357 (9)	3·4 (3)
C(5)	0·039 (1)	0·310 (2)	0·350 (8)	3·1 (3)
C(6)	0·202 (1)	0·117 (2)	0·387 (6)	4·3 (6)
N(2)	0·074 (1)	0·658 (2)	0·37 (1)	5·3 (6)
C(7)	0·100 (1)	0·751 (2)	0·377 (4)	2·7 (5)
O	0·131 (1)	0·842 (2)	0·381 (7)	6·9 (6)

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

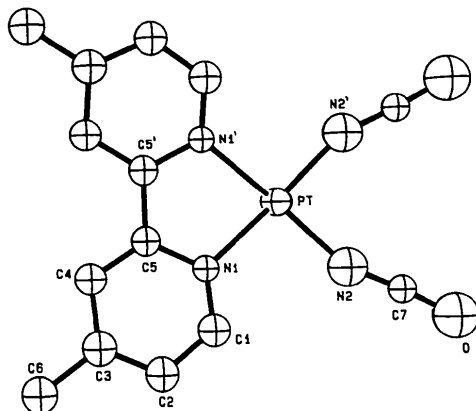|			
Pt—N(1)	2·03 (1)	C(3)—C(4)	1·43 (3)
Pt—N(2)	1·96 (2)	C(3)—C(6)	1·53 (4)
N(1)—C(1)	1·29 (3)	C(4)—C(5)	1·39 (3)
N(1)—C(5)	1·39 (3)	C(5)—C(5')	1·47 (3)
N(1)—C(2)	1·41 (3)	N(2)—C(7)	1·21 (3)
C(2)—C(3)	1·38 (3)	C(7)—O	1·22 (3)
N(1)—Pt—N(2)	93·4 (8)	C(2)—C(3)—C(4)	118 (2)
N(1)—Pt—N(1')	82·3 (6)	C(2)—C(3)—C(6)	122 (2)
N(1)—Pt—N(2')	173 (2)	C(4)—C(3)—C(6)	119 (2)
N(2)—Pt—N(2')	90 (1)	C(3)—C(4)—C(5)	118 (2)
Pt—N(1)—C(1)	126 (1)	N(1)—C(5)—C(4)	121 (2)
Pt—N(1)—C(5)	113 (1)	N(1)—C(5)—C(5')	116 (2)
C(1)—N(1)—C(5)	121 (2)	C(4)—C(5)—C(5')	123 (2)
N(1)—C(1)—C(2)	122 (2)	Pt—N(2)—C(7)	159 (2)
C(1)—C(2)—C(3)	120 (2)	N(2)—C(7)—O	176 (2)

Fig. 1. View of the title compound showing the atom-numbering scheme. The two pseudohalide ligands and the bpy rings are related by a mirror plane.

reported for (1). This distance is comparable to that reported in a number of non-conducting platinum pseudohalide complexes in which the metal atom is exclusively in the divalent state (Williams, 1983).

The infrared, ^{1}H and ^{13}C NMR, and UV-VIS spectroscopies of the title compound are not otherwise remarkable, and will be published elsewhere (Coyer & Herber, 1991).

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Crystal Structures of Bis(di-2-pyridylamine)(acetato)copper(II) Nitrate and Bis(di-2-pyridylamine)(formato)copper(II) Tetrafluoroborate

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Abstract. Bis(di-2-bipyridylamine)(acetato)copper(II) nitrate, [Cu(C$_{10}$H$_9$N$_3$)$_2$(C$_2$H$_3$O$_2$)][NO$_3$], (I), $M_r =$ 526·89, and bis(di-2-bipyridylamine)(formato)copper(II) tetrafluoroborate, [Cu(C$_{10}$H$_9$N$_3$)$_2$(CHO$_2$)][BF$_4$], (II), $M_r =$ 537·64, both crystallize in the monoclinic space group $P2_1/c$. (I), $a =$ 13·216 (3),

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$b = 8.068$ (2), $c = 22.161$ (4) Å, $\beta = 92.01$ (3)°, $V = 2361.50$ Å^3, $Z = 4$, D_m(flotation) $= 1.50$ (1), $D_x = 1.48$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.926$ mm^{-1}, $T = 298$ K, $F(000) = 1084$, $R = 0.048$ for 1887 observed reflections. (II), $a = 13.571$ (2), $b = 7.687$ (1), $c = 22.362$ (3) Å, $\beta = 94.99$ (2)°, $V = 2323.97$ Å^3, $Z = 4$, D_m(flotation) $= 1.52$ (1), $D_x = 1.54$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.960$ mm^{-1}, $T = 298$, $F(000) = 1092$, $R = 0.051$ for 1660 observed reflections. Both structures involve a cis-octahedral CuN$_4$O$_2$ chromophore, but with very asymmetrically coordinated OXO groups, ΔO $=$ {[Cu—O(2)] − [Cu—O(1)]} $= 0.643$ (8) and 0.873 (4) Å, for (I) and (II), respectively. Both structures are best described as involving a square-pyramidal cis-distorted octahedral $(4 + 1 + 1^*)$ CuN$_4$OO' chromophore, but with significantly different angular distortions.

Introduction. The crystal structures of the [Cu^{II}-(chelate)$_2$(OXO)]$^+$ cation, where chelate $=$ di-2-bipyridyl (bpy) and 1,10-o-phenanthroline (phen) and OXO $=$ [ONO]$^-$, [CH$_3$CO$_2$]$^-$ or [HCO$_2$]$^-$ are well characterized (Hathaway, 1984), as fluxional copper(II) stereochemistries (Procter, Hathaway, Billing, Dudley & Nicholls, 1969; Harrison, Hathaway & Kennedy, 1979; Fitzgerald, Murphy, Tyagi, Walsh, Walsh & Hathaway, 1981; Simmons, Hathaway, Amornjarusiri, Santar-Siero & Clearfield, 1987). In order to extend this series to more flexible chelate nitrogen ligands, complexes with the ligand di-2-pyridylamine (dpyam) have been examined, and the structures of (I) and (II) are reported.

Experimental. The complex [Cu(dpyam)$_2$-(O$_2$CCH$_3$)][NO$_3$] (I) was prepared by adding a boiling solution containing 0.48 g (2.0 mmol) Cu(NO$_3$)$_2$.3H$_2$O in 60 ml water, to a warm solution of 0.07 g (4.0 mmol) dpyam in 30 ml ethanol, then 0.33 g 4.0 mmol) CH$_3$COONa was added. After a few days, green crystals of (I) were formed. (I), found: C, 49.18; H, 3.92; N, 18.34; Cu, 11.74%: calculated for C$_{22}$H$_{21}$CuN$_7$O$_5$: C, 50.13; H, 3.99; N, 18.61; Cu, 12.07%. For the complex [Cu-(dpyam)$_2$(O$_2$CH)][BF$_4$] (II), a hot solution containing 0.548 g (3.2 mmol) of dpyam in 30 ml ethanol was added to a boiling solution containing 0.332 g of Cu(O$_2$CH)$_2$.3H$_2$O (1.6 mmol) in 20 ml water, an excess of NaBF$_4$ (0.22 g, 2.0 mmol) was then added and the solution was heated to boiling. After a few days, dark green crystals of (II) were formed. (II), found: C, 47.34; H, 3.69; N, 15.88; Cu, 11.46%; calculated for C$_{21}$H$_{19}$BCuF$_4$N$_6$O$_2$: C, 46.90; H, 3.57; N, 15.63; Cu, 11.81%.

Details of the structure refinement of (I) and (II) are summarized in Table 1. For both complexes the unit-cell and space-group data were determined and

Table 1. Refinement data

Compound	(I)	(II)
Molecular formula	[Cu(dpyam)$_2$-(O$_2$CCH$_3$)][NO$_3$]	[Cu(dpyam)$_2$-(O$_2$CH)][BF$_4$]
Measured reflections	1953	1826
Unique reflections used (N)	1887	1660
Number of parameters (NP)	316	316
N/NP	5.97	5.25
Final weighting: k, g^*	0.8084, 0.002226	1.0363, 0.000640
R	0.048	0.051
wR	0.052	0.053
Max. final shift/e.s.d	0.001	0.001
Max. and min. residual electron density (e Å^{-3})	0.44, −0.42	0.58, −0.39

$^*w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$.

refined on a Philips PW1100 four-circle diffractometer (25 reflections, θ 3–25°). The intensity data were collected using graphite-monochromatized Mo $K\alpha$ radiation, using a θ–2θ scan mode and reflections with $3.0 < \theta < 25°$ in one quadrant were examined. A constant scan speed of 0.05° s^{-1} and a variable scan width of $(0.7 + 0.1\tan\theta)°$ was used. With an acceptance criterion of $I > 2.5\sigma(I)$; for (I), 1953 observed reflections, 1887 unique, with h, −15–15, k, 0–9, l, 0–24 and for (II), 1826 observed reflections, 1660 unique, with h, −17–17, k, 0–8, l, 0–26. Lorentz and polarization corrections were applied, but no correction was made for absorption. The structures were solved using three-dimensional Patterson and Fourier-synthesis techniques, *SHELX*76 and *SHELXS*86 (Sheldrick, 1976, 1986) and refined by full-matrix least-squares minimization of $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic temperature factors were refined for all the non-H atoms. Calculated H positions were used with fixed C—H bond lengths of 1.08 Å and a fixed U_{iso} of 0.07 Å^2; H atoms riding on the associated C or N atom. Complex neutral-atom scattering factors embedded in *SHELX*76 were employed and those for copper were taken from Cromer & Waber (1974). Calculations were carried out using *SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1986), *XANADU* (Roberts & Sheldrick, 1979), *CHEM-X* (Davies, 1980), *ORTEP* (Johnson, 1971) and *PUBTAB* (Henrick, 1980) on the UCC mainframe IBM 4341 and VAX 11/780 computers. The final atomic coordinates with e.s.d.'s are given in Table 2.* Selected bond lengths and angles are given in Table 3. Figs. 1 and 2 illustrate the molecular structures and atom-numbering schemes for (I) and (II), respectively.

Table 2. *Fractional atomic coordinates and isotropic thermal parameters ($\mathring{A}^2$) with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\mathring{A}^2)$
(I)				
Cu	0·17514 (6)	0·52940 (11)	0·62799 (4)	0·0363 (5)
N(1)	0·0419 (4)	0·6492 (7)	0·6305 (2)	0·050 (3)
C(1)	−0·0164 (6)	0·6500 (9)	0·5790 (3)	0·058 (5)
C(2)	−0·1176 (6)	0·6918 (10)	0·5778 (4)	0·067 (5)
C(3)	−0·1602 (6)	0·7344 (11)	0·6316 (4)	0·076 (6)
C(4)	−0·1021 (6)	0·7330 (10)	0·6854 (4)	0·070 (5)
C(5)	0·0005 (5)	0·6905 (9)	0·6823 (3)	0·056 (5)
N(3)	0·0578 (4)	0·6968 (8)	0·7364 (2)	0·061 (4)
C(6)	0·1627 (6)	0·7193 (9)	0·7432 (3)	0·058 (5)
C(7)	0·1982 (7)	0·8005 (11)	0·7948 (3)	0·075 (6)
C(8)	0·2993 (7)	0·8278 (11)	0·8018 (4)	0·079 (6)
C(9)	0·3638 (6)	0·7793 (10)	0·7569 (4)	0·072 (6)
C(10)	0·3246 (5)	0·7005 (9)	0·7078 (3)	0·061 (5)
N(2)	0·2235 (4)	0·6652 (8)	0·7010 (2)	0·058 (4)
N(4)	0·2984 (4)	0·3839 (8)	0·6298 (2)	0·054 (4)
C(11)	0·3199 (6)	0·2957 (11)	0·6808 (4)	0·068 (5)
C(12)	0·3851 (7)	0·1683 (11)	0·6836 (4)	0·077 (6)
C(13)	0·4307 (7)	0·1214 (12)	0·6309 (5)	0·084 (7)
C(14)	0·4117 (6)	0·2078 (11)	0·5782 (4)	0·073 (6)
C(15)	0·3455 (5)	0·3434 (9)	0·5794 (3)	0·050 (4)
N(6)	0·3320 (4)	0·4310 (8)	0·5259 (3)	0·060 (4)
C(16)	0·3053 (5)	0·5951 (10)	0·5190 (3)	0·054 (5)
C(17)	0·3398 (6)	0·6805 (13)	0·4695 (3)	0·076 (6)
C(18)	0·3155 (7)	0·8438 (15)	0·4610 (4)	0·088 (7)
C(19)	0·2567 (7)	0·9263 (11)	0·5026 (4)	0·080 (6)
C(20)	0·2239 (6)	0·8353 (11)	0·5504 (4)	0·070 (6)
N(5)	0·2452 (4)	0·6719 (8)	0·5581 (2)	0·058 (4)
O(1)	0·1067 (3)	0·3507 (6)	0·5767 (2)	0·057 (3)
O(2)	0·0604 (4)	0·2828 (7)	0·6681 (2)	0·077 (4)
C(21)	0·0583 (5)	0·2596 (9)	0·6130 (3)	0·056 (5)
C(22)	−0·0065 (3)	0·1224 (5)	0·5848 (2)	0·092 (7)
N(7)	0·4360 (3)	0·2921 (5)	0·3817 (2)	0·052 (4)
O(3)	0·3983 (3)	0·2283 (5)	0·4255 (2)	0·130 (6)
O(4)	0·4787 (3)	0·4227 (5)	0·3839 (2)	0·184 (9)
O(5)	0·4219 (3)	0·2224 (5)	0·3334 (2)	0·136 (6)
(II)				
Cu	−0·15265 (7)	0·00348 (18)	−0·12624 (4)	0·0377 (5)
N(1)	−0·0244 (5)	0·1148 (10)	−0·1421 (3)	0·039 (4)
C(1)	0·0442 (7)	0·1351 (12)	−0·0961 (4)	0·049 (6)
C(2)	0·1411 (7)	0·1770 (13)	−0·1017 (5)	0·057 (7)
C(3)	0·1690 (8)	0·1896 (16)	−0·1599 (5)	0·072 (8)
C(4)	0·1021 (7)	0·1683 (15)	−0·2090 (4)	0·066 (7)
C(5)	0·0034 (6)	0·1344 (12)	−0·1975 (4)	0·043 (6)
N(3)	−0·0642 (5)	0·1197 (10)	−0·2479 (3)	0·045 (5)
C(6)	−0·1646 (6)	0·1449 (12)	−0·2505 (4)	0·041 (6)
C(7)	−0·2127 (7)	0·2023 (14)	−0·3055 (4)	0·059 (7)
C(8)	−0·3121 (8)	0·2342 (16)	−0·3073 (5)	0·075 (8)
C(9)	−0·3629 (7)	0·2126 (15)	−0·2574 (4)	0·063 (7)
C(10)	−0·3116 (7)	0·1532 (12)	−0·2069 (4)	0·048 (6)
N(2)	−0·2134 (5)	0·1155 (10)	−0·2025 (3)	0·041 (4)
N(4)	−0·2743 (5)	−0·1424 (10)	−0·1185 (3)	0·045 (5)
C(11)	−0·3007 (8)	−0·2578 (15)	−0·1636 (5)	0·064 (7)
C(12)	−0·3748 (9)	−0·3759 (15)	−0·1604 (6)	0·077 (9)
C(13)	−0·4258 (8)	−0·3772 (16)	−0·1105 (7)	0·081 (9)
C(14)	−0·4024 (7)	−0·2627 (15)	−0·0642 (5)	0·065 (7)
C(15)	−0·3245 (6)	−0·1432 (13)	−0·0703 (5)	0·044 (6)
N(6)	−0·3052 (5)	−0·0291 (10)	−0·0226 (3)	0·045 (5)
C(16)	−0·2662 (7)	0·1342 (13)	−0·0221 (4)	0·038 (6)
C(17)	−0·2916 (7)	0·2475 (15)	0·0231 (4)	0·057 (7)
C(18)	−0·2537 (7)	0·4160 (15)	0·0250 (4)	0·058 (7)
C(19)	−0·1919 (7)	0·4668 (12)	−0·0180 (4)	0·051 (7)
C(20)	−0·1703 (7)	0·3487 (13)	−0·0604 (5)	0·053 (7)
N(5)	−0·2044 (5)	0·1851 (10)	−0·0620 (3)	0·040 (4)
O(1)	−0·0779 (4)	−0·1585 (8)	−0·0686 (2)	0·043 (4)
C(21)	−0·0301 (7)	−0·2722 (14)	−0·0949 (5)	0·050 (7)
O(2)	−0·0341 (5)	−0·2945 (10)	−0·1501 (3)	0·071 (5)
B(1)	−0·4472 (10)	−0·3245 (19)	−0·3835 (7)	0·064 (9)
F(1)	−0·5395 (5)	−0·2945 (9)	−0·4024 (4)	0·106 (6)
F(2)	−0·4043 (7)	−0·4543 (11)	−0·4129 (4)	0·150 (8)
F(3)	−0·3917 (5)	−0·1867 (11)	−0·3958 (5)	0·164 (8)
F(4)	−0·4357 (7)	−0·3589 (18)	−0·3277 (4)	0·199 (11)

Table 3. *Selected bond lengths ($\mathring{A}$) and bond angles (°) with e.s.d.'s in parentheses*

	(I)	(II)
(a) Bond lengths		
Cu—N(1)	2·011 (5)	1·999 (7)
Cu—N(2)	2·037 (6)	2·021 (7)
Cu—N(4)	2·007 (6)	2·015 (7)
Cu—N(5)	2·162 (6)	2·164 (7)
Cu—O(1)	2·030 (5)	2·003 (6)
Cu—O(2)	2·673 (5)	2·876 (7)
O(1)—C(21)	1·278 (8)	1·263 (10)
O(2)—C(21)	1·236 (8)	1·243 (11)
N(7)—O(3)	1·220 (1)	
N(7)—O(4)	1·195 (1)	
N(7)—O(5)	1·218 (1)	
B(1)—F(1)		1·307 (13)
B(1)—F(2)		1·354 (14)
B(1)—F(3)		1·343 (14)
B(1)—F(4)		1·271 (14)
(b) Bond angles		
N(1)—Cu—N(2)	88·3 (2)	88·1 (3)
N(5)—Cu—N(1)	99·3 (2)	100·3 (3)
N(5)—Cu—N(2)	98·7 (2)	98·8 (3)
N(4)—Cu—N(2)	93·9 (2)	91·8 (3)
N(4)—Cu—N(1)	172·4 (2)	170·3 (3)
N(4)—Cu—N(5)	87·5 (2)	89·2 (3)
C(6)—N(3)—C(5)	127·1 (6)	127·2 (7)
C(16)—N(6)—C(15)	127·6 (6)	129·4 (8)
O(1)—Cu—N(2)	161·5 (2)	162·6 (3)
O(1)—Cu—N(1)	89·1 (2)	88·8 (3)
O(1)—Cu—N(5)	99·8 (2)	98·6 (3)
O(1)—Cu—N(4)	86·6 (2)	88·4 (3)
O(1)—Cu—O(2)	53·9 (2)	50·3 (5)
O(2)—C(21)—O(1)	122·7 (7)	125·3 (9)
O(4)—N(7)—O(3)	123·0 (1)	
O(5)—N(7)—O(3)	116·8 (1)	
O(5)—N(7)—O(4)	120·0 (1)	

Discussion. The asymmetric units of (I) and (II) are made up of discrete $[Cu(dpyam)_2(O_2CCH_3)]^+$ and $[Cu(dpyam)_2(O_2CH)]^+$ cations, and nitrate and tetrafluoroborate anions, respectively. There is no evidence for semi-coordination of the nitrate or tetrafluoroborate anions to the Cu atoms (Procter, Hathaway & Nicholls, 1968) for (I) and (II), respectively. There are no unusual features in either the bond lengths or the bond angles of the organic ligands present (Stephens, 1969, 1972; Ray & Hathaway, 1978) (see Table 3). The nitrate group (Addison, Logan, Wallwork & Garner 1971) in (I) involves reasonable N—O distances (mean 1·211 $\mathring{A}$) and O—N—O bond angles (mean 119·9°) respectively. In the tetrafluoroborate anion of (II), the B—F bond lengths (mean 1·319 $\mathring{A}$) are shorter than that (1·37 $\mathring{A}$) normally found in the tetrafluoroborate anion, but the bond angles were as expected (mean 109·7°) for the tetrahedral anion. The short B—F distances are not unexpected given the high F-atom U_{eq} values. The main residual electron density (0·58 e $\mathring{A}^{-3}$) is associated with the $[BF_4]^-$ anions, but attempts to represent the anion as disordered failed to improve the model.

The CuN_4O_2 chromophores of (I) and (II) involve a basic *cis*-distorted octahedral stereochemistry [Fig.

3(a)] with a marked asymmetric coordination of the OXO⁻ anion [Fig. 3(b)] (Hathaway, 1984). The Cu atoms of the [Cu(dpyam)₂(OXO)]⁺ cations are basically five-coordinate, but with the second O atom of the acetate group in (I) and the formate group in (II) occupying a sixth coordinate position at a distance greater than 2·6 Å, namely 2·673 (6) and 2·876 (7) Å, respectively. The short Cu—O distances of 2·030 (5) in (I) and 2·003 (6) Å in (II) agree with the typical
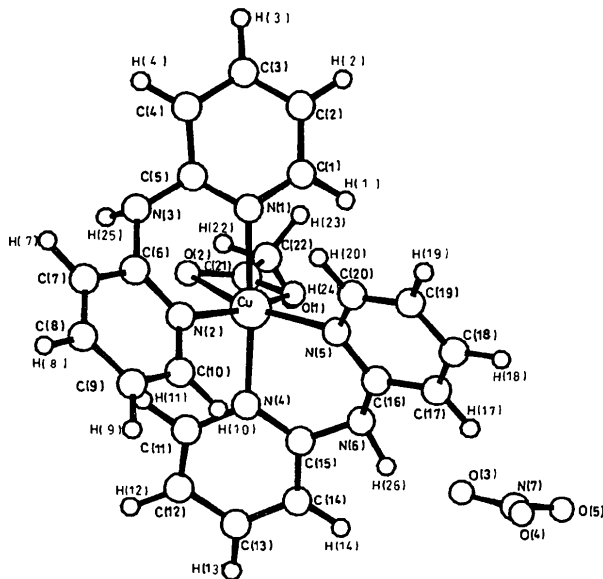
value of 2·00 Å (Hathaway & Hodgson, 1972; Hathaway & Billing, 1970). The coordination of the bidentate acetate group in (I) and the formate group in (II) is extremely asymmetric with $\Delta O_{1,2}$ values of 0·643 (8) and 0·873 (9) Å, respectively. The out-of-plane Cu—N(1) and Cu—N(4) distances are not significantly different with an average Cu—N distance of 2·009 (8) Å [$\Delta N_{1,4}$ 0·004 (8) Å] in (I) and 2·007 (10) Å [$\Delta N_{1,4}$ 0·016 (10) Å] in (II). The mean in-plane Cu—N distances [2·099 (8) in (I) and 2·093 (10) Å in (II)], are significantly longer than the mean out-of-plane Cu—N distances, by ca 0·1 Å. The in-plane Cu—N distances are significantly different with $\Delta N_{2,5} = \{[\text{Cu—N(5)}] - [\text{Cu—N(2)}]\} = 0·125$ (8) in (I) and 0·143 (10) Å in (II).

The out-of-plane N(1)—Cu—N(4) angles in (I) and (II) are nearly linear with values of 172·4 (2) and 170·3 (3)°, respectively. There are no unusual out-of-the N(2), N(5), O(1), O(2) plane angular distortions, with all values between 80 and 100° (Table 3), but the in-plane angles do show significant differences. The O(1)—Cu—N(2) angle is significantly < 180° at 161·5 (2) and 162·6 (3)° in (I) and (II), respectively. The O(1)—Cu—N(5) and N(2)—Cu—N(5) angles [99·8 (2) and 98·6 (2)°, and 98·67 (2) and 98·8 (2)°, respectively] are almost equal but significantly > 90°.

In (I) and (II) the large O(1)—Cu—N(2) angle is opposite the elongated Cu–N(5) direction. This could be taken as the basal angle of the square pyramidal stereochemistry with elongation in the Cu–N(5) direction, especially in view of the near equivalence of the O(1)—Cu—N(5) and N(2)—Cu—N(5) angles (Table 3), to give a square-pyramidal octahedral (4 + 1 + 1*)-type stereochemistry (Hathaway, 1973). The Cu atom is lifted out of the N(1), N(2), N(4), O(1) basal plane by 0·233 Å in (I) and 0·235 Å in (II), in the direction of the N(5) atom. The N(1), N(2), N(4), O(1) basal plane also has a slight trigonal distortion. Consequently this alternative square pyramidal stereochemistry for both complexes is not as regular as in K[Cu(NH₃)₅][PF₆]₃, which has almost equal basal angles of 166 ± 1° (Duggan, Ray, Hathaway, Tomlinson, Brint & Pelin, 1980). A measure

Fig. 1. The molecular structure of [Cu(dpyam)₂(O₂CCH₃)][NO₃] (I) and the atom-numbering scheme.

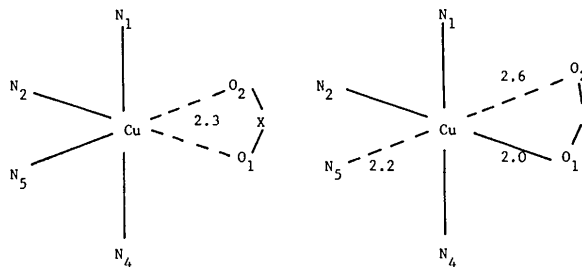Fig. 2. The molecular structure of [Cu(dpyam)₂(O₂CH)][BF₄] (II) and the atom-numbering scheme.

Fig. 3. cis-distorted octahedral CuN₄O₂ chromophore; (a) symmetric OXO⁻ coordination; (b) asymmetric OXO⁻ coordination.

of the trigonal distortion is the τ-value $[\{N(1)\text{—Cu—N}(4)\} - \{N(2)\text{—Cu—O}(1)\}]/60$ (Addison, Nageswara Rao, Reedijk, van Rijn & Verschoor, 1984). This is 0·18 and 0·13 for (I) and (II), respectively, both relatively close to that of a regular square pyramidal CuN_3ON' chromophore, $\tau = 0$.

The sense of the distortion of the N(1), N(2), N(4), O(1) plane is related to the mechanistic pathway of the Berry twist (Berry, 1960), correlating the trigonal and square pyramidal five coordinate stereochemistries of the copper(II) ion (Ray, Hulett, Sheahan & Hathaway, 1978; Ray & Hathaway, 1978; Druhan & Hathaway, 1979), and as previously reported for the $[Cu(bpy)_2X]Y$ system (Harrison, Hathaway & Kennedy, 1979; Walsh, Walsh, Murphy & Hathaway, 1981; Fitzgerald & Hathaway, 1981). However, the structures of both (I) and (II) are best considered to be intermediate between a distorted square-based pyramidal five-coordinate geometry, plus an additional long bonded sixth O(2) ligand, and an asymmetric cis-distorted octahedral geometry, both giving a $(4 + 1 + 1^*)$ type coordination (Fitzgerald & Hathaway, 1981).

The individual pyridine rings in the dpyam ligands in both complexes are planar, to within 0·022 Å. The dpyam ligands as a whole, however, are nonplanar and are slightly twisted about the amine N—C bonds. The pyridine rings involve dihedral angles of 27·90 and 27·41° in (I) and 26·95 and 23·66° in (II) for the ligands defined by the N(1)/N(2) and the N(4)/N(5) atoms, respectively. The dpyam bite angles are 88·3 (2) and 87·5 (2)° in (I) and 88·1 (3) and 89·2 (3)° in (II) for the N(1)/N(2) and N(4)/N(5) ligands, respectively. The mean planes of the dpyam ligands are inclined to each other at 112·16 in (I) and 116·14° in (II).

The acetate group in (I) is planar and reasonably coplanar with the Cu, N(2), N(5) plane and, due to the O(1)—Cu—O(2) bite angle of 53·9 (2)°, O(2) lies well off the z axis of the CuN_3ON' square pyramid, at a distance > 2·6 Å, but close enough to be involved in off-the-z-axis bonding to the Cu^{2+} ion (Hathaway, 1973). The mean C—O distance of the acetate ligand, 1·26 (2) Å, agrees with the reported value, 1·26 Å (Oldham, 1968; Hathaway, Ray, Kennedy, O'Brien & Murphy, 1980; Wells, 1984). The separate C—O distances of 1·236 (8) and 1·278 (8) Å are just significantly different, despite the marked asymmetry in the Cu—O(1) and Cu—O(2) distances. The C—O bond lengths of the formate ligand in (II) are not significantly different at 1·263 (10) for O(1)—C(21) and 1·243 (11) Å for O(2)—C(21). The O(1)—C(21)—O(2) angle of 125·3 (9)°, is larger than the angle of 120° characteristic of a trigonal planar anion, as observed previously (Fitzgerald et al., 1981) and subtends an angle of 50·3 (5)° at the Cu atom.

The plot of the ΔO and ΔN differences for a series of $[Cu(chelate)_2(OXO)]Y$ complexes (Simmons et al., 1987, Fig. 4), where chelate = bpy and phen, has been used to suggest a structural pathway for these fluxional CuN_4O_2 chromophores. The ΔO and ΔN values of (I) and (II) lie in the same range, 0–0·9 Å, and suggest that the dpyam complexes also represent points on a corresponding structural pathway (Hathaway, 1984) and also involve fluxional CuN_4O_2 stereochemistries. In the case of (II), this complex lies near the upper limit of 0·8 Å for the pathway (Fitzgerald et al., 1981). Some evidence for this fluxional description of the CuN_4O_2 chromophore stereochemistry of (I) and (II) can be obtained from the plots of the thermal parameters, Figs. 4(a) and 4(b) (Johnson, 1971). For the Cu, N(2), N(5) and O(1) atoms, the thermal parameters are reasonably spherical. In the case of the O(2) atoms, the thermal parameters are clearly ellipsoidal, with the major axis of the ellipsoid orientated approximately parallel to the Cu—O(2) directions for both (I) and (II) (see Fig. 2 of Simmons et al., 1987).

The electronic spectra of (I) and (II), recorded as previously described (Hathaway & Billing, 1970), involve twin peaks of comparable intensity at 10 000 and 15 200, and 10 500 and 15 600 cm^{-1}, respectively. The spectra differ slightly in the relative energies involved, with the bands of (II) ca 500 cm^{-1} higher in energy than those in (I). The splitting ΔE of approximately 5 100 cm^{-1} is significantly greater than that of the corresponding bpy (Hathaway et al., 1980; Fitzgerald & Hathaway, 1981) and phen (Escobar & Wittke, 1983; Fitzgerald et al., 1985) complexes, of $\Delta E = 4 200$ and 4 500 cm^{-1}, respectively, and may reflect the greater flexibility of the dpyam ligand.
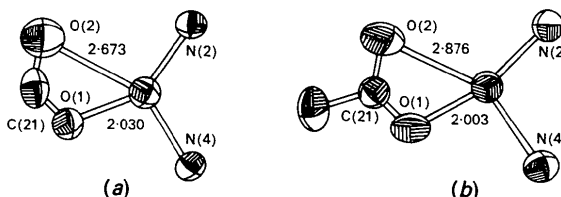
Fig. 4. ORTEP thermal ellipsoid plots; 50% probability ellipsoids for the in-plane CuN_2O_2 atoms of (a) $[Cu(dpyam)_2(O_2CCH_3)][NO_3]$ and (b) $[Cu(dpyam)_2(O_2CH)][BF_4]$.

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Structure of Bis(1,10-phenanthroline)copper(II) Bis(hexafluorophosphate)

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Abstract. [Cu(C$_{12}$H$_8$N$_2$)$_2$][PF$_6$]$_2$, (I), M_r = 713·89, monoclinic, C2/c, a = 17·594 (4), b = 12·603 (3), c = 12·539 (3) Å, β = 111·90 (2)°, V = 2579·72 Å^3, Z = 4, D_m(flotation) = 1·810 (6), D_x = 1·83 Mg m^{-3}, λ(Mo Kα) = 0·71069 Å, μ = 1·017 mm^{-1}, F(000) = 1420, room temperature, R = 0·049 for 1723 unique observed reflections. The crystal contains [Cu(phen)$_2$]$^{2+}$ cations (phen = 1,10-o-phenanthroline) and [PF$_6$]$^-$ anions. The cation involves a compressed tetrahedral CuN$_4$ chromophore and lies on a crystallographic twofold axis of symmetry. The two independent anions are also in special positions of twofold symmetry, with near octahedral stereochemistry, and with the shortest Cu···F distances > 2·75 Å, they are too long even for weak semi-coordination.

Introduction. The compressed tetrahedral CuN$_4$ chromophore is of only limited occurrence in the coordination chemistry of the Cu^{II} ion involving simple neutral chelate N ligands (Hathaway & Billing, 1970; Hathaway, 1987). It was first

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