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SYNTHESES AND CHARACTERISATION OF COMPLEXES [Cu (dpyam)$_2$ (O$_2$CCH$_3$)]X, X = [NO$_3$3]$^-$, [O$_2$CCH$_3$]$^-$, Cl$^-$, Br$^-$, I$^-$AND [PF$_6$]$^-$. CRYSTAL STRUCTURE OF [Cu(dpyam)$_2$ (O$_2$CCH$_3$)] [NO$_3$]

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ABSTRACT

The complexes [Cu(dpyam)$_2$ (O$_2$CCH$_3$3)]X, X=[NO$_3$]$^-$[I], [CH$_3$CO$_2$]$^-$[II], Cl$^-$ [III], Br$^-$[IV], I$^-$[V] and [PF$_6$]$^-$[VI], were prepared directly from their components. A single crystal structural analysis of [I] has been performed and is the first reported crystal structure of this series involving the di-2-pyridylamine (dpyam) and acetate ligands. [I] crystallises in the monoclinic space group P2$_1$/C with a = 13.216(3), b = 8.068 (2), C = 22.161(4) Å, β = 92.011 (3), U = 2361.50 Å^3, D$_m$ = 1.50, D$_c$ = 1.48 Mg m^{-3} and Z = 4. R = 0.0477 for 1887 unique reflections. The structure involves 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) Å. The structure of [I] is best described as a square-pyramidal cis-distorted octahedron (4 + 1 + 1*). Details of the syntheses and electronic spectra are discussed for allcomplexes.

INTRODUCTION

The crystal structures of the Cu(II)(chelate)$_2$(OXO)]$^+$ cation, where chelate = di-2-bipyridyl (bipy) and 1,10-orthophenan-throline (phen) and OXO = [ONO]$^-$, [CH$_3$CO$_2$]$^-$ or [HCO$_2$]$^-$ are well characterised[1] as fluxional copper(II) stereochemistries[2-4]. In order to extend this series to more flexible chelate nitrogen ligands, complexes with the more flexible ligand di-2-pyridylamine (dpyam) has been examined, and the structure of [I] are reported.The structures of [II]-[VI] have been identified by microanalysis, infrared and electronic properties and compared with those of I.

MATERIALS AND METHODS

Preparation

Complexes [I] and [II] were prepared directly, by adding a boiling solution of the corresponding salts 0.48 g (2.0 mmol) Cu(NO$_3$)$_2$. 3H$_2$O for [I] and 0.40 g (2.0 mmol) Cu(O$_2$CCH$_3$)$_2$. H$_2$O for [II] in 60 ml water, to 0.68 g (4.0 mmol) dpyam in 30 ml ethanol and 0.33 g (4.0 mmol) CH$_3$3COONa. The mixed solutions were heated to boiling, filtered and allowed to stand. After a few days, green crystals of [I] and [II] were formed.

Table 1. Elemental analysis of the products $[Cu(dpyam)_2\ (O_2CCH_3)]X$.

Product	**Analysis**									
	Theory(%)					**Found(%)**				
	C	**H**	**N**	**Cu**	**X**	**C**	**H**	**N**	**Cu**	**X**
$[Cu(dpyam)_2\ (O_2CCH_3)][NO_3]$ [I]	50.13	3.99	18.61	12.07	-	49.18	3.92	18.34	11.74	-
$[Cu(dpyam)_2\ (O_2CCH_3)[CH_3CO_2]$ [II]	51.84	5.04	15.12	11.44	-	52.99	4.85	14.73	11.23	-
$[Cu(dpyam)_2\ (O_2CCH_3)]Cl$ [III]	52.80	4.20	16.80	12.71	7.09	52.35	4.16	16.32	12.40	6.96
$[Cu(dpyam)_2\ (O_2CCH_3)]Br$ [IV]	48.49	3.86	15.43	11.67	14.68	48.45	3.83	15.59	11.83	14.94
$[Cu(dpyam)_2\ (O_2CCH_3)]I$ [V]	44.64	3.55	14.20	10.74	21.46	43.70	3.53	14.15	10.53	22.02
$[Cu(dpyam)_2(O_2CCH_3)][PF_6]$ [VI]	43.31	3.44	13.78	10.43	-	42.98	3.41	13.69	10.27	-

The similar procedures were made for complexes [III]-[VI] by adding a boiling solution containing 0.40 g (2.0 mmol) $Cu(O_2CCH_3)_2.H_2O$, to a warm solution of 0.68 g (4.0 mmol) dpyam in 60 ml methanol. The mixtures were warmed, stirred and the corresponding salts 0.12 g (2.0 mmol) NaCl for [III], 0.21 g. (2.0 mmol) NaBr for [IV], 0.30 g (2.0 mmol) NaI for [V], and 0.37 g. (2.0 mmol) KPF_6 and 1.64 g (20.0 mmol) CH_3COONa for [VI] were added. The mixed solutions were heated to boiling, filtered and allowed to stand and yielded green crystals of [III]-[VI]. Table 1 shows the microanalytical results of all products.

Crystal data

The unit cell data and intensities were collected on a Philips 1100 diffractometer with graphite monochromatised Mo-K_α radiation. Reflections with $3.0 < \theta < 25°$ in one quadrant were examined in the θ-2θ scan mode, with a constant scan speed of 0.05° s^{-1}, and a variable scan width of $(0.7+0.1 \tan \theta)°$. 1958 observed reflections were collected [$I > 2.5$]. Lorentz and polarisation corrections were applied, but no correction was made for absorption [μ(Mo-Kα) = 15.36 cm^{-1}]. The structure was solved by the *SHELX76* and *SHELX86* direct methods[5, 6] and by difference Fourier techniques and refined by full matrix least squares analysis, with anisotropic temperature factors on all the non-H atoms. The positions of the H atoms were calculated geometrically and "floated" on the adjacent carbon or nitrogen atoms, assuming C-H and N-H distances of 1.08 Å, and a fixed temperature factor of 0.07 $Å^2$. The data converged when the maximum shift/e.s.d. was < 0.001, with a refined weighting scheme, $w = k\ [\sigma^2\ (F_o o) + g(F_o)^2$ with $k = 1.0000$ and $g = 0.001711$. $R = 0.0372$ and $R_w = 0.0430$. The maximum residual electron density was 0.40 e $Å^{-3}$. Complex atomic scattering factors were employed and those for Cu were corrected for anomalous dispersion[6, 7]. All calculations were carried out with *SHELX76*[5], *SHELX86*[6] and *XANADU*[5] *CHEMX*[9] and *PUBTAB*[10] on the U.C.C. mainframe IBM 4341 and VAX 11/780 computers. Selected bond lengths and angles are given in Table 2, and some mean plane data in Table 3* . Figs. 1 and 2 show the molecular structure of [I], the atom-numbering scheme, and the crystal packing in the unit cell, respectively.

TABLE 2 Selected bond-lengths (Å) and bond-angles (°) with estimated standard deviations in parentheses

(a) Bond lengths

Cu-N(1)	2.011(5)
Cu-N(2	2.037(6)
Cu-N(4)	2.007(6)
Cu-N(5)	2.162(6)
Cu-O(1)	2.030(5)
Cu-O(2)	2.673(5)
O(1)-C(21)	1.278(8)
O(2)-C(21)	1.236(8)
N(7)-O(3)	1.220(1)
N(7)-O(4)	1.195(1)
N(7)-O(5)	1.218(1)

(b) Bond angles

N(1)-Cu-N(2)	88.3(2)
N(5)-Cu-N(1)	99.3(2)
N(5)-Cu-N(2)	98.7(2)
N(4)-Cu-N(2)	93.9(2)
N(4)-Cu-N(1)	172.4(2)
N(4)-Cu-N(5)	87.5(2)
C(6)-N(3)-C(5)	127.1(6)
C(16)-N(6)-C(15)	127.6(6)
O(1)-Cu-N(2)	161.5(2)
O(1)-Cu-N(1)	89.1(2)
O(1)-Cu-N(5)	99.8(2)
O(1)-Cu-N(4)	86.6(2)
O(1)-Cu-O(2)	53.9(2)
N(2)-Cu-N(5)	98.7(2)
O(2)-C(21)-O(1)	122.7(7)
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)

TABLE 3 Equations of least-squares planes in the form 1X+mY+nZ-p = 0, where X, Y, and Z are orthogonal axes, with deviations (A) of relevant atoms from the planes

	1	**m**	**n**	**p**
Plane(1) :	N(1),C(1)-C(5) (r.m.s.d. 0.0039)			
	0.2379	0.9585	-0.1573	2.9578
Plane(2) :	C(6)-C(10), N(2) (r.m.s.d. 0.0143)			
	-0.1251	0.8770	-0.4639	-2.7982
Plane(3) :	N(1), C(1)-C(5), N(3), C(6)-C(10), N(2) (r.m.s.d. 0.2644)			
	0.0542	0.9604	-0.2734	0.2488
	N(3) -0.4541			
Plane(4) :	N(4), C(11)-C(15) (r.m.s.d. 0.0127)			
	0.7572	0.6192	0.2078	7.7873
Plane(5) :	C(16)-C(2),N(5) (r.m.s.d. 0.0120)			
	0.8206	0.2592	0.5094	10.3247
Plane(6) :	N(4), C(11)-C(15), N(6), C(16)-C(20), N(5) (r.m.s.d. 0.2618)			
	0.8345	0.4401	0.3315	9.4607
	N(6) -0.4583			
	C(21) 0.0111			
Plane(7) :	0(1), O(2), C(21), C(22) (r.m.s.d. 0.0064)			
	0.7786	-0.6241	0.0652	0.1655
	C(21) 0.0111			
Plane(8) :	Cu, N(2), N(5), O(1), O(2), C(21), C(22) (r.m.s.d. 0.0330)			
	0.8072	-0.5869	0.0639	0.2370
Plane(9) :	N(1), N(2), N(4), O(1) (r.m.s.d. 0.1035)			
	0.3381	0.5831	-0.7387	-7.1704
	N(1) 0.1047, N(2) -0.1004, N(4) 0.1022, O(1) -0.1066, Cu 0.2229			
Plane (10) :	Cu, N(2), N(5) (r.m.s.d. 0.0000)			
	0.8186	-0.5707	0.0645	0.3481
	Cu 0.0000, N(2) 0.0000, N(5) 0.0000			

Dihedral angle (°) between normals to planes: (1)-(2) 27.90, (4)-(5) 27.41, (3)-(6) 112.16, (7)-(8) 2.69

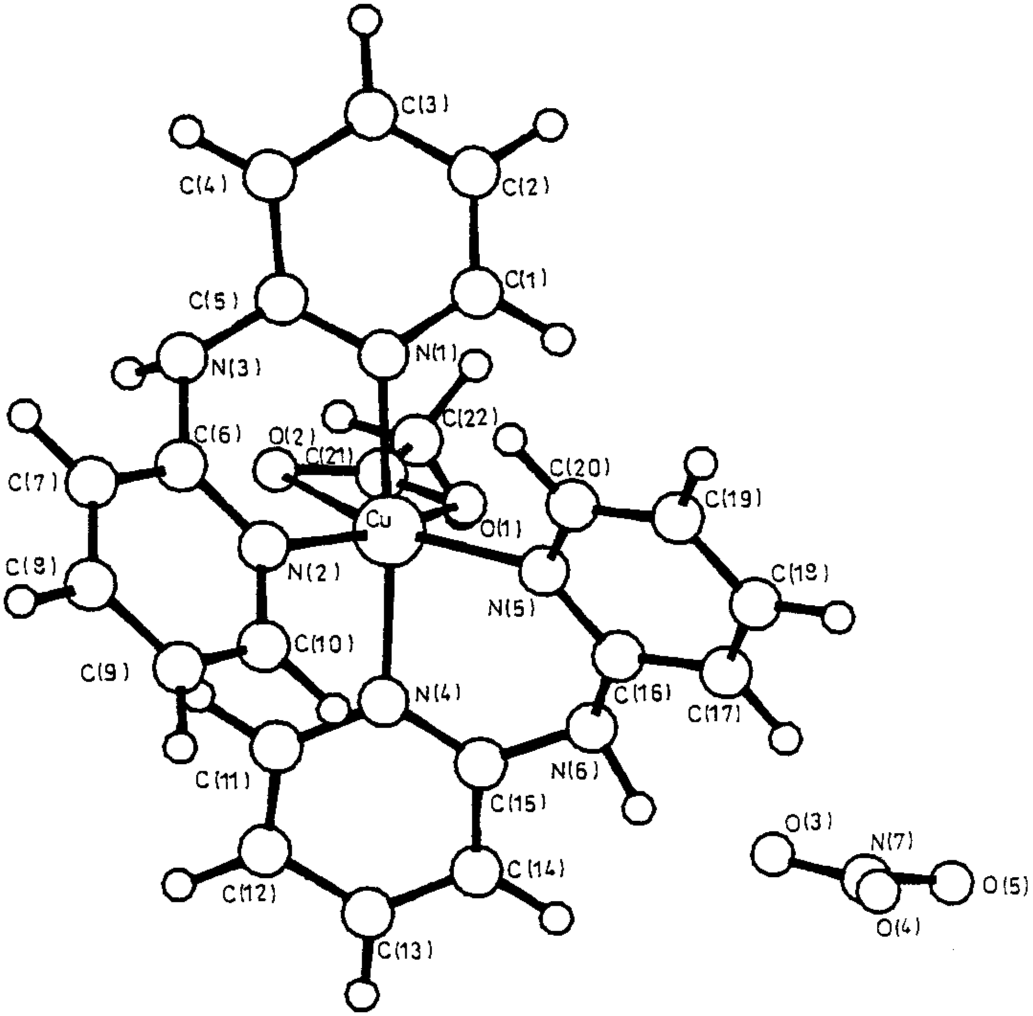

Fig. 1. The molecular structure of $[Cu(dpyam)_2 (O_2CCH_3)] [NO_3]$ [I] and atom-numbering system used

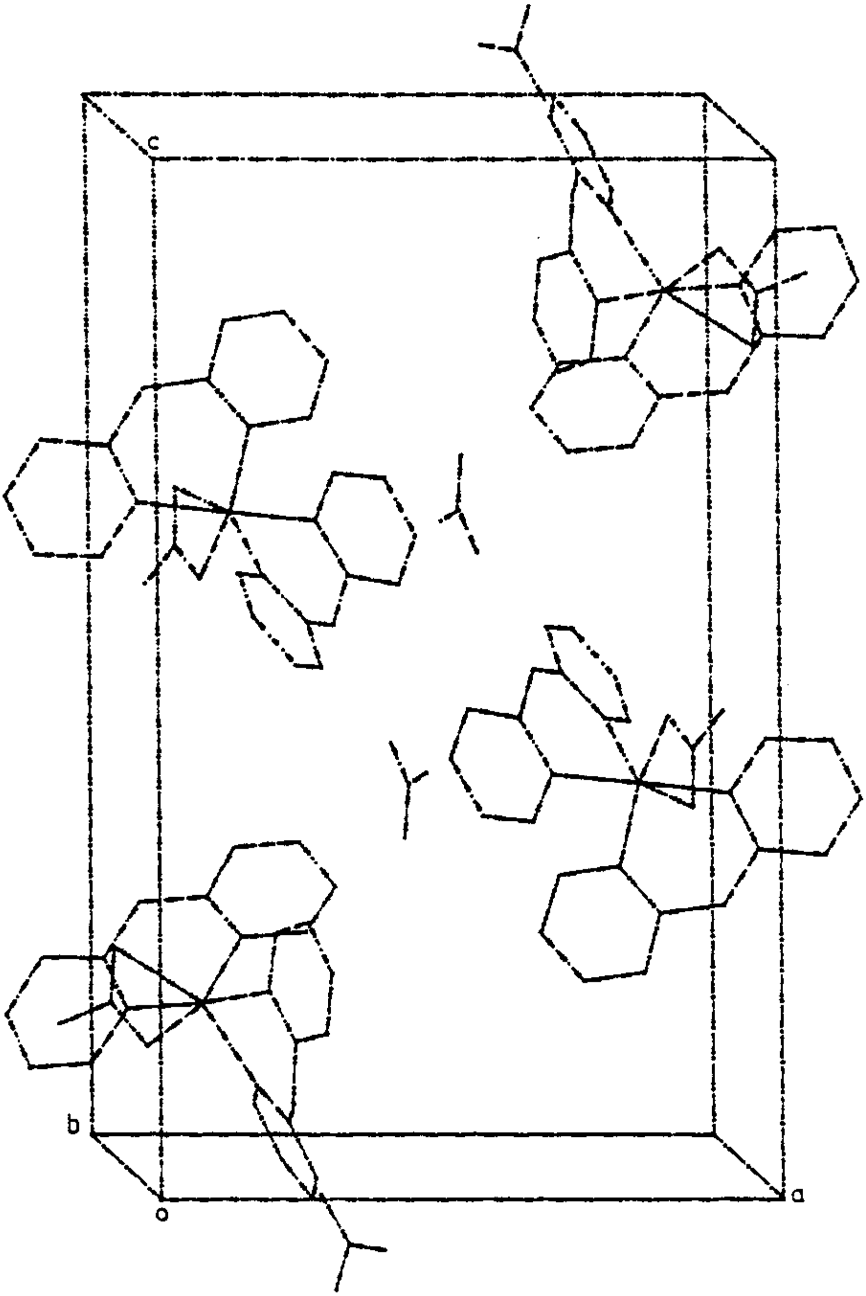

Fig. 2. The molecular packing in the unit cell of $[Cu(dpyam)_2(O_2CCH_3)][NO_3]$ [I]

RESULTS AND DISCUSSION

The structure of [I] consists of a discrete $[Cu(dpyam)_2\ (O_2CCH_3)]^+$ cation and a $[NO_3]^-$ anion. There is no evidence for semi-coordination of the nitrate anion to the copper atom. There are no unusual features in either the bond lengths or the bond angles of the nitrate or in the organic ligands present[11, 12]. The nitrate group[13] involves reasonable N-O distance, mean 1.211 Å and O-N-O bond angle, mean 119.9°, respectively. The copper (II) cation involves CuN_4OO' chromophore with an asymmetric cis-distorted octahedral stereochemistry. The stereo-chemistry of the $[Cu(dpyam)_2\ (O_2CCH_3)]^+$ cation is basically five-coordinate, but with the second oxygen of the acetate group occupying a sixth coordinate position at a distance greater than 2.6 A, namely 2.673(6) Å, to give a (4+1+1*) type coordination[14]. The stereochemistry in best described as a square pyramidal cis-distorted octahedral (4+1+1*). The axial 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). The N(1)-Cu-N(4) angle is nearly linear with the value of 172.4(2)°. The mean in-plane Cu-N distance 2.099(8) Å is significantly longer than the mean out-of-plane Cu-N distance by ca 0.1 A, as previously reported for the trigonal-bipyramidal copper (II) stereochemistry[15]. Nevertheless, the in-plane Cu-N distances are significantly different with ΔN = [Cu-N(5)]-[Cu-N(2)] = 0.125 (8) Å. The short Cu-O distance of 2.030 (5) A is equivalent to a normal short Cu-O distance, ca. 2.00 Å[14, 16]. The coordination of the bidentate acetate group is extremely asymmetric with the $\Delta O_{1,2}$ value of 0.643 (8) Å.

There are no unusual out-of-the-plane angular distortions, values 90±10°, but the trigonal-in-plane angles do show divergences from the 120° of a regular trigonal-bipyramidal stereochemistry: the O(1)-Cu-N(2), α_2, angle is significantly > 120°, 161.5(2) Å. The O(1)-Cu-N(5), α_1 and N(2)-Cu-N(5), α_3 angles, 99.8(2) and 98.6(2)°, respectively, are almost equal, butsignificantly < 120° and together amount to a substantial distortion of the trigonal plane. Nevertheless, the alternative square pyramidal stereochemistry is not regular as in $K[Cu(NH_3)_5][PF_6]_3$, with has almost equal basal angles of 166±1°)[17]. [I] has a clear trigonal distortion of the N(1), N(2), N(4), O(1) plane, Table 3, which N(1)-Cu-N(4) = 172.4(2)° and 0(1)-Cu-N(2) = 161.5(2)°, which results in a large r.m.s.d. of 0.1035 Å, compared to 0.0105 Å in the corresponding basal plane of $K[Cu(NH_3)_5][PF_6]_3$. As the large O(1)-Cu-N(2) angle is opposite the elongated Cu-N(5) direction, it could be taken as the basal angle of the square pyramidal stereochemistry with the Cu-N(5) direction, the elongation direction, especially in view of the near equivalence of the O(1)-Cu-N(5) and N(2)-Cu-N(5) angles. The copper atomis lifted out of this basal plane N(1), N(4), N(2), O(1) by 0.2229 Å, in the direction of the N(5) atom. The sense of the distortion of the N(1), N(2), N(4)

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* Lists of the final atomic coordinates and equivalent isotropic temperature factors, structure factors, anisotropic thermal parameters, calculated H atom coordinates and full bond-length and bond-angle data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP. 53846 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

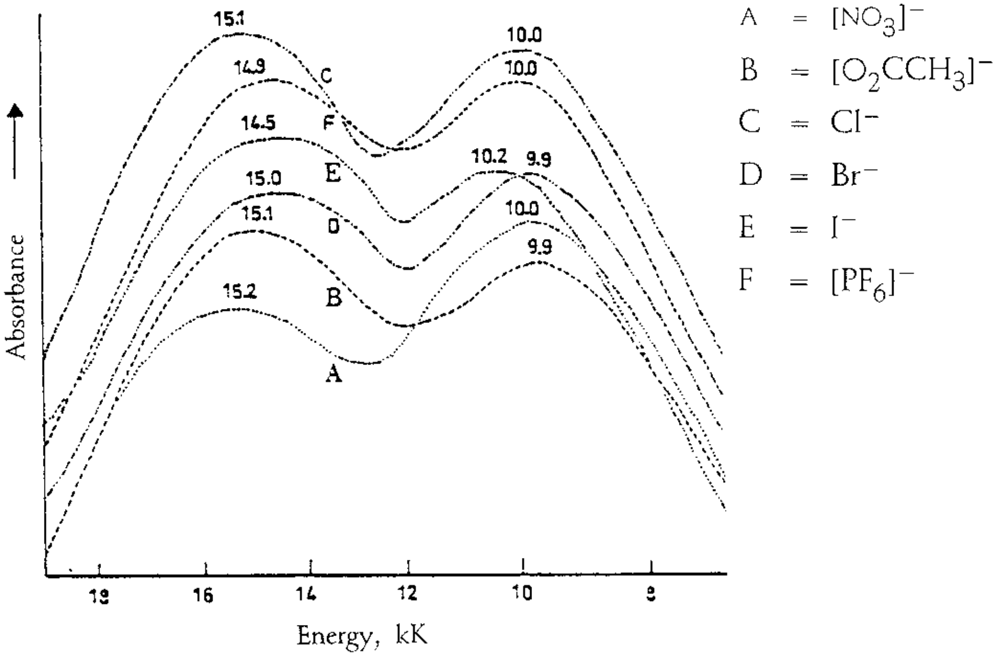

Fig. 3. The electronic reflectance spectra of [Cu(dpyam)$_2$ (O$_2$CCH$_3$)]Y complexes

O(1) plane is related to the mechanistic pathway of the Berry twist[18], correlating the trigonal and square pyramidal stereochemistries of the copper(II) ion[12, 19], and as previously reported for the [Cu(bipy)$_2$ X]Y system[2, 3]. However, the structure of [I] can be considered to be intermediate between a distorted square based pyramidal five coordinate geometry and an asymmetric cis-distorted octahedral geometry, giving a (4+1+1*) type coordination.

The individual pyridine rings in the dpyam ligands are essentially planar, with a r.m.s.d. of 0.022 A, Table 3. The dpyam ligands as a whole, however, are nonplanar and are slightly twisted about the amine nitrogen-carbon bond. The pyridine rings involve a dihedral angle of 27.90 and 27.41° for the ligands defined by N(1)/N(2) and N(4)/N(5) ligands, respectively. consequently, the maximum deviations from the mean planes for both dpyam ligands, Table 3, are not significantly different, 0.454 and 0.458 Å, respectively. The bite angles are 88.3(2)° and 87.5(2)° for the N(1)/N(2) and N(4)/N(5) dpyam ligand, respectively. The mean planes of the dpyam ligands are inclined at 112.16° to each other.

The acetate group is planar and reasonably coplanar with the Cu, N(2), N(5) plane (Table 3) 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 square pyramid at a distance$>$2.6 Å, but close enough to be involved in off-the-z-axis bonding the copper(II) ion[14]. The mean C-O distance of the acetate ligand, 1.26±0.02 Å, agrees with the reported value[20], 1.26 Å. The separate C-O distances of 1.236(8) and 1.278(8) Å are just significantly different, despite the asymmetry in the Cu-O(1) and Cu-O(2) distance involved, $\Delta O = 0.643(8)$ Å. The infrared spectrum of [I] shows strong bands at 1380 and 1325 cm^{-1} and medium band at 1030 cm^{-1} due to nitrate vibrations[21] and two broad and strong bands at 1420 and 1560 cm^{-1} due to acetate vibrations[21]. The electronic reflectance spectrum of [I] consists of two clearly resolved bands of almost equal intensity at ca. 10.0 and 15.2 kK, Fig. 3. The twin-peaked electronic spectrum is typical[2-4] of the cis-distorted CuN_4O_2 chromophore of the fluxional complexes and it can be described as having a d_z2 ground state. The bands may be assigned as the $d_{xy} \rightarrow d_z2$ and d_{xz}, d_{yz}, $d_x2_{-y}2 \rightarrow d_z2$ transitions for the low and high energy bands, respectively. Alternatively, a $d_x2_{-y}2$ ground state would be expected for a square-pyramidal distorted octahedral (4+1+1*) stereochemistry of [I] and the band may be assigned as the $d_z2 \rightarrow d_x2_{-y}2$ and (d_{xy}, d_{yz}, d_{zx}) $\rightarrow d_x2_{-y}2$ transitions for the low and high energy bands, respectively. These two peaks are also consistent with the two transitions predicted from the pseudo-Jahn-Teller potential-energy surface model[22] to be $^2A \rightarrow {}^2B$ and $^2A \rightarrow {}^2T_{2g}$ at ca. 10.0 and 15.2 kK, respectively. The room temperature polycrystalline e.s.r. spectrum of [I] isisotropic with $g_i = 2.100$, which gives no information about the electronic ground state of the copper(II) ion present and arise due to the misalignment of all three local molecular axes in the unit cells, $2\gamma \approx 90°$.

The microanalytical results (Table 1) of complexes [II]-[VI] agree well with [Cu (dpyam)$_2$ (O$_2$CCH$_3$)]Y stoichiometries, Y = Cl$^-$, Br$^-$, I$^-$ and [PF$_6$]$^-$ and the infrared spectra of these complexes are consistent with their being acetate complexes. The polycrystalline e.s.r. spectra are also isotropic with g_i = 2.144, 2.130 and 2.133 for the chloride, bromide

TABLE 4 Electronic reflectance spectra for a series of [Cu(dpyam)$_2$ (OXO)]Y complexes

Complex	**Reflectance spectrum**			
	E$_1$	**E^2**	**ΔE**	ΔO, Å
[Cu(dpyam)$_2$(ONO)][NO$_3$]	9.1	14.7	5.6	0.000
[Cu(dpyam)$_2$(ONO)][NO$_2$]	9.0	14.8	5.8	0.000
[Cu(dpyam)$_2$(ONO)]Br	9.4	14.9	5.6	0.443
[Cu(dpyam)$_2$(ONO)] I	9.8	14.8	5.0	0.226
[Cu(dpyam)$_2$(ONO)][BF$_4$	9.5	15.4	5.9	0.436
[Cu(dpyam)$_2$(ONO)][BF$_6$]	9.5	14.7	5.4	0.225
[Cu(dpyam)$_2$(O$_2$CC$_3$)][NO$_3$][I]	10.0	15.2	5.2	0.643
[Cu(dpyam)$_2$ (O$_2$CCH$_3$)][CH$_3$C$_2$]. 2H$_2$O[II]	9.9	15.1	5.2	–
[Cu(dpyam)$_2$ (O$_2$CCH$_3$)]Cl	10.0	15.1	5.1	–
[Cu(dpyam)$_2$ (O$_2$CCH$_3$)]Br	9.9	15.0	5.1	–
[Cu(dpyam)$_2$ (O$_2$CCH$_3$)] I	10.2	14.5	4.3	–
[Cu(dpyam)$_2$ (O$_2$CCH$_3$)][PF$_0$]	10.0	14.8	4.8	–

and iodide complexes, respectively, which give no information regarding the ground state electron configuration. The electronic reflectance spectra also show a typical cis-distorted octahedral stereo-chemistry for all acetate complexes which are very similar in appearance, Fig. 3. It can be seen from Table 4 that the structures of [Cu(dpyam)$_2$ (ONO)]Y complexes[23] have very similar reflectance spectra even though the structures vary from pseudo cis-distorted octahedral with ΔO = 0.000 Å to asymmetric cis-distorted octahedral with ΔO < 0.600 Å, a result of differing crystalline environments of these cation-distortion isomers. This is because the electronic reflectance spectra are related to the underlying static asymmetric chromophore and not to the time averaged structures found crystallographically. With reference to the similarity of those of the nitrite series, it is possible to suggest that [Cu(dpyam)$_2$ (O$_2$CCH$_3$)] Y complexes have varied cis-distorted octahedral geometries ranging from regular cis-distorted octahedral$^{(4+2)}$ with ΔO = 0.000 Å to the present structure of [I] which has the square-pyramidal distorted octahedral (4+1+1*) with ΔO = 0.643 Å. The small differences in energies of all acetate complexes may arise from the differences in the static CuN$_4$O$_2$ stereochemistry of these cation distortion isomers, owing to the different anion environment present. However, the structures of a series of [Cu(dpyam)$_2$ (O$_2$CCH$_3$)]Y complexes would need to be examined to verify this.

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บทคัดย่อ

ได้เตรียมและศึกษาโครงสร้างของสารประกอบเชิงซ้อน $[Cu(dpyam)_2(O_2CCH_3)]X$, $X = [NO_3]^-$, $[O_2CCH_3]^-$, Cl^-, Br^-, I^- และ $[PF_6]^-$ จากสมบัติทางสเปกโทรสโกปี ได้แก่ infrared spectrum, e.s.r. spectrum และ electronic reflectance spectrum และเปรียบเทียบสมบัติเหล่านี้กับสมบัติทางสเปกโทรสโกปี ของสารประกอบเชิงซ้อน $[Cu(dpyam)_2(O_2CCH_3)][NO_3$ ซึ่งได้ศึกษาโครงสร้างโดยเทคนิค x-ray crystallography