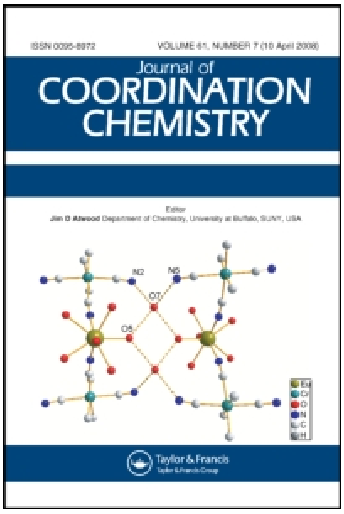

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Crystal structures and electronic properties of three fluxional [Cu(di-2-pyridylamine)$_2$(OXO)]Y complexes

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Crystal structures and electronic properties of three fluxional [Cu(di-2-pyridylamine)$_2$(OXO)]Y complexes

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The crystal structures of three bis(dpyam)copper(II) complexes, [Cu(dpyam)$_2$(ONO)](SO$_4$)$_{0.5}$(H$_2$O) (**I**), [Cu(dpyam)$_2$(O$_2$CCH$_3$)](ClO$_4$) (**II**) and [Cu(dpyam)$_2$(O$_2$CCH$_2$CH$_3$)](ClO$_4$) (**III**) (dpyam = di-2-pyridylamine) have been determined at room temperature by single-crystal X-ray methods. The complexes involve a CuN$_4$O$_2$ chromophore with a symmetric *cis*-distorted octahedral stereochemistry for **I**, and an asymmetric *cis*-distorted octahedral stereochemistry for **II** and **III**. In **I** the copper atom and the oxygen donor atoms of the symmetrically bonded nitrito group lie on a crystallographic C_2 axis. This is the first reported example in the literature of such a complex with this type of stereochemistry, involving the [Cu(dpyam)$_2$(OXO)][Y] series as a whole, where (OXO)$^-$ involves an oxoanion. In contrast, complexes **II** and **III** involve a distortion of the CuN$_4$O$_2$ chromophore towards a square pyramidal (4 + 1 + 1) stereochemistry. Here, the stereochemistries of **I**, **II** and **III** are compared with other closely related complexes. The highly asymmetric geometry of the CuN$_4$O$_2$ chromophores of **II** and **III** suggests that both complexes appear to be static in nature. Electronic spectra of the three complexes involve two bands of similar intensity corresponding to *cis*-distorted octahedral copper(II) stereochemistry.

Keywords: Copper(II); Di-2-pyridylamine; Plasticity effect; Cis-distortion; Fluxional behaviour

1. Introduction

The first crystal structure of a [Cu(chelate)$_2$(OXO)]Y complex (chelate = didentate chelating ligand, 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen) or di-2-pyridylamine (dpyam) and (OXO$^-$) = didentate oxoanion such as acetate, nitrite or formate) to be reported in the literature was that of [Cu(bipy)$_2$(ONO)](NO$_3$) [1]. The stereochemistry of the [Cu(bipy)$_2$(ONO)]$^+$ cation was described as *cis*-distorted octahedral.

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In addition, an analysis of the crystal structures and temperature dependence of the EPR spectra of a series of [Cu(phen)$_2$(O$_2$CCH$_3$]Y "cation-distortion type isomers" (Y = $BF_4^- \cdot 2H_2O$, $ClO_4^- \cdot 2H_2O$, ClO_4^-, and BF_4^-) suggests that the complexes are fluxional (temperature variable) and that the purported *cis*-distorted octahedral geometry is not a genuine static stereochemistry of Cu(II) complexes in general [2, 3]. Symmetric structures with average C_2 symmetries (not static C_2 symmetries) found in [Cu(chelate)$_2$(OXO)]Y complexes actually represent the superpositions of two interconverting asymmetric structures (a "dynamic pseudo Jahn–Teller effect") with equal relative thermal population of the two conformers [4, 5]. These complexes, involving the fluxional *cis*-octahedral CuN_4O_2 chromophore, are susceptible to distortions which appear to be vibronic in origin [6, 7].

In recent studies with the more flexible dpyam ligand, single crystal X-ray crystallography has shown that the complexes [Cu(dpyam)$_2$(ONO)]Y, with Y = NO_2^- [8] and NO_3^- [9] involve an asymmetric *cis*-distorted octahedral CuN_4OO' chromophore although there is crystallographic C_2 symmetry. In order to extend this investigation, the present paper reports the synthesis, crystal structures and spectroscopic properties of three further examples in the [Cu(dpyam)$_2$(OXO)]Y series, [Cu(dpyam)$_2$(ONO)](SO$_4$)$_{0.5}$(H$_2$O) (**I**), [Cu(dpyam)$_2$(O$_2$CCH$_3$)](ClO$_4$) (**II**) and [Cu(dpyam)$_2$(O$_2$CCH$_2$CH$_3$)](ClO$_4$) (**III**). All three are structurally compared with other closely related complexes in the series.

2. Experimental

All reagents were commercial grade materials and used without further purification. Elemental analyses (C, H, N) were performed by the microanalytical service of the Science and Technological Research Equipment Centre, Chulalongkorn University on a Perkin-Elmer PE2400 CHNS/O system. IR spectra were recorded on a Spectrum One Perkin-Elmer FT-IR spectrophotometer (KBr pellets) in the 4000–450 cm^{-1} region. Solid-state (diffuse reflectance) electronic spectra were recorded for polycrystalline samples on a Perkin-Elmer Lambda 2S spectrophotometer over the range 8000–18,000 cm^{-1}. X-band EPR spectra were recorded using polycrystalline samples at room and liquid nitrogen temperatures with a Jeol EPR JES-RE2X spectrometer (X-band) at the Scientific and Technological Research Equipment Centre, Chulalongkorn University.

2.1. *Preparation of [Cu(dpyam)$_2$(ONO)](SO$_4$)$_{0.5}$(H$_2$O) (I)*

An aqueous solution (20 cm^3) of $CuSO_4 \cdot 5H_2O$ (0.125 g, 0.5 mmol) was added to a solution of dpyam (0.171 g, 1.0 mmol) in methanol (5 cm^3), followed by an aqueous solution (20 cm^3) of NaNO$_2$ (0.069 g, 1.0 mmol). After one week, green crystals of **I** were formed. The crystals were filtered off and dried in air. The yield was approximately 60%. Anal. Calcd for $C_{20}H_{20}N_7CuO_5S_{0.5}$ (%): C, 46.37; H, 3.89; N, 18.93 Found: C, 46.28; H, 3.80; N, 18.84.

2.2. *Preparation of [Cu(dpyam)$_2$(O$_2$CCH$_3$)](ClO$_4$) (II)*

Complex **II** was prepared by adding an aqueous solution (25 cm^3) of Cu(O$_2$CCH$_3$)$_2$ (0.181 g, 1.0 mmol) to a solution of dpyam (0.171 g, 1.0 mmol) in methanol (5 cm^3) after which solid KClO$_4$ (0.069 g, 0.5 mmol) was added. The green solution was slowly evaporated at room temperature. Green crystals of **II** were deposited after several days. The yield was approximately 65%. Anal. Calcd for $C_{22}H_{21}N_6CuO_6Cl$ (%): C, 46.82; H, 3.75; N, 14.89. Found: C, 46.64; H, 3.59; N, 14.77.

2.3. *Preparation of [Cu(dpyam)$_2$(O$_2$CCH$_2$CH$_3$)](ClO$_4$) (III)*

A solution of dpyam (0.272 g, 2.0 mmol) in methanol (15 cm^3) was slowly added to an aqueous solution (20 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.0 mmol) after which solid $NaO_2CCH_2CH_3$ (0.163 g, 1.5 mmol) was added. Green needle-like crystals of **III** were deposited after several days. The yield was approximately 68%. Anal. Calcd for $C_{23}H_{23}N_6CuO_6Cl$ (%): C, 47.76; H, 4.01; N, 14.53. Found: C, 47.85; H, 3.95; N, 14.48.

2.4. *Crystallography*

Intensity data for complexes **I**, **II** and **III** were collected at 293 K on a 1 K Bruker SMART CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at a detector distance of 4.5 cm and swing angle of −35°. A hemisphere of reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0, 88, 180°) and each exposure of 15, 15 and 30 s for **I**, **II** and **III**, respectively, covered 0.3° in ω. Data reduction and cell refinements were performed using SAINT [10]. An empirical absorption correction using the SADABS [11] program was applied, which resulted in transmission coefficients ranging from 0.800 to 1.000 for **I**, 0.873 to 1.000 for **II** and 0.806 to 1.000 for **III**. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 [12] software package. Complex **I** is cubic, space group $Pn\bar{3}$, with 12 [Cu(dpyam)$_2$(ONO)]$^+$ cations in the unit cell; Cu lies on a special position. Four sulfates, (S1) also lie in special positions with full occupancy. There are two more sulfates in the unit cell. S2 occupies a special position with point symmetry 2 and a population parameter of 0.0211, and S3 occupies a special position with point symmetry 3 and a population parameter of 0.06219. The oxygen atoms of the S2 and S3 sulphates could not be located. All hydrogen atoms in **II** and **III** were located by difference synthesis and refined isotropically, except those of the acetate and propionate ligands, which were fixed and allowed to ride on attached atoms. Hydrogen atoms in **I** were not located. All non-H atoms were refined anisotropically. Perchlorate groups in **II** and **III** are disordered with site occupancies of 0.50 for both. Two terminal C atoms of the propionato group in **III** are disordered with site occupancies of 0.48 and 0.52. Crystal data and refinement details for **I**, **II** and **III** are listed in table 1. Selected bond lengths and angles are given in tables 2–4. Figures 1, 2 and 3 illustrate the structures of **I**, **II** and **III**, respectively, and the atom numbering schemes used.

Table 1. Crystal data and refinement details for the complexes.

	I	II	III
M	518.00	564.44	578.46
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Cubic	Monoclinic	Monoclinic
Space group	$Pn\bar{3}$	$P2_1/c$	$P2_1/c$
a (Å)	19.5929(2)	13.9072(3)	13.5569(6)
b (Å)	19.5929(2)	7.9208(2)	8.5601(3)
c (Å)	19.5929(2)	22.2935(3)	22.1679(9)
β (°)		92.4710(10)	93.6240(10)
V (Å^3)	7521.01(13)	2453.48(9)	2567.41(18)
Z	12	4	4
D_{Calcd} (g cm^{-3})	1.372	1.528	1.497
Absorption coefficient (mm^{-1})	0.955	1.049	1.005
F(000)	3192	1156	1188
Crystal size (mm^3)	0.20 × 0.30 × 0.25	0.28 × 0.35 × 0.13	0.08 × 0.20 × 0.25
θ range (°)	1.80–30.46	1.47–30.50	1.51–30.48
No. reflections collected	51880	17696	18102
No. unique reflections	3774	7114 ($R_{\mathrm{int}} = 0.0343$)	7366 ($R_{\mathrm{int}} = 0.0420$)
No. observed reflections	2362	4672	4521
Data/restraints/parameter	3774/0/173	7114/0/418	7366/0/444
Goodness-of-fit	1.059	1.026	1.034
Final R indices* [$I > 2\sigma(I)$]	$R_1 = 0.0769$, $wR_2 = 0.1978$	$R_1 = 0.0515$, $wR_2 = 0.1120$	$R_1 = 0.0533$, $wR_2 = 0.0917$
R indices (all data)	$R_1 = 0.1209$, $wR_2 = 0.2300$	$R_1 = 0.0909$, $wR_2 = 0.1300$	$R_1 = 0.1065$, $wR_2 = 0.1095$
Largest difference peak and hole (e Å^{-3})	0.387, −0.485	0.504, −0.486	0.503, −0.295

* $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o\|$, $R_w = [\Sigma w\{|F_o| - |F_c|\}^2/w|F_o|^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[Cu(dpyam)_2(ONO)](SO_4)_{0.5}(H_2O)$ (**I**).

Cu–N(1)	1.999(4)	Cu–N(2)	2.087(4)
Cu–O(2)	2.270(4)	N(7)–O(1)	1.234(6)
N(1)–Cu–N(4)	173.5(2)	N(1)–Cu–N(2)	88.2(2)
N(4)–Cu–N(2)	96.0(3)	N(2)–Cu–N(5)	99.0(2)
N(1)–Cu–O(2)	87.3(2)	N(4)–Cu–O(1)	86.9(2)
N(2)–Cu–O(1)	157.1(1)	N(5)–Cu–O(1)	103.8(2)
O(1)–Cu–O(2)	53.5(3)	O(1)–N(1)–O(2)	111.7(1)
Cu–O(2)–N(7)	97.4(4)		

3. Results and discussion

3.1. *Crystal structures*

The crystal structures of **I**, **II** and **III** consist of discrete $[Cu(dpyam)_2(ONO)]^+$, $[Cu(dpyam)_2(O_2CCH_3)]^+$ and $[Cu(dpyam)_2(O_2CCH_2CH_3)]^+$ cations and SO_4^{2-}(**I**), or ClO_4^- (in the case of **II** and **III**) anions, respectively. Complex **I** also involves a lattice molecule of water. All cations possess a *cis*-distorted octahedral CuN_4O_2 chromophore with **I** involving a symmetrically coordinated nitrito group. In contrast, **II** and **III** involve an asymmetrically coordinated acetato or propionato ligand. The copper atom

Table 3. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[\mathrm{Cu(dpyam)_2(O_2CCH_3)}](\mathrm{ClO_4})$ (**II**).

Cu–N(1)	2.002(2)	Cu–N(2)	2.032(2)
Cu–N(4)	2.012(2)	Cu–N(5)	2.162(2)
Cu–O(1)	2.013(2)	Cu–O(2)	2.718(2)
C(21)–O(1)	1.266(3)	C(21)–O(2)	1.239(4)
N(1)–Cu–N(4)	173.6(2)	N(1)–Cu–N(2)	88.3(2)
N(4)–Cu–N(2)	94.0(2)	N(1)–Cu–N(5)	98.5(2)
N(4)–Cu–N(5)	87.2(2)	N(2)–Cu–N(5)	96.4(2)
N(1)–Cu–O(1)	88.2(2)	N(4)–Cu–O(1)	87.6(2)
N(2)–Cu–O(1)	160.6(2)	N(5)–Cu–O(1)	103.0(2)
O(2)–Cu–N(1)	79.5(2)	O(2)–Cu–N(2)	107.7(2)
O(2)–Cu–N(4)	94.1(2)	O(2)–Cu–N(5)	155.6(2)
O(2)–Cu–O(1)	52.9(2)	O(1)–C(21)–O(2)	122.6(2)
Cu–O(1)–C(21)	108.4(2)	Cu–O(2)–C(21)	75.8(2)

Table 4. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[\mathrm{Cu(dpyam)_2(O_2CCH_2CH_3)}](\mathrm{ClO_4})$ (**III**).

Cu–N(1)	1.986(2)	Cu–N(2)	2.028(2)
Cu–N(4)	2.007(2)	Cu–N(5)	2.156(2)
Cu–O(1)	2.025(2)	Cu–O(2)	2.669(2)
C(21)–O(1)	1.278(3)	C(21)–O(2)	1.241(4)
N(1)–Cu–N(4)	172.1(2)	N(1)–Cu–N(2)	88.8(2)
N(4)–Cu–N(2)	96.1(1)	N(1)–Cu–N(5)	98.4(2)
N(4)–Cu–N(5)	86.9(2)	N(2)–Cu–N(5)	101.3(2)
N(1)–Cu–O(1)	88.1(3)	N(4)–Cu–O(1)	84.8(2)
N(2)–Cu–O(1)	153.3(2)	N(5)–Cu–O(1)	105.4(2)
O(2)–Cu–N(1)	82.3(2)	O(2)–Cu–N(2)	99.6(2)
O(2)–Cu–N(4)	90.7(1)	O(2)–Cu–N(5)	159.1(2)
O(2)–Cu–O(1)	53.7(2)	O(1)–C(21)–O(2)	123.1(3)
Cu–O(1)–C(21)	106.7(2)	Cu–O(2)–C(21)	76.3(2)

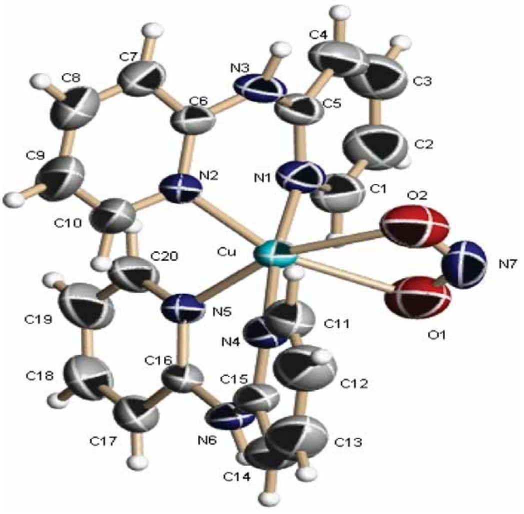


Figure 1. The molecular structure of $[\mathrm{Cu(dpyam)_2(ONO)}]^+$ (**I**).

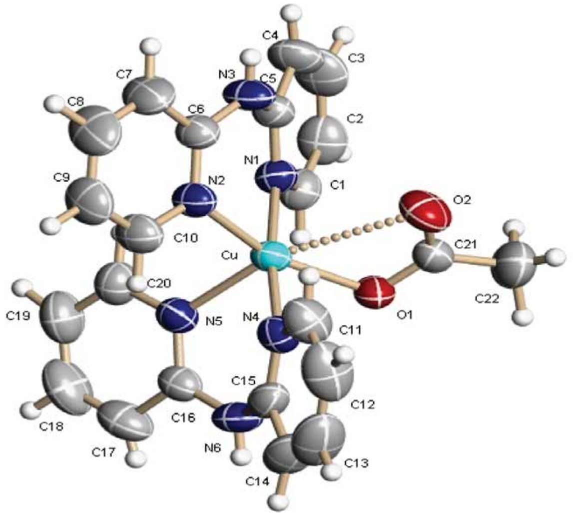


Figure 2. The molecular structure of $[Cu(dpyam)_2(O_2CCH_3)]^+$ (**II**).

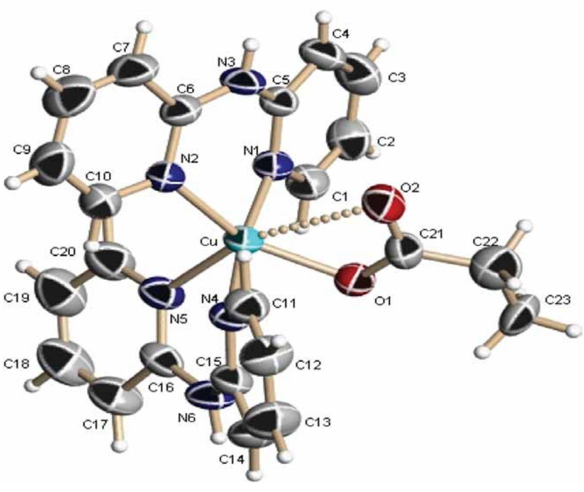


Figure 3. The molecular structure of $[Cu(dpyam)_2(O_2CCH_2CH_3)]^+$ (**III**).

in all three complexes is surrounded by four nitrogen atoms from the two dpyam ligands and two oxygen atoms from the coordinated oxyanion. A terminal nitrogen of each dpyam ligand occupies axial positions while remaining nitrogen atoms of dpyam and oxygen atoms from the $(OXO)^-$ anion occupy equatorial positions.

Compound **I** is the first example in the $[Cu(chelate)_2(OXO)]Y$ series (chelate = 2,2′-bipyridyl, 1,10-phenanthroline, di-2-pyridylamine; $(OXO)^-$ = nitrite, formate, acetate, propionate), reported crystallographically to involve a cubic lattice with a symmetrically *cis*-distorted octahedral CuN_4O_2 chromophore and crystallographic C_2 symmetry. In recent work on the dpyam family, we found that the monoclinic complexes [Cu(dpyam)$_2$(ONO)]Y, where Y = NO_2^- [8] and NO_3^- [9], involve marked disorder of the asymmetrically bonded nitrito group although there is crystallographic C_2 symmetry. This is distinct from the previously reported, pseudo regular, *cis*-distorted, octahedral CuN_4O_2 chromophores of the bipy and phen complexes [4, 5, 13]. Hence, compound **I** is also the first example in the dpyam family found to exhibit a pseudo symmetrically, *cis*-distorted octahedral CuN_4N_2 chromophore. In the [Cu(dpyam)$_2$(ONO)]$^+$ cation, the two Cu–O bonds (2.270(4) Å) are significantly longer than the four Cu–N distances (av. 2.043(4) Å) to give a typical (4 + 2) coordination sphere.

In contrast, the stereochemistry of the CuN_4O_2 chromophores in **II** and **III** is basically five-coordinate with a second oxygen of the $(OXO)^-$ anion occupying a sixth position at a distance greater than 2.4 Å [2.718(2) Å for **II** and 2.666(3) Å for **III**], to give a (4 + 1 + 1*)-type coordination sphere. The large O(1)–Cu–N(2) angles of 160.7(2)° and 153.3(3)° for **II** and **III**, respectively, lie *trans* to the elongated Cu–N(5) direction. This could be taken as the basal angle of a square-based pyramid with elongation in the Cu–N(5) direction [14]. The Cu atom is displaced from the basal plane by 0.21 Å in **II** and 0.27 Å in **III**, in the direction of the N(5) atom. The basal planes of both complexes also show slight tetrahedral distortion with dihedral angles between the CuN_2 and CuO_2 planes of 19.8(2) and 26.9(2)° for **II** and **III**, respectively. As the τ values (τ = /[{N(1)–Cu–N(4)}–{N(2)–Cu–O(1)}]/60) [15] are 0.21 for **II** and 0.31 for **III**, complexes **II** and **III** are distorted toward a regular square pyramidal CuN_3ON' chromophore, which has $\tau = 0$. Hence, both structures are best described as a square pyramidal, *cis*-distorted, octahedral (4 + 1 + 1*), but differ significantly in their angular distortions. In addition, $\Delta O_{1,2}$ is equal to 0.705(2) Å in **II**, which is larger than the corresponding value of 0.644(2) Å in **III**. For all three complexes, axial N–Cu–N angles are almost linear, with values of 173.5(2), 173.6(2) and 172.1(2)°, for **I**, **II** and **III**, respectively.

The pyridine rings form dihedral angles of 20.6° in **I**, 27.0 and 30.7° in **II** and 22.5 and 29.4° in **III** for the ligands defined by N(1)/N(2) and N(4)/N(5), respectively. The dpyam bite angles are 88.2(2)° for **I**, 88.3(2) and 87.2(2)° for **II** and 88.8(2) and 86.9(2)° for **III**. The coordinated nitrito group in **I** involves symmetric N–O distances with N(7)–O(1) equal to1.234(6) Å; the O(1)–N(1)–O(2) angle is to 111.7(1)° and the bite angle is 53.5(3)°. These are in good agreement with values previously reported for the symmetrically coordinated nitrito group in corresponding [Cu(chelate)$_2$(ONO)]Y complexes (N–O = 1.236(7) Å, O–N–O = 112.6°, bite angle = 55.4°) [16]. The coordinated acetato and propionato groups of **II** and **III** involve asymmetric C–O distances with C(21)–O(1) and C(21)–O(2) values of 1.266(3) and 1.239(4) Å for **II** and 1.278(3) and 1.241(4) Å for **III.** This is not significantly different from previously reported values for the coordinated carboxylato group (C–O = 1.236(3)–1.286(3) Å). The O–C–O angles of 122.6(2)° in **II** and 123.1(3)° in **III** lie in the previously reported range (122.2(3)–126.2(1)°) [17–19]. All three crystal structures are stabilized by moderate to weak hydrogen bonding networks [N–H $\cdots$ O(NO_2) in **I**; N–H $\cdots$ O(H_3CCO_2) and N–H $\cdots$ O(ClO_4) in **II** and N–H $\cdots$ O($CH_3CH_2CO_2$) and N–H $\cdots$ O(ClO_4) in **III**].

3.2. *Comparison of crystal structures*

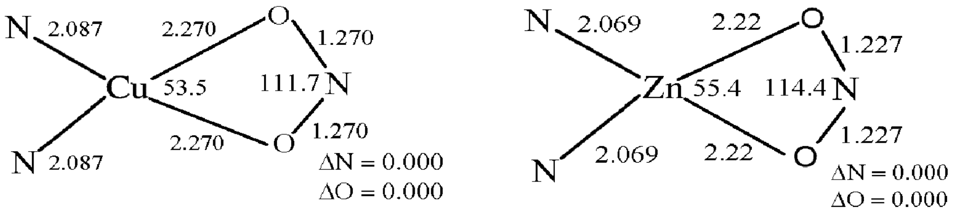
The structures of **I**, **II** and **III** are clearly different from the equally elongated rhombic-octahedral (4 + 2) chromophore in [Cu(bipy)$_2$(S_3O_6)] [20] and [Cu(bipy)$_2$(S_4O_6)] [21], and the unequally elongated rhombic-octahedral (4 + 1 + 1*) chromophore of $[Cu(bipy)_2(O_2ClO_2)](ClO_4)$ [22, 23]. The structure of **I** is similar to the pseudo symmetric *cis*-distorted octahedral geometries of $[Cu(phen)_2(O_2CMe)]Y$ ($Y = ClO_4$, BF_4) [4, 5] and $[Cu(phen)_2(O_2CH)]Y$ ($Y = BF_4$, ClO_4) [6, 13] with two Cu–O distances of 2.26–2.36 Å, figure 4(e) and (f). The structures of **II** and **III** are similar to those previously reported for $[Cu(dpyam)_2(OXO)]^+$ cations, $(OXO)^- =$ formate [24], acetate [19, 24], propionate [25, 26] and nitrite [9, 16, 25], all of which involve (4 + 1 + 1*) coordination (square pyramidal/*cis*-distorted octahedral CuN_4OO' chromophore with Cu–O(2) > 2.400(1) and $\Delta O > 0.400(1)$ Å). Furthermore, the crystal structures of $[Cu(dpyam)_2(NO_2)](NO_2)$ [8], with $\Delta O = 0.477(1)$ Å and the $[Cu(dpyam)_2(ONO)](NO_3)$ [9], with $\Delta O = 0.420(1)$ Å, shown in figures 4(c) and (d) and table 5, show some similarity to that of **I** involving a crystallographic C_2 axis but with apparent disorder of the asymmetrically bonded nitrito group.

In conclusion, the CuN_4O_2 chromophore in **I** shows greatest similarity to the ordered $[Zn(dpyam)_2(ONO)]^+$ cation [27], represented in figure 4(b) and table 5, which has static C_2 symmetry, and $[Cu(phen)_2(O_2CH)](BF_4)$ and $[Cu(phen)_2(O_2CCH_3)](ClO_4) \cdot 2H_2O$, shown in figures 4(e) and (f), table 5, which have average C_2 symmetry. The coordination geometries of selected $[M(chelate)_2(OXO)]^+$ cations, where chelate = phen or dpyam, are shown in figure 4 for comparison.

3.3. *Spectroscopic properties*

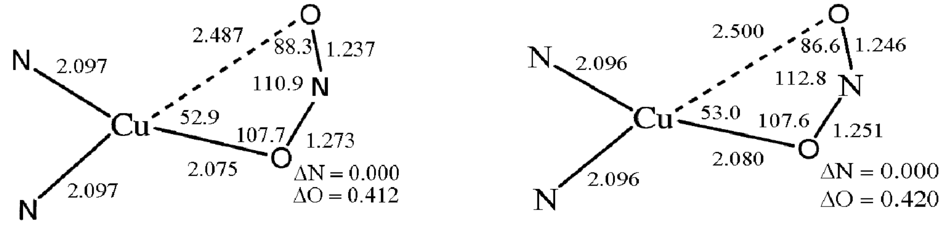
3.3.1. EPR spectra. Polycrystalline EPR spectra of **I** are isotropic at both room and liquid nitrogen temperatures (77 K) with $g_i = 2.154$ and 2.143, respectively, which gives no information regarding the electronic ground state and no information to suggest any fluxional behaviour [28]. In contrast, for **II**, the room temperature spectrum is rhombic but only two g values are seen, $g_1 = 2.047$ and $g_2 = 2.162$; the third is not resolved due to exchange narrowing. Upon lowering the temperature to that of liquid nitrogen the spectrum is more resolved with $g_1 = 2.039$, $g_2 = 2.112$ and $g_3 = 2.196$. The g values obtained in the EPR spectrum of **III** are axial at both room temperature ($g_\parallel = 2.274$, $g_\perp = 2.066$) and liquid nitrogen temperature ($g_\parallel \approx 2.444$, $g_\perp = 2.049$), consistent with the $d_{x^2-y^2}$ ground state of a square-pyramidal/*cis*-distorted octahedral CuN_4O_2 chromophore [6, 17, 29]. The static nature of the crystal structures of **II** and **III** is supported by the EPR spectra. However, in the case of **I** EPR spectra at room temperature and 77 K are isotropic with similar g values, although in different orientations. Hence, single-crystal X-ray diffraction studies need to be carried out at low temperature for **I** to probe changes in bond lengths of the CuN_4O_2 chromophore. As the symmetric structure of **I** actually involves interconverting asymmetric structures giving rise to an average, not static, C_2 structure, the sensitivity of the coordination mode to temperature suggests a small difference in energy between the two conformers (extreme geometries) [6].

3.3.2. Electronic spectra. Electronic spectra of the complexes consist of two clearly resolved peaks with almost equal intensity at approximately 14,700 and 9,800 cm^{-1} for **I**, 14,510 and 10,110 cm^{-1} for II and 14,680 and 10,020 cm^{-1} for III. These values are similar to those previously reported for other $[Cu(chelate)_2(OXO)]Y$ complexes involving the *cis*-distorted octahedral CuN_4O_2 chromophore. The slight difference in



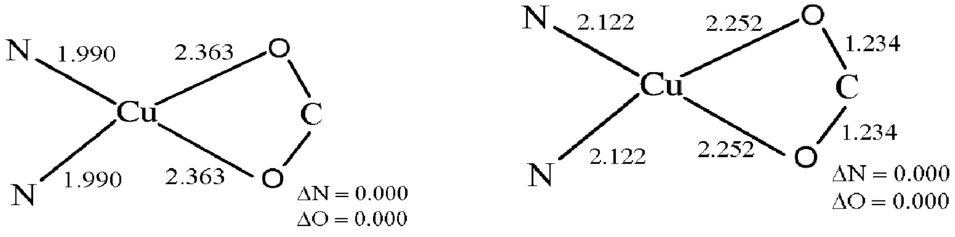
(a) [Cu(dpyam)$_2$(ONO)](SO$_4$)0.5(H$_2$O) (**I**)

(b) [Zn(dpyam)$_2$(ONO)](NO$_2$) (**1**)



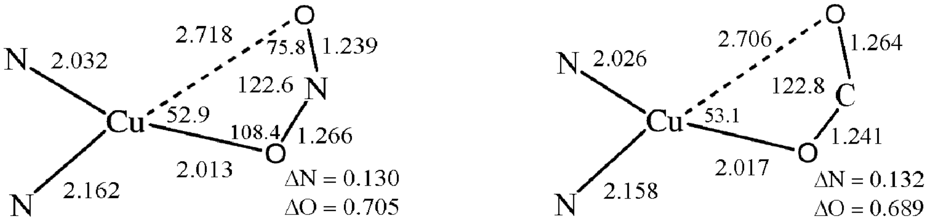
(c) [Cu(dpyam)$_2$(ONO)](NO$_2$) (**2**)

(d) [Cu(dpyam)$_2$(ONO)](NO$_3$) (**3**)



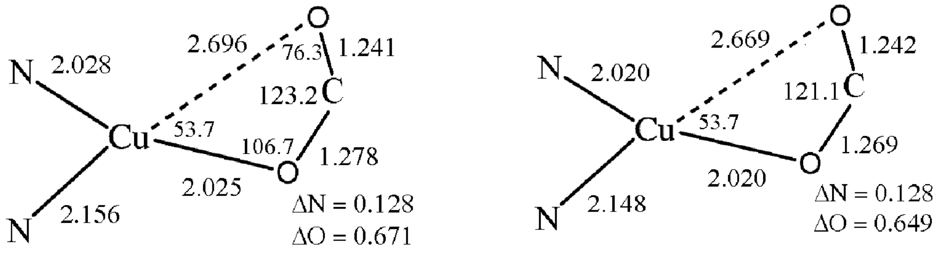
(e) [Cu(phen)$_2$(O$_2$CH)](BF$_4$) (**4**)

(f) [Cu(phen)$_2$(O$_2$CCH$_3$)](ClO$_4$)·2H$_2$O (**5**)



(g) [Cu(dpyam)$_2$(O$_2$CCH$_3$)](ClO$_4$) (**II**)

(h) [Cu(dpyam)$_2$(O$_2$CCH$_3$)](BF$_4$) (**6**)



(i) [Cu(dpyam)$_2$(O$_2$CCH$_2$CH$_3$)](ClO$_4$) (**III**)

(j) [Cu(dpyam)$_2$(O$_2$CCH$_2$CH$_3$)](NO$_3$) (**7**)

Figure 4. Comparison of [M(chelate)$_2$(OXO)]$^+$ coordination geometries.

Table 5. Molecular dimension of the complexes [M(chelate)$_2$(OXO)]Y.

M	Cu	Zn	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
chelate	dpyam	dpyam	dpyam	dpyam	phen	phen	dpyam	dpyam	dpyam	dpyam
OXO	ONO	NO_2	NO_2	NO_2	O_2CH	O_2CCH_3	O_2CCH_3	O_2CCH_3	$O_2CCH_2CH_3$	$O_2CCH_2CH_3$
Y	$(SO_4)_{0.5}(H_2O)$	NO_2	NO_2	NO_3	BF_4	$ClO_4 \cdot 2H_2O$	ClO_4	BF_4	ClO_4	NO_3
Reference	This work	[27]	[8]	[9]	[6]	[5]	This work	[19]	This work	[20]
M–N(1)	1.999(4)	2.163	2.132(12)	2.009(2)	2.111(6)	1.999(2)	2.002(2)	2.000(2)	1.987(2)	2.005(2)
M–N(2)	2.087(4)	2.069	2.097(2)	2.096(2)	1.990(6)	2.122(2)	2.032(2)	2.026(2)	2.028(2)	2.020(2)
M–N(4)	1.999(4)	2.163	2.132(12)	2.009(2)	2.111(6)	1.999(2)	2.012(2)	2.002(2)	2.007(2)	1.989(2)
M–N(5)	2.087(4)	2.069	2.097(2)	2.096(2)	1.990(6)	2.122(2)	2.162(2)	2.158(2)	2.156(2)	2.148(2)
M–O(1)	2.270(4)	2.22	2.075(4)	2.080(8)	2.363(8)	2.252(2)	2.013(2)	2.017(2)	2.025(2)	2.020(2)
M–O(2)	2.270(4)	2.22	2.487(2)	2.500(2)	2.363(8)	2.252(2)	2.718(2)	2.706(2)	2.696(2)	2.669(3)
X–O(1)	1.234(6)	1.227	1.273(6)	1.246(3)		1.234(3)	1.266(3)	1.264(3)	1.278(3)	1.269(4)
X–O(2)	1.234(6)	1.227	1.237(8)	1.251(3)		1.234(3)	1.239(4)	1.241(4)	1.241(4)	1.242(4)
O(1)–X–O(2)	111.7(1)	114.4	110.9(8)	112.8(2)			122.6(2)	122.8(3)	123.1(3)	121.1(3)
O(1)–M–O(2)	53.5(3)	55.4	52.9(2)	53.0(2)			52.9(2)	53.1(3)	53.7(2)	53.7(2)
$\Delta N_{1,4}$	0.0	0.0	0.0	0.0	0.0	0.0	0.010	0.002	0.020	0.016
$\Delta N_{2,5}$	0.0	0.0	0.0	0.0	0.0	0.0	0.13	0.132	0.128	0.128
ΔO	0.0	0.0	0.412	0.420	0.0	0.0	0.705	0.689	0.671	0.649

electronic spectra of this series is due to the nearly comparable distortion of the extreme stereochemistries of the underlying static $(4+1+1^*)$ CuN_4O_2 chromophores. The one electron energy sequence of the Cu(II) ion in the asymmetrically distorted CuN_4O_2 geometries is approximately the same as that predicted for the square-based pyramidal geometry, namely $d_{x^2-y^2} > d_z^2 > d_{xy} > d_{xz} \approx d_{yz}$. The higher energy bands may be tentatively assigned to d_{xy}, d_{yz}, $d_{zx} \rightarrow d_{x^2-y^2}$, whereas the lower energy bands can be assigned to $d_z^2 \rightarrow d_{x^2-y^2}$ transitions.

3.3.3. Infrared spectra. IR spectra of **I** show $\nu_{as}(NO_2)$, $\nu_s(NO_2)$ and $\delta(NO_2)$ bands at 1365, 1150 and $840\,cm^{-1}$, respectively. **II** and **III** display characteristic bands of the asymmetric acetato group and propionato group: $\nu_{as}(COO)$ at 1560s, $\nu_s(COO)$ at 1420m, δ(O–C–O) at 675w for **II** and $\nu_{as}(COO)$ at 1585s, $\nu_s(COO)$ at 1420m, δ(O–C–O) at 671w for **III**. The SO_4^{2-} group in **I** appears at 1130 and $1019\,cm^{-1}$. **II** and **III** also show a strong band corresponding to the ClO_4 vibration near $1100\,cm^{-1}$ with three sharp peaks at 1110s, 1065s and $625s\,cm^{-1}$ for **II** and 1120s, 1090s and $625s\,cm^{-1}$ for **III**.

Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 289156, 234506 and 234507 for **I**, **II** and **III**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336033, E-mail: deposit@ccdc.cam.ac.uk].

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