The Crystal Structures of [Cu(phen)₂(O₂CMe)]X (phen = 1,10-phenanthroline) Complexes: Pseudo *cis*-Distorted Octahedral Structures and Fluxional Copper(II) Stereochemistries

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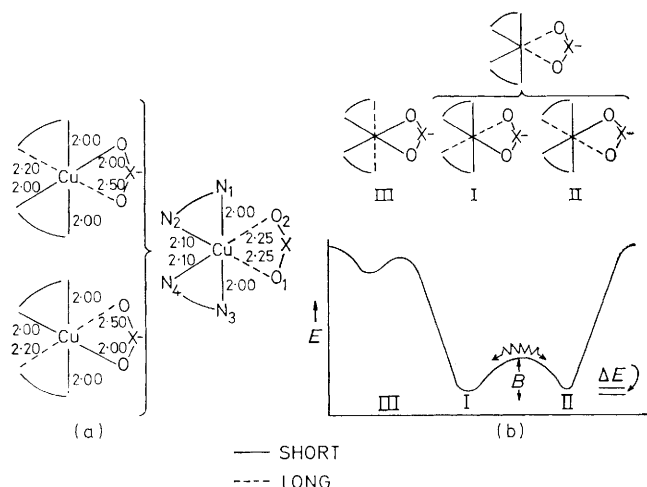[b] *The Chemistry Department, The University of Hawaii at Manoa, Honolulu, Hawaii, U.S.A.*

The X-ray crystal structures of four cation-distortion isomers of the [Cu(phen)₂(O₂CMe)]⁺ (phen = 1,10-phenanthroline) cation are reported and shown to contain the *cis*-octahedral CuN₄O₂ chromophore; X-ray and e.s.r. data are consistent with a fluxional CuN₄O₂ structure, which is best described as a psuedo *cis*-distorted octahedral copper(II) stereochemistry in three of the complexes, and consequently these structural variations can be related to the dynamic pseudo-Jahn–Teller effect.

The *cis*-distorted octahedral structure[1] of [Cu(bipy)₂(ONO)]- [NO₃] (1), (bipy = 2,2'-bipyridyl) is unique in the stereochemistry of the copper(II) ion, as it involves a *cis*- rather than a *trans*-distortion of the CuN₄O₂ chromophore structure. The crystal structures[2] of the corresponding [Cu(bipy)₂- (O₂CMe)][BF₄] and [ClO₄] complexes still involve a *cis*-distorted octahedral CuN₄O₂ chromophore, but with very asymmetrically co-ordinated acetate groups, $\Delta O = \{[Cu-O(2)] - [Cu-O(1)]\} = 0.62$—$0.64$ Å, whose structure is best described as a square-pyramidal distorted octahedron (4 + 1 + 1*). Attempts to prepare the corresponding [Cu(phen)₂(O₂CMe)][BF₄] and [ClO₄] complexes (phen = 1,10-phenanthroline) resulted in the formation in aqueous alcohol solution of the dihydrates[3] (2) and (3) (see Table 1) and in

Table 1. Molecular structures of the *cis*-distorted octahedral [Cu(chelate)₂(OXO)]X system.

	[Cu(bipy)₂(ONO)]- [NO₃] (1)	[Cu(phen)₂(O₂CMe)]- [BF₄], 2H₂O (2)	[Cu(phen)₂[O₂CMe)]- [ClO₄], 2H₂O (3)	[Cu(phen)₂(O₂CMe)]- [ClO₄] (4)	[Cu(phen)₂- (O₂CMe)][BF₄] (5)
Space group	$P2_1/n$	$P2/c$	$P2/c$	$P2_1/c$	$P\bar{1}$
Cu–N(1)	1.980(11)	2.000(4)	1.994(5)	1.994(4)	2.009(5)
Cu–N(2)	2.065(10)	2.123(4)	2.124(4)	2.098(4)	2.061(5)
Cu–N(3)	2.006(10)	2.000(4)	1.994(5)	2.006(4)	2.023(5)
Cu–N(4)	2.100(10)	2.123(4)	2.124(4)	2.130(4)	2.215(4)
Cu–O(1)	2.238(10)	2.261(5)	2.257(5)	2.220(4)	1.999(4)
Cu–O(2)	2.329(10)	2.261(5)	2.257(5)	2.421(5)	2.670(5)
ΔN	0.035(20)	0.0	0.0	0.032(8)	0.154(9)
ΔO	0.091(20)	0.0	0.0	0.201(10)	0.671(10)

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Figure 1. [Cu(phen)$_2$(O$_2$CMe)]X; (a) static disorder and (b) fluxional disorder model [for which a potential energy surface (E) is also given].

Figure 2. The single-crystal e.s.r. spectra of (a) 10% copper-doped [Zn(phen)$_2$(O$_2$CMe)][BF$_4$], 2H$_2$O; (b) [Cu(phen)$_2$(O$_2$CMe)][ClO$_4$] 2H$_2$O; both measured in the Cu, N(2), N(4), O(1), O(2) plane, at room temperature (——), and at liquid nitrogen temperature (– – –) (i = isotropic) (units of A 10^{-4} cm^{-1}).

acetonitrile of the anhydrous complexes[3,4] (4) and (5). All four complexes were prepared† and characterised by C, H, N, and Cu analysis and their crystal structures determined.‡

The four complexes represent a series of cation distortion isomers[5] of the cis-octahedral CuN$_4$O$_2$ chromophore, Figure 1, but while (2) and (3) involve a regular cis-distorted octahedral structure, vide infra, (4) and (5) involve an asymmetrically bonded acetate with ΔO-values of 0.20 and 0.67 Å, respectively, such that (5) should best be described as a square-pyramidal distorted octahedral (4 + 1 + 1*) structure (Table 1). In the cis-distorted octahedral structures of (2) and (4) the acetate oxygen atoms have large anisotropic thermal motion,[4] with the major component of the thermal ellipsoids nearly parallel to the Cu–O bonds (ca. 13°), suggesting marked disorder of the acetate groups in the plane of the Cu, O(1), O(2), and acetate C atoms. This large thermal motion is consistent with either static or fluxional disorder of the whole CuN$_4$O$_2$ chromophore, Figure 1(a) and (b), respectively.[6] Attempts to refine the complete [Cu(phen)$_2$(O$_2$CMe)]$^+$ cation of (3), with static disorder about the twofold axis, were unsuccessful.

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† Complexes (2) and (3) were prepared from a twofold excess of 1,10-phenanthroline and the corresponding hexa-aquo copper(II) salt in 1:1 water–acetone with, in addition, a tenfold excess of Na$_2$O$_2$CMe.3H$_2$O. The anhydrous complexes (4) and (5) were prepared from the corresponding hydrated complex by recrystallisation from 5:1 acetonitrile–2,2-dimethoxypropane kept at 0 °C for a few days.

‡ Crystals of [Cu(phen)$_2$(O$_2$CMe)][BF$_4$], 2H$_2$O are monoclinic, space group P2/c, a = 9.639(2), b = 8.237(2), c = 17.575(4) Å, β = 108.66(2)°, U = 1322.1 Å^3, Z = 2, μ(Mo-$K\alpha$) = 8.62 cm^{-1}. 1834 unique reflections gave R = 0.070. Crystals of [Cu(phen)$_2$(O$_2$CMe)][ClO$_4$], 2H$_2$O are monoclinic, space group P2/c, a = 9.671(2), b = 8.282(2), c = 17.595(3) Å, β = 109.63(2)°, U = 1327.4 Å^3, Z = 2, μ(Mo-$K\alpha$) = 9.33 cm^{-1}. 2921 unique reflections gave R = 0.055. Crystals of [Cu(phen)$_3$(O$_2$CMe)]-[ClO$_4$] are monoclinic, space group P2$_1$/c, a = 8.258(3), b = 19.070(9), c = 16.755(3) Å, β = 111.79(3)°, U = 2450.0 Å^3, Z = 4, μ(Mo-$K\alpha$) = 10.5 cm^{-1}. 2607 unique reflections gave R = 0.043. Crystals of [Cu(phen)$_2$(O$_2$CMe)][BF$_4$] are triclinic, space group P$\bar{1}$, a = 16.073(3), b = 10.615(2), c = 8.443(2) Å, α = 106.43(2), β = 76.67(2), γ = 109.40(2)°, U = 1209.3 Å^3, Z = 2, μ(Mo-$K\alpha$) = 9.22 cm^{-1}. 3345 unique reflections gave R = 0.037. All four structures were solved by the heavy atom method, and their atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.
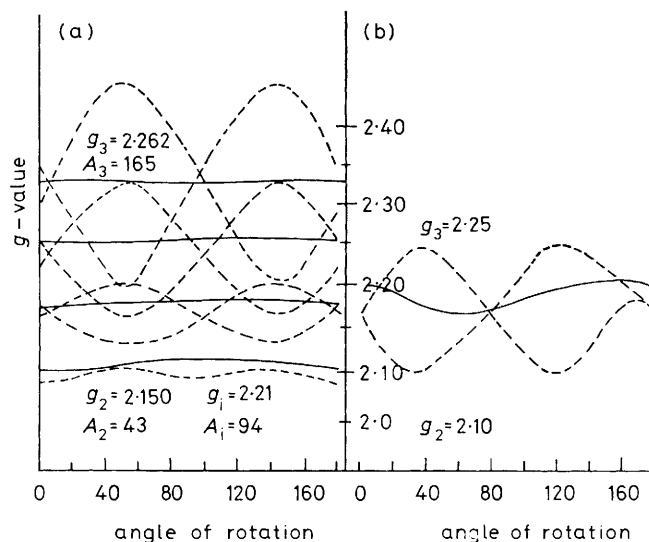
The polycrystalline e.s.r. spectra of complexes (2)—(5), Table 2, are anisotropic at room temperature, and the spectra of (2), (3), and (4) show significant changes with decreasing temperature, while that of (5) shows less change. The e.s.r. spectra of the 10% copper-doped [Zn(phen)$_2$(O$_2$CMe)]X systems of (2) and (3) involve copper hyperfine structure (A) on the highest g-values, Table 2. At room temperature the g-values are consistent with a compressed octahedral CuN$_4$O$_2$ chromophore,[7] ($g_{||}$ > $g_\perp$ > 2.0), while at liquid nitrogen temperature the spectra are consistent with an elongated rhombic octahedral CuN$_4$O$_2$ chromophore ($g_{||}$ ≫ $g_\perp$ > 2.0).[7,8] Figure 2(a) shows the effect of temperature on the single-crystal e.s.r. spectrum of the 10% copper-doped (2) system measured in the Cu, N(2), N(4), O(1), and O(2) plane. At room temperature the spectrum is isotropic in all directions, while at liquid nitrogen temperature the angular variation is consistent with two magnetic centres whose maximum g-values correspond to the direction of the Cu–O(1) and Cu–O(2) bonds in the measured plane. Comparable behaviour is observed in the single-crystal e.s.r. spectrum of (3), Figure 2(b), but the magnitude of the effect is not so marked, owing to the co-operative Jahn-Teller effect. The observation of two magnetic sites at liquid nitrogen temperature is then consistent with two crystal domains. The large anisotropic temperature factors for the acetate oxygen atoms of (2) and (4), and the marked temperature variation of the e.s.r. spectra for both the concentrated and doped systems of these isomers, are consistent with the fluxional behaviour of the CuN$_4$O$_2$ chromophore, Figure 1(b), rather than static disorder, Figure 1(a), which can both be rationalised in terms of the dynamic pseudo-Jahn-Teller effect.[10]

In the two-dimensional fluxional model for (2) and (3), two static square-pyramidal distorted octahedral (4 + 1 + 1*) structures are involved [wells I and II, Figure 1(b)], with the elongation axes misaligned by 90°. In (2) and (3) at room temperature, both wells I and II are energetically equivalent (as they are related by the twofold axis), are equally occupied and, as the energy B < kT, are thermally accessible. Consequently, the room temperature structures (as determined by X-ray crystallography), are a time average of the two static elongated CuN$_4$O$_2$ chromophores of wells I and II, and 'appear' to be cis-distorted octahedral.[8] As this cis-distorted octahedral stereochemistry is really an artifact of the fluxional behaviour

Table 2. Temperature variable e.s.r. data (polycrystalline samples).

	Room temperature			Liquid nitrogen temperature		
	g_1	g_2	g_3	g_1	g_2	g_3
(2) $[Cu(phen)_2(O_2CMe)][BF_4]$, $2H_2O$	2.035	—	2.220	2.050	2.083	2.260
$[10\% \ Cu-Zn(phen)_2(O_2CMe)][BF_4]$, $2H_2O$	2.050	—	2.213	—	2.085	2.260
(3) $[Cu(phen)_2(O_2CMe)][ClO_4]$, $2H_2O$	2.028	—	2.223	2.032	2.083	—
$[10\% \ Cu-Zn(phen)_2(O_2CMe)][ClO_4]$, $2H_2O$	—	—	2.210	—	2.087	2.275
(4) $[Cu(phen)_2(O_2CMe)][ClO_4]$	2.040	—	2.200	—	2.082	—
(5) $[Cu(phen)_2(O_2CMe)][BF_4]$	2.060	2.105	2.260	2.065	2.087	2.280

at room temperature, it is best described as *pseudo cis*-distorted octahedral *and is not a genuine static six-co-ordinate stereochemistry of the copper*(II) *ion*. At liquid nitrogen temperature B may be greater than the thermal energy, wells I and II are no longer thermally related, and the low-temperature e.s.r. spectra indicate the presence of the two individual CuN_4O_2 chromophores with their elongation axes misaligned by 90°, separated into two crystal domains. Because the room temperature X-ray crystal structure of (5) shows that the acetate ion is very asymmetrically co-ordinated to Cu^{II}, giving an essentially square pyramidal distorted octahedral $(4 + 1 + 1^*)$ structure, only well I is significantly populated [wells I and II are not energetically equivalent for (5) as it crystallised in the space group $P\bar{1}$ at room temperature], and only a small temperature variation of the e.s.r. spectrum is observed. The structure of (4) then involves a fluxional situation ($\Delta O = 0.201$ Å), intermediate between the regular *pseudo cis*-distorted octahedral structure of (2) and (3) and the essentially static structure of (5).

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