The *X*-Ray Crystal Structure and Electronic Properties of $[Cu(bipy)_2(ONO)][NO_3]$(bipy = 2,2′-bipyridyl) at 298 and 165 K, a Fluxional *cis*-Distorted Octahedral CuN_4O_2 Chromophore

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The *X*-ray crystal structures of $[Cu(bipy)_2(ONO)][NO_3]$ (bipy = 2,2′-bipyridyl) are reported at 298 and 165 K; significant differences occur which are consistent with a fluxional behaviour of the CuN_4O_2 chromophore, and enable the underlying static stereochemistry to be predicted and rationalised using the i.r. spectrum of the nitrito-group and the electronic reflectance spectrum of the CuN_4O_2 chromophore.

For ten years the stereochemistry[1] of $[Cu(bipy)_2(ONO)][NO_3]$ (**1**) (bipy = 2,2′-bipyridyl) was considered to involve a unique *cis*-distorted octahedral stereochemistry for the copper(II) ion, but in the past few years approximately 14 structures of $[Cu(chelate)_2(OXO)]Y$ complexes have been reported, where chelate = 2,2′-bipyridyl, 1,10-phenanthroline, and 2,2′-bipyridylamine, and OXO^- = nitrite, acetate, and formate.[2] From the analysis of the temperature variation of the e.s.r. spectra of the copper(II)-doped $[Zn(bipy)_2(ONO)][NO_3]$ complex[3] and of a series of cation distortion isomers, $[Cu(phen)_2(O_2CCH_3)]X$ (phen = 1,10-phenanthroline) complexes,[2] where X = $[ClO_4]^-\cdot 2H_2O$, $[ClO_4]^-$, $[BF_4]^-\cdot 2H_2O$, and $[BF_4]^-$, it has been suggested that the stereochemistry of the CuN_4O_2 chromophore is fluxional,[4] and that the *cis*-distorted octahedral stereochemistry is not a genuine *static* stereochemistry of the copper(II) ion, but an artefact of the fluxional behaviour present. To test this suggestion the low-temperature crystal structure of (**1**) has been determined,† and the determination repeated at room temperature† [Figure 1(a)]. The latter structure is not significantly different from the original structure determination,[1] which used visually estimated data (*R* 0.081), but is more accurately determined, (*R* 0.0456). The low-temperature structure still involves a *cis*-distorted octahedral stereochemistry, but with some significant copper–ligand differences in the Cu, N(2), N(4), O(1), O(2) plane. At 165 K there is a significant increase in the Cu–O(2) distance and a significant decrease in the Cu–O(1) distance such that the value of ΔO = {[Cu–O(2)] − [Cu–O(1)]} increases from 0.090 Å at 298 K to 0.147 Å at 165 K. There is a corresponding increase in the value of Cu–N(4) and a decrease in Cu–N(2) at 165 K, to give ΔN = {[Cu–N(4)] − [Cu–N(2)]} = 0.027 Å, but these changes are of little significance. All of these bond-length changes are consistent with the change to a square-pyramidal-distorted *cis*-distorted octahedral (4 + 1 + 1*) structure as observed in the structure[5] of $[Cu(bipy)_2(ONO)][BF_4]$ (**2**) [Figure 1(b)]. In (**2**) the extent of the asymmetric distortion is significantly greater, ΔN = 0.088 Å, and ΔO = 0.346 Å, and the changes are consistent with an increasing distortion along the structural pathway from a regular *cis*-distorted octahedral CuN_4O_2 stereochemistry to a square-pyramidal-distorted *cis*-distorted octahedral (4 + 1 + 1*) CuN_4O chromophore stereochemistry [ref. 5, Figure 3(b)]. The change in the structure of (**1**) with decreasing temperature is then consistent with a fluxional behaviour of the $[Cu(bipy)_2(ONO)]^+$ cation as previously suggested[3] for this ion doped in the isomorphous diamagnetic host lattice, $[Zn(bipy)_2(ONO)][NO_3]$. The relatively small change in bond distance with decreasing temperature accounts for the lack of clear evidence for the fluxional behaviour in (**1**) from the e.s.r. spectrum, as this was masked by exchange coupling.[3]

The temperature variable structure of (**1**) may be used to obtain structural information on the underlying static CuN_4O_2 chromophore of the fluxional model by assuming a linear relationship between the Cu–O(1) and Cu–O(2) distances and the temperature. The extrapolation to 0 K yields Cu–O(1) and Cu–O(2) distances of 2.170 and 2.385 Å respectively, ΔO = 0.215 Å, and using a Boltzmann distribution, $\ln(n_1/n_2) = \Delta E/kT$, where n_1 and n_2 represent the thermal populations[4,6] of Wells I and II, repectively, and ΔE their energy difference

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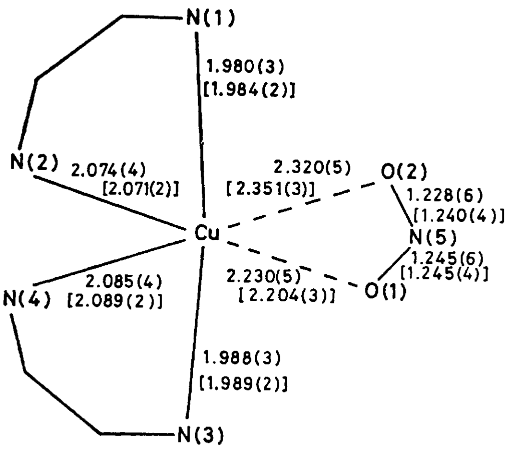
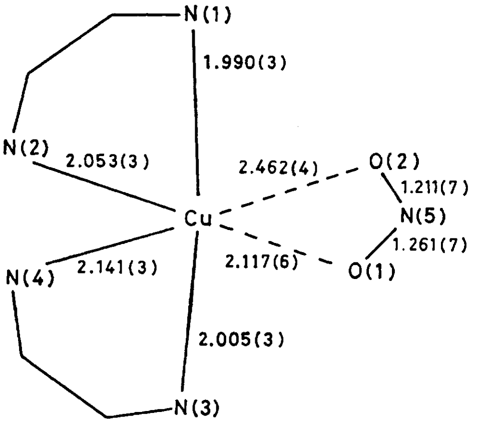
† Complexes (**1**) and (**2**) were prepared as previously reported.[1] Crystals of [(**1**)-298 K] are monoclinic, space group $P2_1/n$, a = 11.225(2), b = 12.035(5), c = 15.109(5) Å, β = 99.55(2)°, U = 2013(2) Å^3, Z = 4, $\mu(\text{Mo-}K_\alpha)$ = 11.3 cm^{-1}. 2142 Unique reflections gave *R* 0.0456. Crystals of [(**1**)-165 K] have a = 11.217(2), b = 11.936(5), c = 14.969(6) Å, β = 99.14(2)°, U = 1979(2) Å^3, Z = 4, $\mu(\text{Mo-}K_\alpha)$ = 11.5 cm^{-1}. 2921 Unique reflections gave *R* 0.0463.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



(a) ΔN = 0.011[0.027]
ΔO = 0.090[0.147]



(b) ΔN = 0.088
ΔO = 0.346

Figure 1. The local molecular structures of (a) $[Cu(bipy)_2(ONO)][NO_3]$ at 298 and 165 K and of (b) $[Cu(bipy)_2(ONO)][BF_4]$. Low temperature data are given in square brackets.

$[Cu(bipy)_2(ONO)][NO_3]$
(1)

$[Cu(bipy)_2(ONO)][BF_4]$
(2)

[see Figure 1(b), ref. 2], a mean $\Delta E = 190\ cm^{-1}$ is obtained. This value is close enough to thermal energy ($kT = 207\ cm^{-1}$) to indicate why the structure of (1) is temperature variable. The extrapolation of the Cu–O distances of (1) with temperature also indicate that the regular *cis*-distorted structure will occur at *ca.* 510 K with a Cu–O distance of 2.275 Å. The ΔO value of 0.215 Å at 0 K, for the extrapolated static CuN_4O_2 chromophore, then represents the upper limit for fluxional behaviour; it is also of interest with respect to the observed geometry[5] of (2) [Figure 1(b)]. As (2) has a ΔO value of 0.346 Å, this ΔO value lies well above the limit of fluxional behaviour, namely, 0.215 Å, and implies that the structure of (2) is a genuine static CuN_4O_2 structure in its own right, with a distorted square pyramidal ($4 + 1 + 1^*$) structure. Some support for this lies in the N–O distances of the nitrito-group (Figure 1). In the fluxional system of (1), these are averaged values, *ca.* 1.23 Å, and are not significantly different, whereas in the static structure of (2), these are significantly different, Δ(N–O) = 0.05 Å, and are consistent with the single bond character of the N(5)–O(1) distance, and the higher double bond character of the N(5)–O(2) distance, predicted for the asymmetrically bonded nitrito-ligand[7] of (2). While the bonding role of the nitrito-ligand in (1) is still asymmetric, the asymmetry in the N–O distances is averaged out owing to the fluxional behaviour of the CuN_4O_2 chromophore. This accounts for the similarity in the i.r. spectra of (1) and (2), both of which involve bands at 1350s, 1115s, and 830s cm^{-1}, in view of the short lifetime (10^{-13} s) of i.r. transitions[8] which relate to the underlying static stereochemistry.

Nevertheless, the most significant consequence of the fluxional behaviour of the CuN_4O_2 chromophore in (1) is the explanation of the comparable electronic reflectance spectra observed[3] for (1) and (2), both of which involve twin-peaked electronic spectra, with two clearly resolved bands at 9 500 and 14 600 cm^{-1} and 9 500 and 15 000 cm^{-1}, respectively. The comparability arises as the electronic transitions relate to the underlying static CuN_4O_2 geometry of the fluxional system, owing to the short lifetime[8] of the electronic transition (10^{-15} s), and not to the time-average structure determined by *X*-ray crystallographic techniques (*ca.* 1 s). The small difference in energy of the spectra of (1) and (2) then arises from small differences in the basic static CuN_4O_2 stereochemistry of these two cation distortion isomers,[9] owing to the different anion environments present. The electronic transitions of (1) and (2) may then be confidently assigned[3] as a square pyramidal ($4 + 1 + 1^*$) stereochemistry with a $d_{x^2-y^2}$ ground state with the band at 9 500 cm^{-1} assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition and that at *ca.* 15 000 cm^{-1} as the $(d_{xy}, d_{zx}, d_{yz}) \rightarrow d_{x^2-y^2}$ transition.

Consequently, the low-temperature crystal structure of (1) not only establishes crystallographic evidence for the fluxional behaviour of (1), but also defines the limit of the fluxional behaviour, ΔO *ca.* 0.215 Å, and rationalises the i.r. and electronic spectra of complexes (1) and (2).

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