A Comment on the Crystal Structure and Electronic Properties of Bis(2,9-dimethyl-1,10-phenanthroline)nitratocopper(II) Trichloroacetate Trichloroacetic Acid

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A re-examination of the electronic properties and structure of $[Cu(dmphen)_2(O_2NO)][CCl_3CO_2]{\cdot}CCl_3CO_2H$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) suggests that it is best described as a distorted square-pyramidal *cis* octahedral CuN_4O_2 chromophore (4 + 1 + 1*) as suggested by the electronic reflectance spectrum, but involving a novel sense of distortion.

The crystal structure[1] of $[Cu(dmphen)_2(O_2NO)][CCl_3CO_2]{\cdot}CCl_3CO_2H$ (1) (dmphen = 2,9-dimethyl-1,10-phenanthroline) [Figure 1(*a*)] has recently been described as a five-co-ordinate or a severely distorted six-co-ordinate octahedral structure. This description failed to suggest the position of the structure of the CuN_4O_2 chromophore of (1) in the structural pathway (Figure 2) relating the regular *cis* distorted CuN_4O_2 chromophore to the distorted square-pyramidal *cis* octahedral (4 + 1 + 1*) chromophore, which are connected by the appropriate combination of the modes of vibration of the CuN_4O_2 chromophore (Figure 2) in $[Cu(chelate)_2(OXO)]Y$ (X = N, CMe, CH, or NO; Y = NO_3^-, BF_4^-, ClO_4^-, PF_6^-) complexes.[2] As the electronic spectrum of (1) was only reported in solution,[1] in which state the environment of the copper(II) ion may be different from that reported in the crystalline state, the electronic properties of (1) in the solid state have been determined, and have been used to describe more precisely the structure of (1).

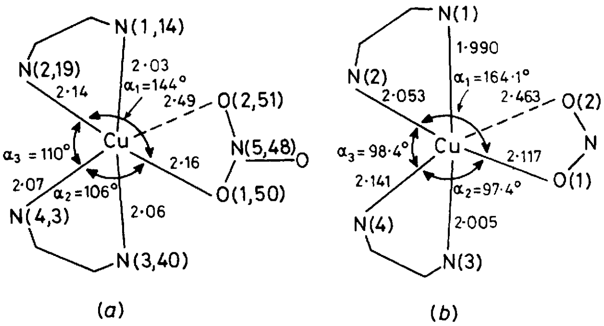

Figure 1. The molecular structure of (*a*) $[Cu(dmphen)_2(O_2NO)][CCl_3CO_2]{\cdot}CCl_3CO_2H$ (1) [ΔO = 0.33, ΔN = 0.07 Å] and (*b*) $[Cu(bipy)_2(ONO)][BF_4]$ [ΔO = 0.346, ΔN = 0.088 Å], with standard and original [for (*a*)] atom-numbering schemes (distances in Å)

Experimental

The electronic reflectance spectrum and polycrystalline e.s.r. spectrum of (1) were obtained as described previously.[3]

Results and Discussion

The electronic reflectance spectrum of (1) displays two equally intense resolved bands at 9 260 and 12 900 cm^{-1}, compared with the single peak observed[1] in solution at 13 500 cm^{-1}. The twin-peaked electronic spectrum is typical[2] of the *cis* distorted CuN_4O_2 chromophore of the fluxional complex, $[Cu(bipy)_2(ONO)][BF_4]$ (2) (bipy = 2,2′-bipyridyl) [Figure 1(*b*)], which has peaks at 9 500 and 14 600 cm^{-1}.

The polycrystalline e.s.r. spectrum of (1) at room temperature is of the exchange type,[3] consistent with the presence of two-dimensional exchange coupling with g values of 2.032 and 2.242, neither of which corresponds to the local molecular g values[3] due to the exchange coupling present. At 77 K the e.s.r. spectrum shows no change in the lowest g value, but the highest g factor broadens to suggest the presence of two components with a shift to a lower value of an intermediate g value consistent with fluxional behaviour[2,4] of the CuN_4O_2 steterochemistry.

The local CuN_4O_2 chromophore stereochemistry of (1) [Figure 1(*a*)] is remarkably similar to the fluxional distorted square-pyramidal *cis* octahedral (4 + 1 + 1*) structure[2] of (2) [Figure 1(*b*)]. Both involve comparable mean Cu–N and Cu–O bond distances and bond differences, ΔO = [Cu–O(2)] – [Cu–O(1)] and ΔN = [Cu–N(4)] – [Cu–N(2)], but they differ in the sense that while the longest Cu–O and Cu–N in-plane distances of (2) are *trans* to each other, in (1) they are *cis*. In this respect the structure of (1) is different from that of 13 other complexes containing the *cis* distorted octahedral CuN_4O_2 chromophore.[5] However, (1) is the only complex to involve the 2,9-dimethyl-1,10-phenanthroline ligand, and the only one to involve a nitrate anion as the chelate oxyanion, although the nitrate anion does co-ordinate in this way in $[Zn(bipyam)_2(O_2NO)][NO_3]$ (bipyam = di-2-pyridylamine).[6] Although the bond angles are comparable in (1) and (2) (Figure 1), there are significant differences in the in-plane angles α_1—α_3, with a maximum difference of 20° in the value of α_1, which can be related to the difference in the peak separation of the electronic spectra, 3 640 cm^{-1} in (1) and 5 100 cm^{-1} in (2).[2] Despite these differences the CuN_4O_2 chromophore is still considered to be fluxional[2,4] in the solid state. The most significant evidence for this is the high thermal parameters associated[7] with the long bonded nitrate oxygen atoms, see Table 1 of ref. 1.

Figure 1(*a*) shows that the N(1)–Cu–N(3) angle (169°), although only marginally smaller than the value of 174—178° previously observed in the $[Cu(chelate)_2(OXO)]Y$ complexes,[5] is bent towards the NO_3^- rather than towards the N(2)–Cu–N(4) angle. This imposes a slight tetrahedral as opposed to a trigonal distortion to the CuN_4 chromophore, the significance of which has been discussed elsewhere (see ref. 8). In order to understand the unique structure of (1) it is necessary to re-examine the combination of vibrational modes that produce the structural pathway of Figure 2. For a regular CuN_4O_2 chromophore of C_{2v} symmetry,[9] the S_{1a} mode (a_1 symmetry),

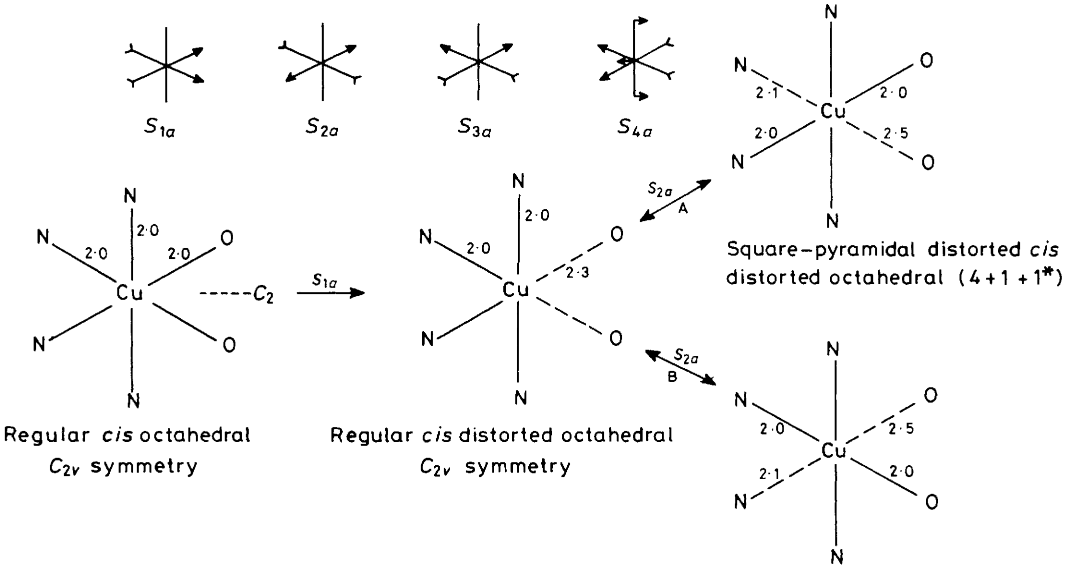

Figure 2. The structural pathway for a *cis* octahedral CuN_4O_2 chromophore plus some modes of vibration of the chromophore of C_{2v} symmetry

Figure 2, produces the clear *cis*-Cu–O elongation (mean 2.322 Å) and the S_{2a} mode (b_2 symmetry) produces the asymmetry in the in-plane distances (ΔO = 0.334 Å and ΔN = 0.067 Å). If only a linear combination of S_{1a} and S_{2a} is involved, the alternative, but equivalent, routes A and B of Figure 2 are produced. However, the novel structure of (1) requires that other modes of vibration, such as S_{3a}, Figure 2, as a linear combination $S_{1a} + S_{2a} + S_{3a}$, with $S_{1a} \gg S_{2a} \approx S_{3a}$, are also included. In general, coupling may involve a linear combination of any number of the vibrational modes of the CuN_4O_2 chromophore of C_{2v} symmetry,[9] as $\Gamma_{\text{vib.}} = 6a_1 + 2a_2 + 3b_1 + 4b_2$. To date the crystal structures [7,10] of the [Cu(chelate)$_2$(OXO)]Y complexes have fitted a one-mode vibronic coupling model, but the structure of (1) emphasises that other possible modes of vibration must not be overlooked. Thus, the atypical bending of the N(1)–Cu–N(3) angle towards the nitrato-group of (1) may well require the inclusion of a mode such as S_{4a} (Figure 2) in the linear combination, in order to account for the direction of this out-of-the-plane distortion.

Redox Properties of (1).—The structure of (1) is of interest as it is obtained by aerial oxidation [11] of a [Cu$^{\text{I}}$(dmphen)$_2$][NO$_3$] complex. Two reports have appeared recently, which also involve the oxidation by air of a [Cu$^{\text{I}}$(chelate)$_2$]X complex to the corresponding *cis* distorted octahedral copper(II) complexes; *i.e.* [Cu(phen)$_2$][ClO$_4$] (phen = 1,10-phenanthroline) in dimethylformamide (dmf) to give [Cu(phen)$_2$(HCO$_3$)][ClO$_4$]·dmf [12] and [Cu(bipy)$_2$][ClO$_4$] in nitroalkanes to give [Cu(bipy)$_2$(ONO)][ClO$_4$].[13] These reports suggest that the fluxional *cis* distorted octahedral structure may have a role in the copper(I)–copper(II) redox process and may involve a similar role in the redox properties of copper blue proteins, involving a distorted tetrahedral CuN_4 site, such as plastocyanin and azurin.[14,15]

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