The Single-crystal Electronic Properties and Stereochemistry of Tripotassium Penta(nitro/nitrito)cuprate(II) †

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The polarised single-crystal electronic and e.s.r. spectra of $K_3Cu(NO_2)_5$ have been determined and are shown to be consistent with the stereochemistry of the two non-equivalent copper(II) environments present namely, a *seven*-co-ordinate $[Cu(NO_2)_3(ONO)_2]^{3-}$ and a *cis*-distorted six-co-ordinate $[Cu(NO_2)_2(ONO)_2(ONO)]^{3-}$ species. The i.r. spectrum is shown to be compatable with the presence of nitro- and unidentate and bidentate nitrito-ligands, but cannot distinguish the two types of nitrito-co-ordination. A structural pathway is suggested between the seven-co-ordinate and *cis*-distorted species.

THE complex $K_3Cu(NO_2)_5$ (1) has been known for a considerable time [1-3] and has aroused much interest [4,5] as a possible five-co-ordinate copper(II) complex involving five potentially equivalent nitro-ligands. The recent *X*-ray crystal-structure determination [6] of (1) has established that there are two types of non-equivalent copper(II) ion environments, neither of which is five-co-ordinate: one involves a seven-co-ordinate pentagonal-bipyramidal $[Cu(NO_2)_3(ONO)_2]^{3-}$ anion, and the other a *cis*-distorted $[Cu(NO_2)_2(ONO)_2(ONO)]^{3-}$ anion, Figure 1(*a*) and (*b*), respectively. The nitrite ligands involve three distinct types of co-ordination,[7] namely nitro, unidentate nitrito, and bidentate nitrito. As the original e.s.r. spectrum [5] of (1) was reported as axial, consistent with an elongated tetragonal-octahedral stereochemistry, and as the original electronic spectrum [4] was reported as a single peak at 14 710 cm^{-1} in contrast to the twin peaks predicted for a *cis*-distorted octahedral structure,[8] the electronic properties have been redetermined and are now reported in the light of the known crystal structure [6] of (1).

EXPERIMENTAL

Preparation.—Complex (1) was prepared by adding ethanol (80 cm^3) to aqueous $Cu(NO_2)_2$ solution [0.05 mol; prepared by metathesis from $CuSO_4\cdot5H_2O$, and $Ba(NO_2)_2$] and KNO_2 (0.20 mol) in water (80 cm^3); slow evaporation of the mother-liquor produced green-black needles [4] of (1), which were examined without recrystallisation. All attempts to recrystallise (1) from methanol were unsuccessful.[4]

Physical Properties.—These were recorded as previously described.[9,10] The i.r. spectrum of (1) was determined as a Nujol mull and a KBr disc on a Perkin-Elmer 621 spectrometer.

RESULTS AND DISCUSSION

Crystallographic Data.—The structure [3-6] of $K_3Cu(NO_2)_5$ involves four independent $[Cu(NO_3)_5]^{3-}$ species located at special positions of two-fold symmetry [Figure 1(*a*) and (*b*)], of which two of the species in pairs are not significantly different. The two non-equivalent copper(II) environments are completely different. One involves a *seven*-co-ordinate $[Cu(NO_2)_3(ONO)_2]^{3-}$ species, three of the nitrite groups co-ordinating as nitro-groups, and two as unsymmetrical nitrito-groups to give a geometry that is closely comparable [11] to that of $[Cu(py)_3(NO_3)_2]$ (2) (py = pyridine), Figure 1(*c*). In the second, Figure 1(*b*), two of the nitrite groups co-ordinate

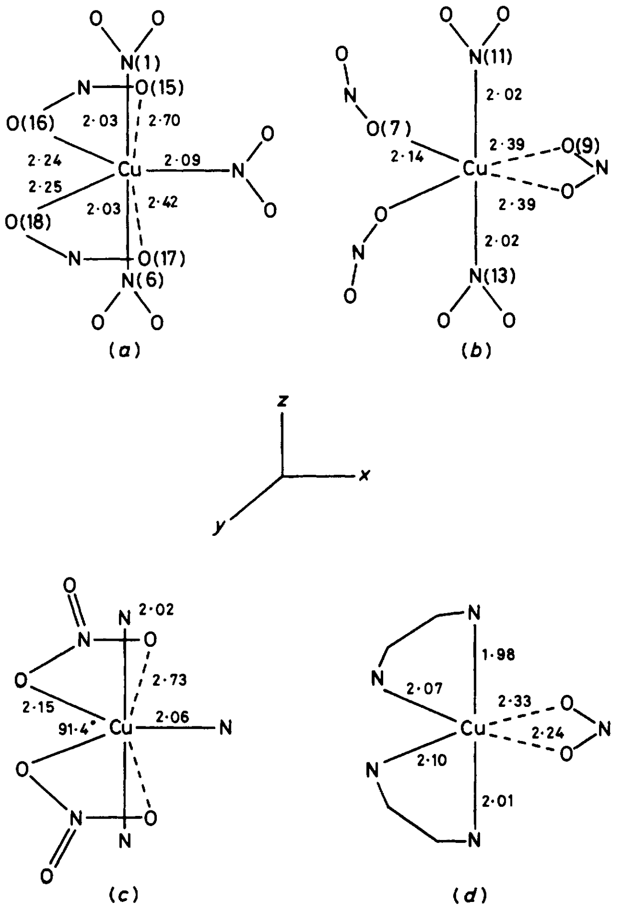

FIGURE 1 The molecular structure of (*a*) $[Cu(NO_2)_3(ONO)_2]^{3-}$, (*b*) $[Cu(NO_2)_2(ONO)_2(ONO)]^{3-}$, (*c*) $[Cu(py)_3(NO_3)_2]$ (2), and (*d*) $[Cu(bipy)_2(ONO)][NO_3]$ (3)

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† Hexapotassium di(nitrito-*OO*′)tri(nitro-*N*)cuprate(II) di(nitrito-*O*)(nitrito-*OO*′)di(nitro-*N*)cuprate(II).

as nitro-groups, two as unidentate nitrito-groups, and one as a symmetrical bidentate nitrito-group with relatively long Cu–O distances of 2.39 Å to give a *cis*-distorted octahedral $CuN_2O_2O'_2$ chromophore, whose geometry is closely comparable to the $CuN_2N'_2O_2$ chromophore[12] of [Cu(bipy)$_2$(ONO)][NO$_3$] (3), Figure 1(*d*). In the four non-equivalent copper(II) species in the unit cell the two seven-co-ordinate species and the two *cis*-distorted species have their local molecular axes aligned parallel, but between the seven-co-ordinate and the *cis*-distorted species the *z* and *y* axes are misaligned by 90° with the *x* axes parallel, Figure 2(*a*)—(*c*).

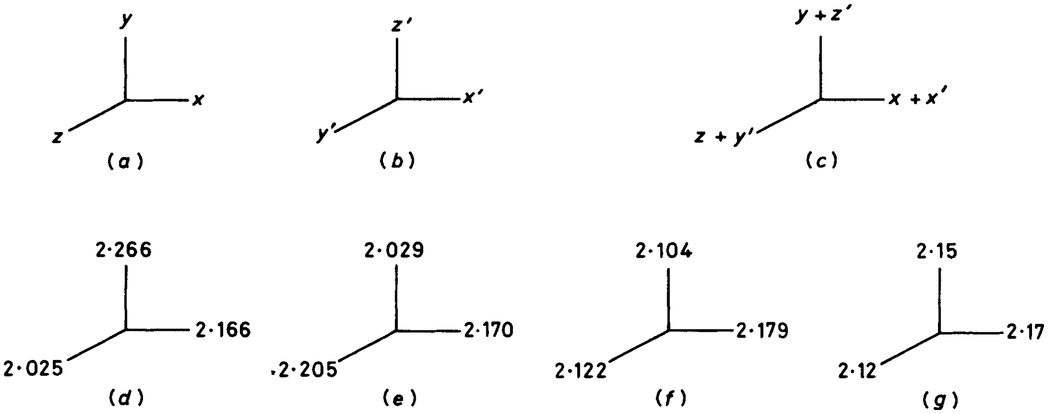

FIGURE 2 The definition of local molecular axes for (*a*) the seven-co-ordinate species of (1), (*b*) the *cis*-distorted species of (1), and (*c*) their misalignment in (1). Also shown are single-crystal e.s.r. data (*d*) for (2), (*e*) (3), (*f*) (1), and (*g*) the composite e.s.r. spectrum of (2) and (3) misaligned as in (1)

Electronic Properties.—The polycrystalline e.s.r. spectrum of (1) is of the exchange type[10] with one crystal *g* value of 2.127, which only changes slightly at the temperature of liquid nitrogen to 2.133. At room temperature, the single-crystal *g* values are 2.122 parallel to the *c* axis (needle axis), and 2.104 and 2.179 parallel to the *a* and *b* axis, respectively. As the crystal *g* values do not equate with the local molecular *g* values no information is available on whether or not the two independent copper(II) environments have a d_{z^2} ground state.[10] As the local molecular stereochemistries are so comparable to (2) and (3), Figure 1(*c*) and (*d*), respectively, their local molecular *g* values have been used to predict the crystal *g* value[8,13] of the complexes (2) and (3), misaligned as in (1). These are shown in Figure 2(*d*)—(*f*), and compared with the data for (1) in Figure 2(*g*). There is reasonable agreement with the *g* values measured along the *a* and *b* axis, but a significant difference along the *c* axis. This suggests that the highest *g* of the seven-co-ordinate environment of (1) is not as high as 2.266, that observed for (2), which is consistent[11] with the shorter Cu–O distance (2.73 Å) and mean (2.56 Å) in (2) and (1) respectively. Consequently, it is possible to rationalise the single-crystal *g* values for (1) in terms of the two misaligned seven-co-ordinate and *cis*-distorted environments present.

The electronic reflectance spectrum of (1) consists of two equally intense resolved peaks at 10 400 and 14 500 cm^{-1}, Figure 3, and not the single peak at 14 710 cm^{-1}, as previously reported,[4] due to the failure of these authors to measure reflectance spectra into the near-i.r. region, which is all important for copper(II) complexes.[14] The polarised single-crystal spectra of (1), Figure 3, have been measured for the main (010) face of the crystal only; the *c*-axis spectrum shows a main band at 14 900 cm^{-1}, with a clearly resolved band at 9 600 cm^{-1}, while the *a*-axis spectrum shows a main band at 15 300 cm^{-1}, with two poorly resolved shoulders at 12 600 and 9 200 cm^{-1}. The bands of the *c*-axis spectrum are then consistent with the two bands at 14 600 and 9 500 cm^{-1} in the reflectance spectrum[8] of (3), while the shoulder at 12 600 cm^{-1} in the *a*-axis spectrum of (1) is consistent with the single peak[13] at 11 400 cm^{-1} in the electronic reflectance spectrum of (2). Consequently, although it is not possible to assign the polarised single-crystal spectra of (1) in terms of the two misaligned local molecular

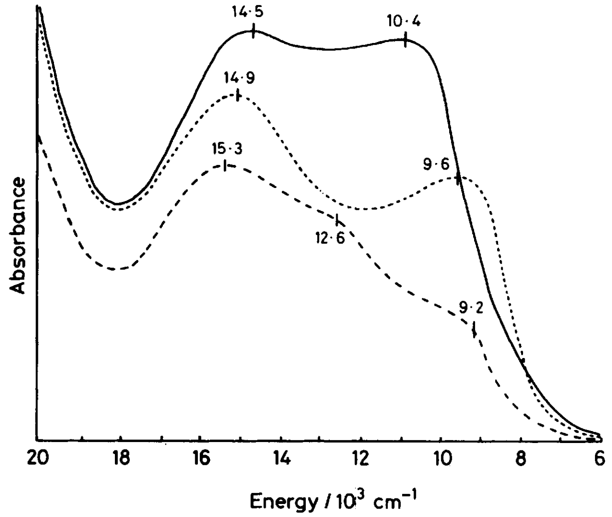

FIGURE 3 The electronic reflectance spectrum of $K_3Cu(NO_2)_6$ (——), and the polarised single-crystal electronic spectra parallel to the *a* axis (*z* + *y'* polarised) (— — —) and parallel to the *c* axis (needle, *y* + *z'* polarised) (· · · ·)

chromophores, the single-crystal spectra *are* of value in revealing the position of bands which are masked in the reflectance spectrum and which are consistent with the two types of stereochemistry present. Consequently, the single-crystal electronic spectrum of (1) has some value as an electronic criterion of stereochemistry[14] for the two independent chromophores present.

Infrared Spectra.—The i.r. spectrum was reported previously[4] to involve two types of co-ordinated nitrite ion. The Table reports i.r. data[4,8,15,16] of $K_2BaCu(NO_2)_6$, complex (3), and $[Cu(bipy)(ONO)_2]$ (4), which involve nitro-,[17] symmetrical bidentate nitrito-,[12] and unsymmetrical bidentate nitrito-co-ordination[18] of the nitrite groups present, respectively. The i.r. spectrum clearly distinguishes[7] nitro- from nitrito-co-ordination, but is not able to distinguish the symmetrical bidentate nitrito-co-ordination[12] of (3) from the asymmetric bidentate nitrito-co-ordination[18] of (4). Consequently, in the i.r. spectrum of (1), while the bands at 1 275, 1 225, and 816 cm^{-1} may be associated with nitro-co-ordination, and those at 1 360, 1 184, and 821 cm^{-1} with nitrito-co-ordination of the nitrite groups, it is not possible to distinguish the symmetrical and the very asymmetrical bidentate nitrito-co-ordination present in (1).

TABLE The polyanion i.r. spectra (cm^{-1}) of some nitrite complexes of copper(II)

Complex[a]	NO_2^- Co-ordination									
$K_3Cu(NO_2)_5$ [4]			1 360s		1 275 (sh)	1 225s	1 184s	821 (sh)	816s	
$K_2BaCu(NO_2)_6$ [15]	Nitro	1 420m (sh)		1 332s	1 260s				816s	800
$[Cu(bipy)_2(ONO)][NO_3]$ [8]	Nitrito bidentate		1 350s[b]				1 115s		830s	
$[Cu(bipy)(ONO)_2]$ [16]	Nitrito unidentate		1 372s				1 150		844	

[a] bipy = 2,2′-Bipyridyl. [b] Band at 1 390 cm^{-1} due to NO_3^-.

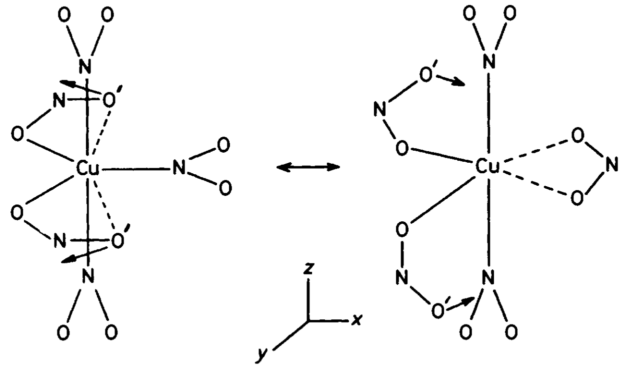

FIGURE 4 The structural pathway connecting the seven-co-ordinate $[Cu(NO_2)_3(ONO)_2]^{3-}$ species and the *cis*-distorted $[Cu(NO_2)_2(ONO)_2(ONO)]^{3-}$ species of $K_3Cu(NO_2)_5$

Structural Profiles.—The crystal structure of (1) indicates the presence of two cation distortion isomers[19] of the $[Cu(NO_2)_5]^{3-}$ cation, which arise due to the Plasticity Effect[20] of the copper ions. It has already been suggested[6] that the two isomers are related by a ready bond-breaking and -forming mechanism, which accounts for their existence in the same lattice and suggests a structural pathway,[21] Figure 4, connecting the seven-co-ordinate species to the *cis*-distorted species. In this process the symmetrical Cu–O′ bond-lengthening process in the seven-co-ordinate species allows the in-plane nitro-co-ordination to switch to the greater space-filling symmetrical bidentate nitrito-co-ordination, during which the plane of the in-plane nitro-group is turned through 90° about the in-plane Cu–N direction. In this non-rigid structure,[6] it is not surprising that the e.s.r. spectrum of (1) measured in a dry ethanol–dimethylformamide solution[6] at liquid-nitrogen temperature yielded an axial type e.s.r. spectrum, which is totally inconsistent with the observed structures, as the process of dissolution will inevitably change the ligand environment about the copper(II) ion.

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