Molecular Helicity in Inorganic Complexes; The Preparation, Crystal and Molecular Structure of Bis(2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine)acetatodicopper(II) Hexafluorophosphate Monohydrate

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2,2′:6′,2″:6″,2‴:6‴,2⁗-Quinquepyridine (L, quinquepy) forms 2:2 complexes with transition metal ions in which the ligands are twisted about the metals in a double helical arrangement reminiscent of nucleic acids.

There has been considerable interest in molecular helicity since the revelation of a double helical structure for nucleic acids.[1] Although helicity is a relatively common feature in organic molecules, it is extremely rare in inorganic compounds.[2] To date, helicity has been demonstrated in a trinuclear copper(I) complex and postulated for a binuclear copper(I) complex of sterically restricting 2,2′-bipyridyl ethers.[3] We report herein the preparation of a series of complexes of the type $[M_2(\text{quinquepy})_2]^{n+}$, quinquepy = 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine, and the structural characterisation of the double helical bis-copper(II) complex.

The ligand quinquepy (L) is readily prepared by the reaction of 2,6-bis(3′-dimethylammonio-1′-oxopropyl)pyridine dichloride with two equivalents of [2′-(2″-pyridyl)-2′-oxoethyl]pyridinium iodide in the presence of ammonium acetate.[4] The addition of copper(II), cobalt(II), zinc(II), or nickel(II) acetate to a suspension of quinquepy in boiling methanol led to the formation of clear solutions, from which salts of $[M_2L_2]^{4+}$ could be isolated by the addition of $[NH_4][PF_6]$. These stoicheiometries were confirmed by microanalysis, and the molecularity established by fast atom bombardment (f.a.b.) mass spectrometry.

A number of species were isolated from the reaction with copper(II) acetate, in which varying numbers of water, hydroxy, or acetate ancilliary ligands were present. All exhibited peaks in the f.a.b. mass spectrum at m/z 900 corresponding to $[Cu_2L_2]$. Molecular models indicated that a 2:2 stoicheiometry could only be achieved if a helical arrangement of ligands was present. The e.s.r. spectra exhibited broad, near isotropic, signals for frozen glasses at 196 and 4 K. Cyclic voltammograms of acetonitrile solutions of all the copper(II) complexes exhibited two fully reversible reduction waves [$E_{\frac{1}{2}}$ +0.15, −0.37 V *vs.* Fc/Fc$^+$ (Fc = ferrocene), $E_a - E_p$, 60—65 mV].

The crystal and molecular structure of the cation in a material analysing as $[Cu_2L_2(OAc)][PF_6]_3{\cdot}H_2O$ is shown in Figure 1.[†] Two views of the cation are shown. The structural analysis clearly demonstrates the presence of the binuclear cation, and shows the double helical arrangement of the ligands around the two copper centres. The two metal ions are 4.50 Å apart, and are not bonded to each other. Each quinquepy ligand acts as a bidentate donor to one metal and a

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[†] *Crystal data* for $[Cu_2L_2(OAc)][PF_6]_3{\cdot}H_2O$, $Cu_2N_{10}C_{52}H_{39}O_3P_3F_{18}$, M = 1414.0, triclinic, a = 11.829(8), b = 12.575(11), c = 20.917(22) Å, α = 103.0(1), β = 82.9(1), γ = 114.4(1)°, U = 2758.6 Å^3, space group $P1$, $F(000)$ = 1420, D_m = 1.68, D_c = 1.70 g cm^{-3}, Z = 2, Mo-K_α radiation (λ = 0.7107 Å), μ(Mo-K_α) = 10.1 cm^{-1}. 7173 Independent reflections with 2θ max. of 50° were measured on a diffractometer, of which 3543 with $I > 2\sigma(I)$ were used in the calculations. The structure was solved by heavy atom methods and refined [Cu, P, F, O, N, C anisotropic, H isotropic in calculated positions] to R 0.072 (R_w 0.075). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

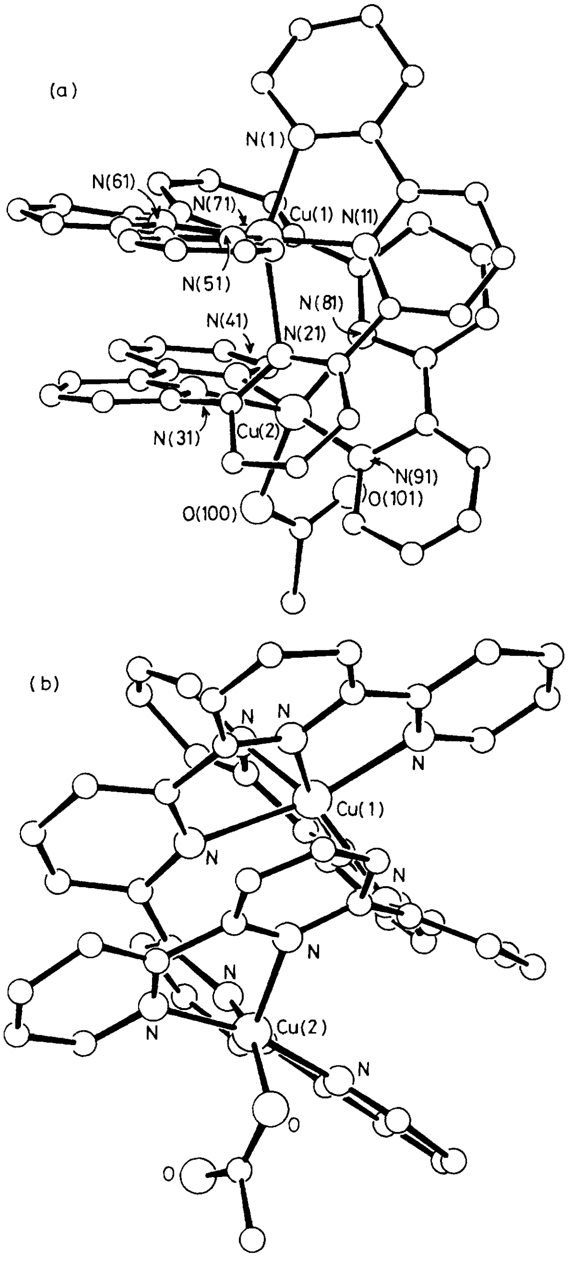

Figure 1, (a) and (b). Two views of the crystal and molecular structure of the cation $[Cu_2(quinquepy)_2(OAc)]^{3+}$ showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity. Some relevant bond lengths are: Cu(1)–N(1), 2.161(13), Cu(1)–N(11), 2.017(13), Cu(1)–N(21), 2.319(10), Cu(1)–N(51), 2.160(18), Cu(1)–N(61), 1.964(14), Cu(1)–N(71), 2.378(15), Cu(2)–N(31), 2.212(15), Cu(2)–N(41), 1.994(12), Cu(2)–N(81), 2.079(13), Cu(2)–N(91), 1.995(11), Cu(2)–O(100), 2.038(11), Cu(2)–O(101), 2.683 Å.

terdentate to the other. Thus, Cu(1) is bonded to two 'terpyridyl' fragments in a very distorted octahedral N_6 environment, whilst Cu(2) is in a highly distorted trigonal bipyramidal environment, co-ordinated to two 'bipyridyl' residues and the oxygen of one acetate group. The six Cu–N distances about the six co-ordinate copper vary considerably in the range 1.964—2.378 Å, whilst those about the five co-ordinate copper are in the range 1.994—2.212 Å. The acetate is bonded to Cu(2) through one oxygen (Cu–O, 2.038 Å), but there is a weak interaction with the other oxygen of the acetate (Cu–O, 2.683 Å).

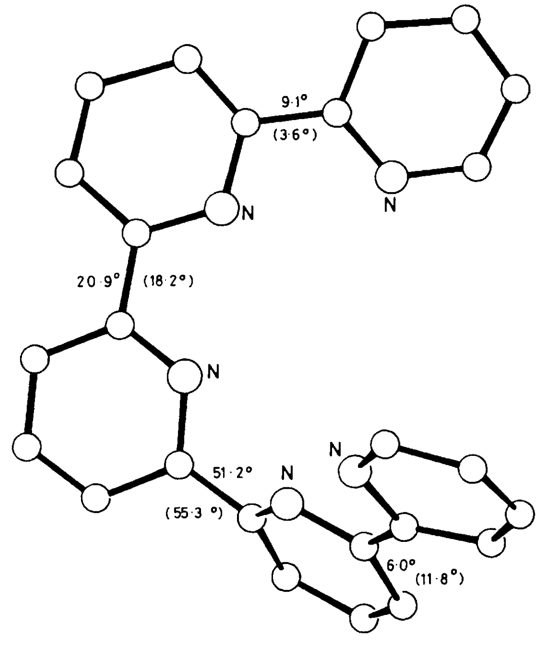

Figure 2. A view of one of the two independent ligands in the $[Cu_2(quinquepy)_2(OAc)]^{3+}$ cation, showing the twist angles about the C–C bonds (angles in parentheses refer to the other independent ligand in the cation).

The quinquepy ligand is twisted about the C–C bond linking the terdentate and bidentate portions of the molecule; the two ligands are not identical, but exhibit twist angles of 55.3° and 51.2°. The molecule exhibits a marked stacking interaction between the planar parts of the ligand, reminiscent of the base-pair stacking in nucleic acids. The terpyridyl fragment of one ligand is arranged nearly parallel to the bipyridyl fragment of the other with angles of intersection of 5.5 and 4.4° for the two interactions; this is illustrated in Figures 1(a) and (b). The average distance of an atom in the bipyridyl fragment from the plane of the approximately parallel terpyridyl fragment in the other ligand is 3.25 and 3.35 Å in the two ligands.

The molecule is chiral, and the unit cell consists of the two enantiomers of a double helix. The molecular helicity persists in the reduced forms of the complex; we have recently determined the structure of $[Cu_2L_2][PF_6]_3$ in which one copper is six- and one four-co-ordinate.[5] The interaction with small molecules at the terminal binding site occupied by the acetate, and at the planar binding site between the stacked pyridyl rings will be of interest, as will resolution of the cation into its enantiomers.

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References

1 J. D. Watson and F. H. C. Crick, *Nature (London)*, 1953, **171**, 737.
2 L. Pauling, R. B. Corey, and H. R. Branson, *Proc. Natl. Acad. Sci. USA*, 1951, **37**, 205; P. J. Flory and W. G. Miller, *J. Mol. Biol.*, 1966, **15**, 284; J. H. Brewster, *Top. Curr. Chem.*, 1974, **47**, 29; K. Mislow, D. Gust, P. Finnocchiaro, and R. J. Boettcher, *ibid.*, 1974, **47**, 1; K. P. Meurer and F. Vogtle, *ibid.*, 1985, **127**, 1.
3 J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, and D. Moras, *Proc. Natl. Acad. Sci. USA*, 1987, **84**, 2565.
4 F. Krohnke, *Synthesis*, 1976, 1.
5 M. Barley, E. C. Constable, S. Corr, M. G. B. Drew, J. Nutkins, and M. D. Ward, unpublished results.