

Double-helical Complexes from Simple 2,2':6',2"-Terpyridines; the Crystal and Molecular Structure $[\text{Cu}_2(\text{Ph}_2\text{tpy})_2][\text{PF}_6]_2$ ($\text{Ph}_2\text{tpy} = 6,6''\text{-diphenyl-2,2':6',2''-terpyridine}$)

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2,2':6',2"-Terpyridines form dinuclear complexes with copper(I) which are double-helical; the introduction of 6-phenyl substituents stabilises the helicate, and the crystal and molecular structure of $[\text{Cu}_2(\text{Ph}_2\text{tpy})_2][\text{PF}_6]_2$ described.

We are interested in the self-assembly of helical metallo-supramolecules,¹ and we and others have shown that oligopyridines act as versatile metal-binding domains in such systems.² Simple double helicates result from the partitioning of 2,2':6',2"-quaterpyridines into two didentate domains upon coordination to copper(I) or silver(I) centres.^{3,4} Isolated examples of dinuclear double helicates assembled from ligand arrays of six donor atoms are known,⁴⁻⁷ and we speculated upon the nature of copper(I) complexes of 2,2':6',2"-terpyridines.

Complexes of copper(I)⁸ with 2,2':6',2"-terpyridine (tpy) have been known for many years, but remarkably little is known about their constitution. The complexes formed from the interaction of equimolar quantities of tpy and copper(I) salts are effective oxygen-activation and -transfer catalysts.^{8,9} We have now reinvestigated these complexes. An orange, very air-sensitive solution is obtained from the reaction of tpy with $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ in MeOH. Exposure to air yields blue-green solutions containing $[\text{Cu}(\text{tpy})_2]^{2+}$ salts. In the absence of oxygen, the red salt $\{\text{Cu}(\text{tpy})(\text{PF}_6)\}_n$ may be isolated which exhibits intense peaks in its FAB mass spectrum corresponding to $\{\text{Cu}_2(\text{tpy})_2(\text{PF}_6)\}$ (m/z 737) and $\{\text{Cu}_2(\text{tpy})_2\}$ (m/z 592). We suggest that the initially formed species is a double-helical complex, but that this is unstable with respect to oxidation to copper(II). In order to probe the structure of these copper(I) tpy complexes, we have introduced sterically demanding phenyl groups into the 6- and 6"-positions of the tpy ligand which are expected to minimise solvation effects and stabilize the double helix.

The ligand Ph_2tpy was prepared by Kröhnke methodology¹⁰ by the reaction of phenacylpyridinium bromide with the bis(Mannich) salt derived from 2,6-diacetylpyridine, para-

formaldehyde and dimethylammonium chloride. The reactions of Ph_2tpy with $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ or $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ led to the formation of $\{\text{Cu}(\text{Ph}_2\text{tpy})(\text{BF}_4)\}_n$ or $\{\text{Cu}(\text{Ph}_2\text{tpy})(\text{PF}_6)\}_n$ as red solids. The mass spectroscopic properties resembled those of the complexes with the parent tpy ligand [m/z 984, $\text{Cu}_2(\text{Ph}_2\text{tpy})_2(\text{BF}_4)$ and 898, $\text{Cu}_2(\text{Ph}_2\text{tpy})_2$]. The copper(I) complex of Ph_2tpy is air-stable, and we have determined the molecular structure of the complex $[\text{Cu}_2(\text{Ph}_2\text{tpy})_2][\text{PF}_6]_2$; a view of the cation is presented in Fig. 1.† The cation is double-helical, with a Cu...Cu distance of 2.570(2) Å. The helix is formed by a series of twists about the interannular C-C bonds of the ligand. The ligands have essentially distributed themselves to present didentate domains to one metal centre, and a single pyridine donor to the other, to give a {4 + 2} double-helicate.¹ The two copper atoms are in different environments; Cu(2) is in a distorted tetrahedral environment and is bonded to N(31), N(41), N(81) and N(91) [Cu-N, 1.959(6)–2.224(7) Å] whilst Cu(1) is in an approximately linear [N(71)–Cu(1)–N(21) = 175.8(3)°] two-coordinate environment. However, Cu(1) also shows two longer-range interactions with the 'bridging' pyridine rings (Cu-N, 2.544, 2.467 Å). In independent studies, Potts has very recently reported the analogous structure of the copper complex with the more highly functionalised ligand 6,6"-diphenyl-4,4"-bis(methylthio)-2,2':6',2"-terpyridine.⁷

It is constructive to compare the known dicopper(I) double helicates constructed from two N,N'N"-donor ligands. Our intermetallic distance [2.570(2) Å] is significantly shorter than those reported by Nelson *et al.* [2.626(1) Å]⁶ or Williams *et al.* [2.854(2) Å]⁵ and most importantly, it is shorter than that in the complex described by Potts [2.631(2) Å].⁷ The differences from the 6,6"-diphenyl-4,4"-bis(methylthio)-2,2':6',2"-terpyri-

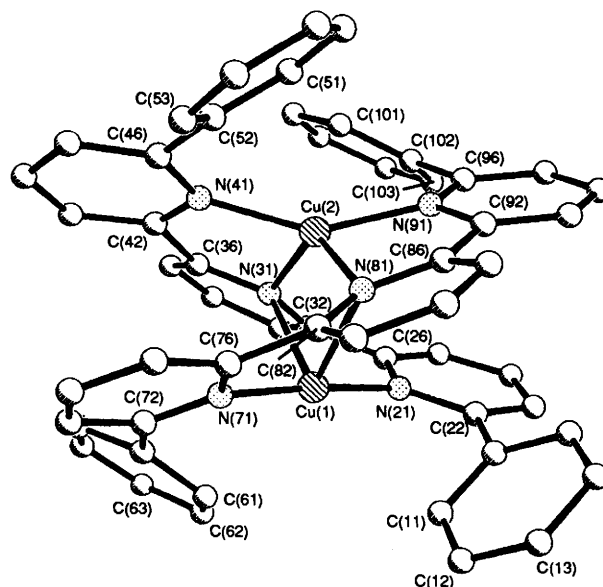
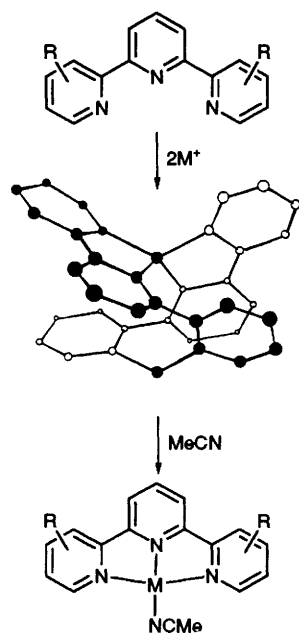


Fig. 1 Crystal and molecular structure of the $[\text{Cu}_2(\text{Ph}_2\text{tpy})_2]^{2+}$ cation in $[\text{Cu}_2(\text{Ph}_2\text{tpy})_2][\text{PF}_6]_2$ showing the numbering scheme adopted

dine complex are of particular importance; the varying metal-metal distance results from a change in the pitch of the helix achieved by small but cumulative differences in the interannular C-C bonds. This introduces a new structural feature: the two phenyl substituents of one ligand 'sandwich' the central pyridine of the other. Each phenyl ring forms an coplanar angle of *ca.* 30° with the pyridine, with centroid-to-centroid distances of about 3.8 Å. Presumably, this is not possible when the methylthio substituent is present. This emphasizes once again the critical observation that the gross structural features of double-helicate complexes are determined by the ligand donor set, but that the detailed molecular geometry is dependent upon the presence and character of the substituents that may be present.^{1,2}

In conclusion, from the above data and those of Potts⁴ we can now suggest that the solid-state complexes of 1:1 stoichiometry formed from copper(I) with 2,2':6',2''-terpyridine ligands should be regarded as double-helical dinuclear species. The solution properties of these complexes vary, depending upon the availability of donor solvents and the ease of oxidation of the metal centres. It is of interest to note that the silver(I) complex of tpy is dinuclear but *not* double-helical, whereas the silver complex of Ph₂tpy is mononuclear.¹¹

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Footnote

† Crystal data: C₅₄H₃₈Cu₂F₁₂N₆P₂, red crystals, *M* = 1267.92, monoclinic, space group *P*2₁/*c*, *a* = 24.051(5), *b* = 14.639(3), *c* = 15.270(3) Å, β = 95.87(3)°, *U* = 5348 Å³, *Z* = 4, *D*_c = 1.575 g cm⁻³, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) = 0.952 mm⁻¹. 7150

Reflections were collected at 153 K on a four-circle diffractometer with 2θ(max) 45.0° of which 6958 were unique and were used in structure solution using SHELX 93 and refined (Cu, P, F, N, C anisotropic) to *R*1 = 0.1134, *wR*2 = 0.2888. Both PF₆⁻ groups were severely disordered. A complex model was used in the refinement in which two positions [three for F(3) and F(8)] were located for five out of the six F atoms in each PF₆⁻ group; the sums of the occupancies were set to unity for the individual F atoms. All F atoms were refined with isotropic displacement parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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