

A Polynuclear Copper(I) Complex with a Single Helical Structure

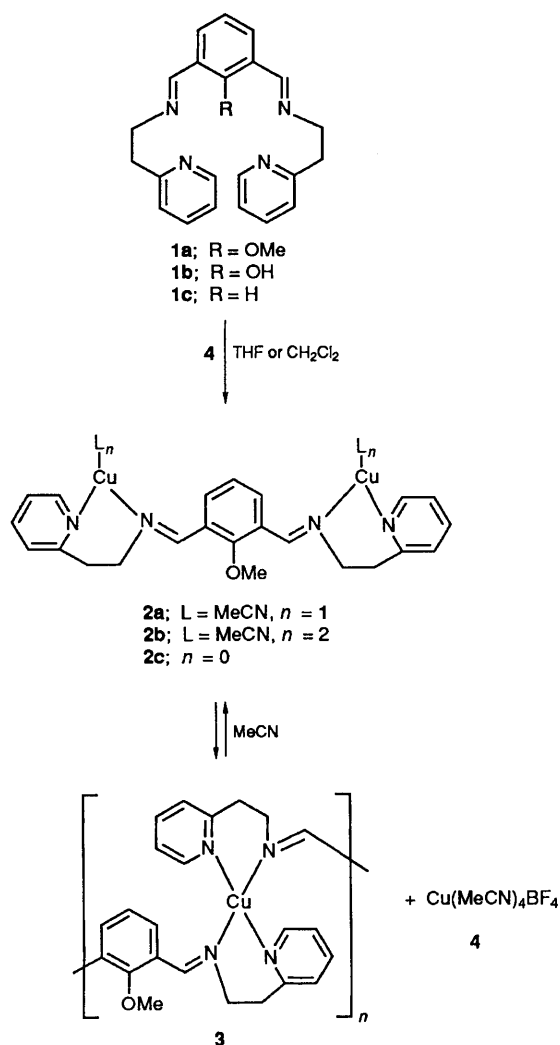
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The synthesis and crystal and molecular structure of a single helical polynuclear Cu^I complex are described.

Molecular recognition by design and self-assembly of (supra)molecular structures are currently being extensively investigated and a crucial role for molecular helicity has been revealed.¹⁻⁴ Based on oligopyridines as ligands, spontaneous assembly of double helical polynuclear metal complexes has been demonstrated. Thus, ligands containing two to five

2,2'-bipyridine units separated by oxapropylene spacers form double helical Cu^I complexes^{3,5} and similar molecular topology was found in Ni^{II}, Cd^{II}, Pd^{II} and Cu^I complexes of various oligopyridines.^{4,6} A single stranded diruthenium(II) helical complex has recently been discovered by Constable, Tocher and co-workers.⁷



Scheme 1 THF = tetrahydrofuran

We report in this communication the synthesis and crystal and molecular structure of a single helical copper(1) coordination polymer. When the new ligand 2,6-bis[*N*-(2-(2-pyridyl)ethyl)formimidoyl]-1-methoxybenzene **1a** was allowed to react with two equivalents of $\text{Cu}(\text{MeCN})_4\text{BF}_4$, dinuclear copper(1) complexes **2a-c** were formed.⁸ The formation of **2a-c** is strongly dependent upon the amount of MeCN present; heating of **2b** at reflux in CH_2Cl_2 for 10 min provided the acetonitrile-free and presumably two-coordinated dinuclear Cu^1 complex **2c**. Addition of MeCN (4 equiv.) to a CHCl_3 solution of **2c** reconverted it into acetonitrile complex **2b** (80–90% yield).⁸ When, however, excess (≥ 10 equiv.) of MeCN was added to **2c** in CHCl_3 and the resulting solution allowed to crystallize at room temperature for a period of 50 h, white crystalline and orange crystalline material could be obtained in a 50:50 (± 5) ratio. The white compound was $\text{Cu}(\text{MeCN})_4\text{BF}_4$ **4**, whereas the orange compound showed a ligand-copper stoichiometry of 1:1 and a copper-nitrogen ratio of 1:2 indicating a mononuclear or polynuclear 1:1 complex. This complex, in solution, is very sensitive to molecular oxygen and when a 1:1 mixture of **3** and **4** in CHCl_3 is oxidized with O_2 the same oxygenated ligand⁸ **1b** is obtained as is the case with **2a-c**.⁹ These results indicate an intact bis-imine ligand in **3** and an equilibrium between **3+4** and **2a-c** in solution.

Bright-orange crystals of **3** suitable for X-ray analysis were obtained from CHCl_3 -MeCN. The crystal and molecular

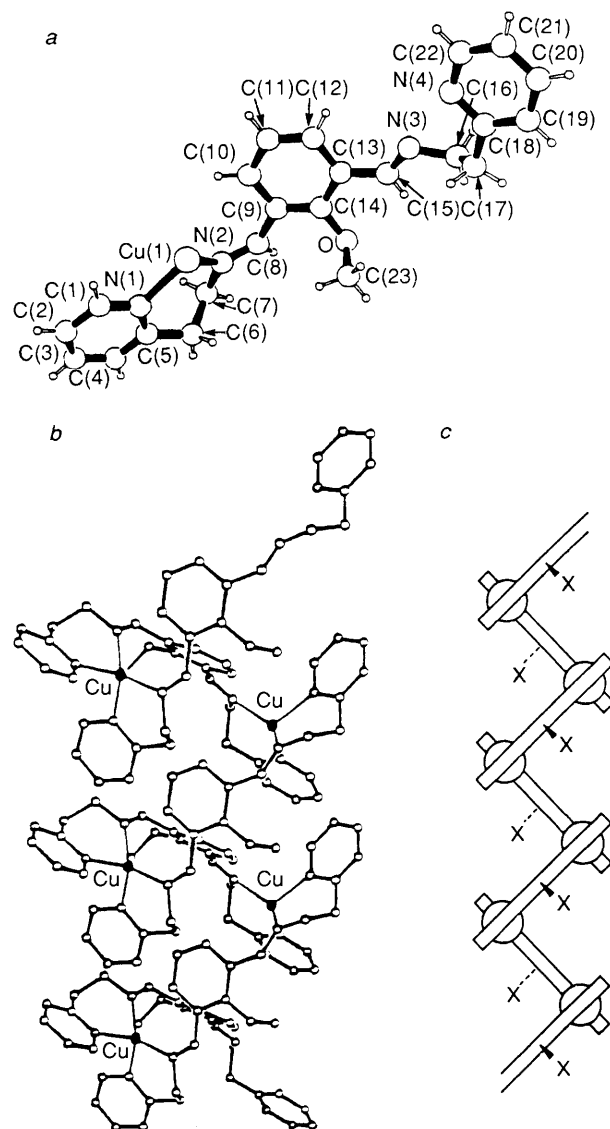


Fig. 1 (a) A view of the cation of **3** with adopted numbering scheme. Selected bond lengths (\AA) and angles ($^\circ$): Cu(1)-N(1) 2.097(5), Cu(1)-N(2) 2.032(5), Cu(1)-N(3)¹ 2.048(4), Cu(1)-N(4)¹ 2.073(5), Cu(1)-Cu(1)¹ 7.650(4); N(1)-Cu(1)-N(2) 97.0(2), N(1)-Cu(1)-N(3)¹ 107.4(2), N(1)-Cu(1)-N(4)¹ 109.6(2), N(2)-Cu(1)-N(3)¹ 131.2(2), N(2)-Cu(1)-N(4)¹ 111.9(2), N(3)¹-Cu(1)-N(4)¹ 98.9(2). (b) Crystal structure of part of the coordination polymer **3**. (c) Schematic view of the single-helical arrangement (X = OMe).

structure of **3** is shown in Fig. 1.[†] Each Cu^1 atom in **3** is four-coordinated with two pyridylethylimine bidentate units from two different ligand molecules **1a**, in a distorted tetrahedral geometry. A dihedral angle between the $\text{CuN}(1)\text{-N}(2)$ and $\text{CuN}(3)\text{-N}(4)$ planes of 83.6° is observed. Upon

[†] *Crystal data*: $\text{C}_{24}\text{H}_{25}\text{N}_4\text{BCl}_3\text{F}_4\text{OCu}$, monoclinic, space group $P2_1/n$, $a = 13.826(3)$, $b = 9.938(2)$, $c = 20.555(6)$ \AA , $\beta = 102.58(2)^\circ$, $U = 2756.5$ \AA^3 , $Z = 4$, $D_c = 1.55$ g cm^{-3} , Mo-K α radiation ($\lambda = 0.71073$ \AA), $\mu(\text{Mo-K}\alpha) = 11.4$ cm^{-1} .

Data were collected on a Nonius CAD4F diffractometer at 130 K in the range $1^\circ \leq \theta \leq 27^\circ$. 3618 Unique reflections with $I \geq 3\sigma(I)$ were used in the refinements. The structure was partly solved by direct methods; the remaining atoms including all the H-atoms were located in succeeding difference Fourier synthesis. Block-diagonal least-squares on F , with unit weights, converged to a final $R = 0.059$ and $R_w = 0.065$ using anisotropic thermal parameters for the non-hydrogen atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

coordination of Cu^I the ligand **1a** has formed a linear coordination polymer with two helical strains, lying next to each other in the infinite unit cell [Fig. 1(b)].

Furthermore, one BF₄⁻ anion and one molecule of CHCl₃ are present for each Cu^I unit. The copper–nitrogen distances are nearly the same (2.03–2.09 Å) and on the average slightly longer than the Cu–N distance in the three-coordinated Cu^I complex derived from **1c**⁹ as might be expected on the basis of steric repulsion. The Cu–N_{pyr} bonds (average 2.085 Å) are rather long compared to the Cu–N_{pyr} bond lengths generally found for four-coordinated Cu^I ions (2.0–2.05 Å)¹⁰ and those in helical (oligo-)bipyridine Cu^I complexes (average 2.02 Å).³ Not unexpectedly, the N_{imine}–Cu–N_{pyridine} bond angles are relatively small (97.0, 98.9°) compared to the other four N–Cu–N angles (average 115.0°). The 1,3-bis-imine substituted anisole group bridges two Cu^I centres 7.650 Å apart; the Cu–Cu distance is considerably longer than the distance of 4.952 Å observed in the binuclear Cu^I complex derived from ligand **1c**.⁹

In complex **3** the Cu^I ions are an integral part of the polymer backbone and the two bidentate units of each ligand **1a** are twisted with respect to each other. Other polymers with backbone metals are known which form linear, planar or three-dimensional structures depending on the identity of the ligand and the coordination abilities of the metal ion.¹¹ As far as copper(I) coordination polymers are concerned, Reedijk and coworkers recently described a reaction of *N,N,N',N'*-tetrakis(pyrazol-1'-ylmethyl)-1,2-diaminoethane (tpde) with Cu(MeCN)₄BF₄ which produced a white Cu(tpde)BF₄MeCN linear polymer. The Cu^I ions are coordinated by four pyrazole N-atoms in an almost tetrahedral arrangement.¹²

Fares and coworkers reported a polymeric cyano-2,2'-biquinoline-Cu^I complex containing both linear and tetrahedrally coordinated Cu^I in the chain.¹³ In the Cu^I coordination polymer **3** the two helices in the infinite unit cell are single stranded, one of which is left handed and the other right handed [schematically shown in Fig. 1(c)]. The ability of ligands such as **1a** to assemble in the presence of Cu^I ions to single stranded helical complexes provides flexible and synthetically easy accessible alternatives to double stranded

polypyridine Cu^I systems in approaches towards supramolecular recognition and electroactive systems. The fact that the methoxy substituent in the ligand points outside the helicate, thereby minimizing steric hindrance, allows attachment of functional units that arrange in a helical geometry. We are currently investigating these molecular arrangements.

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References

- 1 J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89.
- 2 J. K. Barton, *J. Biomol. Struct. Dyn.*, 1983, **1**, 621; J. K. Barton, *Chem. Eng. News*, 1988, **66**, 30.
- 3 J. M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. USA*, 1987, **84**, 2565.
- 4 E. C. Constable, M. G. B. Drew and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1987, 1600.
- 5 J. M. Lehn and A. Rigault, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1095.
- 6 E. C. Constable, M. D. Ward, M. G. B. Drew and G. A. Forsyth, *Polyhedron*, 1989, **8**, 2551; E. C. Constable, M. D. Ward and D. A. Tocher, *J. Am. Chem. Soc.*, 1990, **112**, 1256; E. C. Constable, S. M. Elder, J. Healy, M. D. Ward and D. A. Tocher, *J. Am. Chem. Soc.*, 1990, **112**, 4590.
- 7 C. J. Cathey, E. C. Constable, M. J. Hannon, D. A. Tocher and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1990, 621.
- 8 O. J. Gelling and B. L. Feringa, *J. Am. Chem. Soc.*, 1990, **112**, 7599.
- 9 O. J. Gelling, F. van Bolhuis, A. Meetsma and B. L. Feringa, *J. Chem. Soc., Chem. Commun.*, 1988, 552.
- 10 K. D. Karlin, R. W. Cruse, Y. Gultneh, A. Faroog, J. C. Hayes and J. Zubieta, *J. Am. Chem. Soc.*, 1987, **109**, 2668, and references cited therein.
- 11 B. M. Foxman and S. W. Gersten in *Encyclopedia of Polymer Science and Engineering*, ed. J. I. Kroschwitz, 1985, Wiley, New York, vol. iv, p. 175; J. T. Wroblewski and D. B. Brown, *Inorg. Chem.*, 1979, **18**, 498; M. Hanack, *Chimia*, 1983, **37**, 238.
- 12 W. L. Driessen, F. B. Hulsbergen, J. Reedijk and G. C. Verschoor, *Transition Met. Chem.*, 1985, **10**, 390.
- 13 G. Dessy, V. Fares, P. Imperatori and G. O. Morpurgo, *J. Chem. Soc., Dalton Trans.*, 1985, 1285.