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

O. J. Gelling, F. van Bolhuis and Ben L. Feringa*

Department of Organic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

The synthesis and crystal and molecular structure of a single helical polynuclear Cu¹ 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 Cu¹ complexes³,⁵ and similar molecular topology was found in Ni²⁺, Cd²⁺, Pd²⁺ and Cu¹ complexes of various oligopyridines.⁴,⁶ A single stranded diruthenium(II) helical complex has recently been discovered by Constable, Tocher and co-workers.⁷
We report in this communication the synthesis and crystal and molecular structure of a single helical copper(I) 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 Cu(MeCN)4BF4, dinuclear copper(I) 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 CH2Cl2 for 10 min provided the acetonitrile-free and presumably two-coordinated dinuclear Cu(I) complex 2c. Addition of MeCN (4 equiv.) to a CHCl3 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 CHCl3 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 Cu(MeCN)4BF4 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 CHCl3 is oxidized with O2 the same oxygenated ligand 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 CHCl3–MeCN. The crystal and molecular structure of 3 is shown in Fig. 1.† Each CuI 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 CuN(1)–N(2) and CuN(3)–N(4) planes of 83.6° is observed. Upon

† Crystal data: C24H25N4BCl3F4OCu, monoclinic, space group P21/n, a = 13.826(3), b = 9.938(2), c = 20.555(6) Å, β = 102.58(2)°, U = 2756.5 Å3, Z = 4, D = 1.55 g cm–3, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) = 11.4 cm–1. Data were collected on a Nonius CAD4F diffractometer at 130 K in the range 1° ≤ θ ≤ 27°. 3618 Unique reflections with F ≥ 3σ(F) 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 wR = 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⁺ 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 Cu¹ complex derived from 1c as might be expected on the basis of steric repulsion. The Cu–N₄coord bonds (average 2.085 Å) are rather long compared to the Cu–N₃coord bond lengths generally found for four-coordinated Cu⁺ ions (2.0–2.05 Å)¹⁰ and those in helical (oligo-)bipyridine Cu⁺ complexes (average 2.02 Å).³

Not unexpectedly, the N₄coord–Cu–N₄pyridine bond angles are relatively small (97.0, 98.9°) compared to the other four N–Cu–N angles (average 115.0°).¹ The 1,3-bis-imine substituted anisole group bridges two Cu¹ centres 7.650 Å apart; the Cu–Cu distance is considerably longer than the distance of 4.952 Å observed in the binuclear Cu¹ complex derived from ligand 1c.³

In complex 3 the Cu⁺ 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.¹³ As far as copper(i) coordination polymers are concerned, Reedijk and coworkers recently described a reaction of Cu(MeCN)₄BF₄ and coworkers recently described a reaction of Cu(N₃)₂ with Cu(tpde)BF₄ which produced a white Cu(tpde)BF₄ ≈ 3 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⁺ ions to single stranded helical complexes provides flexible and synthetically easy accessible alternatives to double stranded polypyridine Cu⁺ 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.

Received, 3rd September 1990; Com. 0/03983G

References