Helical transition-metal compounds: preorganisation of the ligands by a paracyclophane group

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The synthesis of a bis-diiminedithia substituted [2.2]paracyclophane, with a novel high-yielding [1 + 2] condensation reaction, and of its double helical dicopper(I) complex, characterized by a crystal structure analysis are reported.

Helicity is an important structural motif in biological systems, and helical metal complexes have attracted much attention in recent years.[1] Polypyridine based ligands have been studied extensively in this field.[1,2] With a series of dicopper(I) complexes of large macrocyclic Schiff-base type ligands [$(N_2S_2)_2$ donor sets; 30–36-membered cycles] we have discovered and studied a new type of double helicity, induced by metal-ion coordination.[3] A similar metal-ion induced folding of large natural macrocycles has been observed with certain cyclic octapeptides [*e.g.* in the dicopper(II) complex of Patellamide D].[4] Propellicenes have a similar topology, and crown ether-substituted paracyclophanes have also been investigated.[5]

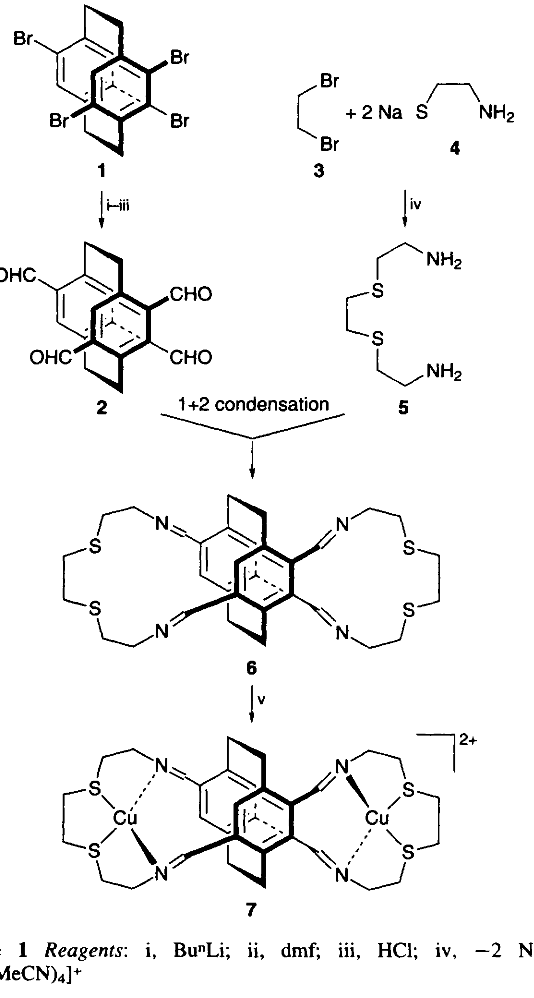
The 'figure-of-eight' configuration of our compounds is stabilized by π stacking of the phenylene spacer groups and by the preference of copper(I) centres for (distorted) tetrahedral coordination geometry.[3,6] An obvious idea to investigate the strain induced by π stacking of the substituted phenylene spacer groups was to investigate the structures of dicopper(I) compounds of ligands with a preorganized double-helical configuration. A tetrasubstituted paracyclophane was assumed to be an ideal anchor group for the two Schiff-base ligand units. This would also lead to a new type of highly preorganized ligands, which might be of importance for various applications, where high complex stabilities or metal-ion selectivities are an advantage.[7]

The novel [1 + 2] condensation reaction with the new *trans*-tetraformylparacyclophane leads, in analogy to the well known [2 + 2] condensation reaction of dialdehydes with diamines,[8] in high yield to the desired [2.2]paracyclophane linked dinucleating ligand with imine and thioether donor sets (Scheme 1). Addition of 0.5 equiv. of *trans*-tetraformylparacyclophane (4,7,13,16-tetraformyl-[2.2]paracyclophane) **2** to a solution [MeCN–toluene (3 : 1)] of 3,6-dithia-1,8-diaminononane **5** affords ligand **6** as a white solid in 70–80% yield. A Bouveault reaction yields the tetraformyl–paracyclophane **2** by lithiation of the corresponding *trans*-tetrabromoparacyclophane with Bu^{n}Li, followed by reaction with dmf and acid hydrolysis. Analytical data (elemental analyses, FABMS, IR, ^{1}H NMR) are compatible with the structure of **6**. Addition of $[Cu(MeCN)_4]ClO_4$ in MeCN to **6** in MeCN–toluene (3 : 1) affords a yellow–orange solution, from which crystals, suitable for X-ray diffraction, were isolated after slow evaporation of the solvent.

The structural analysis of **7** (Fig. 1)‡ reveals, as expected, that the dicopper(I) compound has structural features that are very similar to those of the analogous double-helical compounds with unsubstituted phenylene spacer groups.[3,6] Specifically, there are only minimal structural differences to the parent compound with an identical ligand backbone (Table 1).[6] Thus, the strain induced by the paracyclophane anchor unit is minimal, and **6** is a highly preorganized ligand for copper(I). An important factor is that the solution ^{1}H NMR data of the coordination sites of the two compounds are also very similar (see Table 1). This supports our earlier conclusion that the dicopper(I) compounds with the open macrocyclic ligands have also a chiral folded structure in solution.[3]

All significant structural differences are related to the central paracyclophane anchor unit. As usually observed with paracyclophanes, the two benzene rings are slightly folded along the four ethylene bridged carbon atoms (7°). The carbon atoms linking the paracyclophane unit to the coordinating side-chains are only slightly bent out of these planes. The imine donor groups are planar but, as observed in all our double-helical dicopper(I) compounds,[3,6] their coordination to copper(I) enforces a torsion of 32° (av.) around the $C^{arom}C^{imine}$ bond.

The electrochemical properties of **7** have been studied by cyclic voltammetry in MeCN.§ Oxidation of Cu^I to Cu^{II} occurs at $E_{1/2}$ = 1.29 V (*vs.* NHE), *i.e.* 230 mV more anodically than



Scheme 1 *Reagents*: i, Bu^{n}Li; ii, dmf; iii, HCl; iv, −2 NaBr; v, $[Cu(MeCN)_4]^+$

the dicopper(I) complex with the parent compound with a similar chelate ring size.

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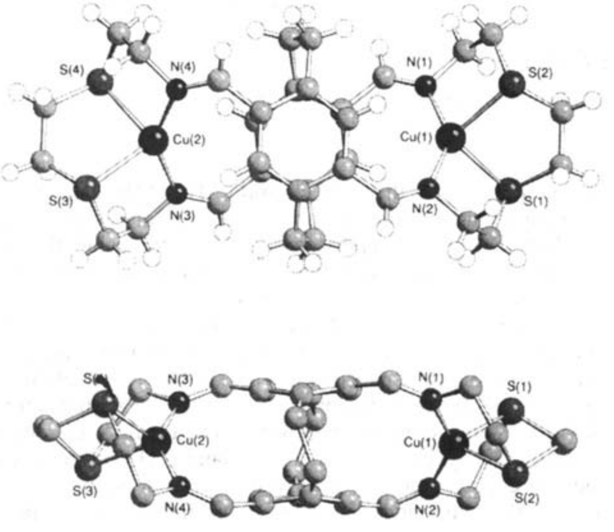

Fig. 1 Two orientations (rotation of 90° around the pseudo-C_2 axis) of the molecular structure [(*P*)-enantiomer] of **7**$[ClO_4]_2$·MeCN

Table 1 Comparison of the experimentally determined average bond distances (d_{av}) and valence angles (θ_{av}), and of the ^{1}H NMR (in $MeNO_2$) parameters of the ethylene bridges between the paracyclophane-based dicopper(I) compound **7** and the analogous compound with the unbridged phenylene spacer groups[6]

	Paracyclophane **7**	Unbridged
d_{av}/Å		
Cu–S	2.376	2.380
Cu–N	1.962	2.013
Cu···Cu	8.221	7.825
Ar···Ar	3.055	3.588
θ_{av}/°		
S–Cu–S	91.5	91.0
S–Cu–N	117.4	115.1
S–Cu–N^{chelate}	90.2	90.8
N–Cu–N	141.2	144.1
^{1}H NMR δ, *J*/Hz		
SCH_2	3.75 (d, 4 H, $^2J_{AX}$ 9.8), 2.61 (d, 4 H, $^2J_{AX}$ 9.8), Δν = 341.3 Hz	3.65 (d, 4 H, $^2J_{AX}$ 10.1), 2.80 (d, 4 H, $^2J_{AX}$ 10.2), Δν = 257.3 Hz
NCH_2CH_2	4.01 (mt, 4 H, $^2J_{AX}$ 12.5), 3.16 (dt, 4 H, $^2J_{AX}$ 13.7, $^3J_{AX}$ 4.9), Δν 257.2 Hz	4.01 (mt, 4 H, $^2J_{AX}$ 11.8), 3.17 (dt, 4 H, $^2J_{AX}$ 12.9, $^3J_{AX}$ 4.8) Δν 252.8 Hz
NCH_2	4.13 (dd, 4 H, $^2J_{AX}$ 13.4, $^3J_{AX}$ 4.1), 3.39 (dd, 4 H, $^2J_{AX}$ 14.7, $^3J_{AX}$ 2.8) Δν 223.3 Hz	4.12 (td, 4 H, $^2J_{AX}$ 14.0, $^3J_{AX}$ 4.0) 3.30 (td, 4 H, $^2J_{AX}$ 14.2, $^3J_{AX}$ 3.4) Δν 212.8 Hz

Footnotes

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‡ Crystal structure determination of **7**$[ClO_4]2$·MeCN, $C_{34}H_{43}Cl_2Cu_2$-$N_5O_8S_4$, M = 975.95; orange crystals (0.20 × 0.25 × 0.20 mm^3); monoclinic, space group $P2/n$; a = 1993.7(9), b = 1281.3 (5), c = 1560.9(7) pm; β = 90.18(4)°; U = 3987.30(3) pm^3; Z = 4; D_c = 1.626 g cm^{-3}; $F(000)$ = 2008; μ = 14.67 cm^{-1}; 8411 reflections (Siemens Nicolet Syntex R3m/V diffractometer; 200 K; Mo-Kα radiation, graphite monochromator); λ = 0.71073 Å; ω–2θ scan, $3.8 < 2\theta < 50°$; data reduction, Lorentz and polarisation absorption correction were carried out by direct methods.[9,10] Data refinement (full-matrix, r.m.s., basis F^2) of 516 variables, using 3083 reflections with $I > 2.0\sigma(I)$ converged at R = 0.0799 and R_w = 0.1575, residual electron density 0.706, −0.423 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/163.

§ The cyclic voltammogram of **7** (0.01 mmol dm^{-3} in dry MeCN with 0.1 mol dm^{-3} tetrabutylammonium perchlorate as electrolyte) was recorded on a BAS 100B instrument, equipped with a glassy carbon working electrode, a Pt auxiliary electrode and a $AgNO_3$–Ag^0 reference electrode; the potential of ferrocene (+0.067 V) was used as reference, and the potential was converted to the NHE scale.

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