Molecular Structure of a Catenand and its Copper(I) Catenate: Complete Rearrangement of the Interlocked Macrocyclic Ligands by Complexation

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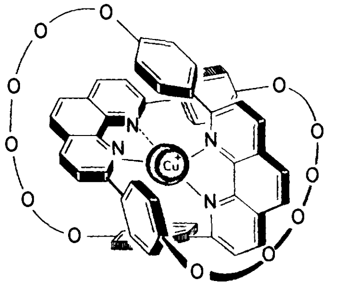
The first crystal structures of a catenane and of a metallo-catenate are reported; upon complexation with Cu^I, there is a dramatic change in molecular shape.

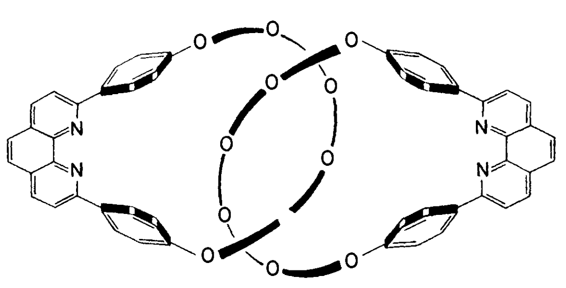
Recently, a new family of molecules has been reported whose topological and co-ordinating properties are of interest: the catenands.[1] These are interlocked macrocyclic ligands, while metallo-catenates[2] are obtained by complexation to a metal.

The topology of catenanes was first discussed more than twenty years ago,[3] but their practical preparation has been extremely limited.[4,5] Templated synthesis[1] allows gram scale preparation and crystallization of these compounds. The present report describes the first crystallographic study of a catenane.

The catenane structure forces the two co-ordinating sub-units to remain in close proximity but it does not impose a rigid shape to the molecule, provided each macrocycle is large enough to allow the chain of the other ring to slide freely within its cavity. Consequently, although the metallo-catenate (**1**) and the catenand (**2**) differ by only one atom (Cu^+) and the



(1)



(2)

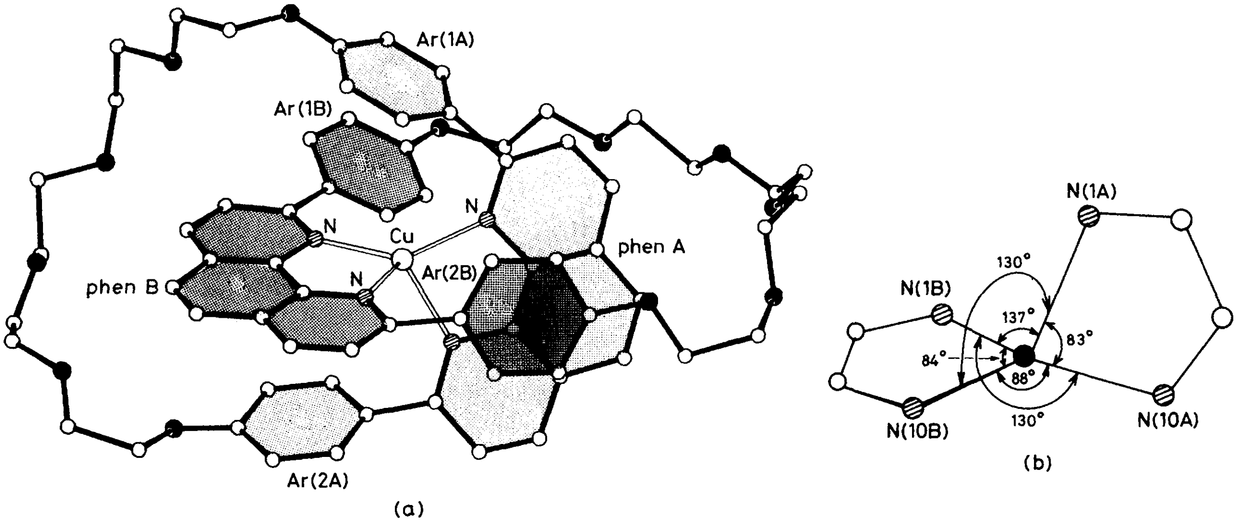


Figure 1. (a) Structure of the copper(I) catenate (**1**) and (b) the co-ordination polyhedron of Cu^{I}.

bond connectivity of the organic skeleton is identical for both compounds, their respective molecular shapes are totally different, as shown by the present *X*-ray study.

The molecular structure of the copper(I) catenate, (**1**),[†] Figure 1, shows the interlocking of the two macrocycles, confirming the molecular topology of (**1**) postulated by ^{1}H n.m.r. measurements.[2] The copper atom is bound to the two phenanthrolines (phen) *via* four nitrogen atoms. The N–Cu distances range from 2.0 to 2.09 Å; they are close to the values found in other copper(I) complexes of related ligands.[7,8] The two phen nuclei (phen A and phen B, Figure 1) are far from being perpendicular to one another, in contrast to Cu(dmp)$_2^+$ (dmp = 2,9-dimethylphenanthroline),[8] their dihedral angle being *ca.* 60°.

Unlike Cu(dmp)$_2^+$, the co-ordination polyhedron around Cu^{I} is highly distorted with respect to tetrahedral geometry, as depicted in Figure 1. The chelate bite of the phen ligand imposes two N–Cu–N angle values of *ca.* 83°, but the other N–Cu–N angles vary from 88° to 137°. The geometry around Cu^{I} is thus notably 'open', making the metal centre potentially accessible to additional ligands. The pronounced distortion around the copper atom might originate from charge-transfer interactions between the phen nucleus of a macrocyclic subunit and one anisoyl moiety of the other. Indeed, phen A (see Figure 1) is almost parallel to one of the phenyl groups [Ar(2B)] substituted on phen B (dihedral angle *ca.* 7°) and phen B is roughly parallel to Ar(2A) (dihedral angle *ca.* 11°). The phenanthroline (π-acceptor) to phenyl (π-donor) distance is *ca.* 3.35 Å; similar interactions have recently been shown to occur in the adduct formed between a platinum(II) complex and a large macrocyclic polyether.[9] In addition the two

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[†] Crystals of (**1**) were grown from a mixture of hexane–ethanol. *Crystal data:* $C_{68}H_{68}N_4O_{12}CuBF_4$, triclinic, space group $P\bar{1}$, a = 20.667(10), b = 17.965(9), c = 8.738(6) Å, α = 95.90(7), β = 90.62(5), γ = 108.71(8)°, U = 3053 Å^3, Z = 2. The 1328 observed data were collected on an automatic 4-circle diffractometer. The structure was solved by the Patterson method. Owing to the small amount of data the least-squares refinement was performed with isotropic thermal parameters to an *R*-value of 14.6%.

Crystals of (**2**) were grown from benzene. *Crystal data:* $C_{68}H_{68}N_4O_{12}{\cdot}C_6H_6{\cdot}H_2O$, triclinic, space group $P\bar{1}$, a = 23.012(6), b = 13.034(5), c = 13.053(5) Å, α = 121.58(3), β = 86.30(2), γ = 100.32(3)°, U = 3279 Å^3, Z = 2. The structure was solved by direct methods using a local program.[6] One benzene molecule and one disordered water molecule were located in the asymmetric unit. Isotropic refinement led to an *R*-factor of 16.4% for 2254 reflections and 160 atoms (including 68 theoretical H atoms). The high *R* factors are a result of weakly diffracting crystals, maximum 2θ = 2 × 68°.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

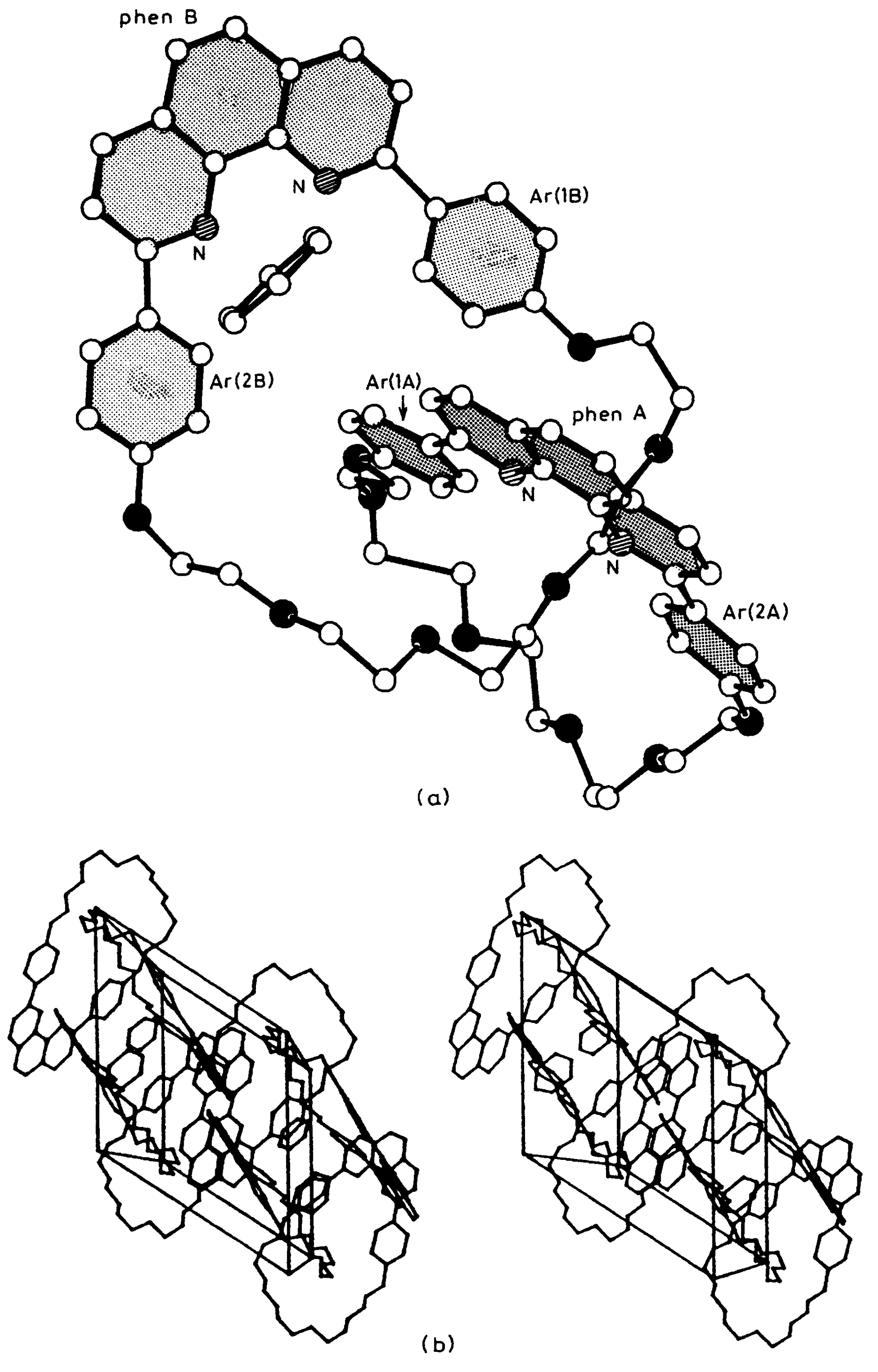

Figure 2. (a) Structure of the catenand (**2**) and (b) a stereoscopic view of the packing within the crystal.

remaining phenyl groups [Ar(1A) and Ar(1B)] are also parallel to one another and in very close proximity.

The molecular arrangement of the free ligand (**2**) is strikingly different from that of the catenate (**1**). In (**1**) the two diphenyl phenanthroline fragments interpenetrate, but they are fully disentangled in the catenand (**2**).† The two virtual co-ordinating sites assigned to each phen are *ca.* 11.2 Å apart. In the free ligand (**2**) each diphenyl phenanthroline subunit is almost planar, in contrast to the copper(I) catenate (**1**). The packing forces probably influence the molecular assembly within the crystal, as represented in Figure 2. Aromatic nuclei superpositions exist as in the copper(I) catenate but only between catenand molecules related by inversion centres.

Recomplexation of (**2**) by copper(I) can be quantitatively carried out, the rearrangement of the molecular geometry being reversible. The complexation process displays an allosteric character;[10] the long distance between the two phen nuclei of the catenand is dramatically shortened during the complexation process, while the two pentaethyleneoxy chains, originally in close proximity, are progressively unravelled. Interestingly, in contrast to many complexing agents which are preorientated in a conformation appropriate to the interaction with a given substrate, the catenand (**2**) has no geometrical analogy with its corresponding complex, the metallo-catenate (**1**), although the stability[1] and the kinetic inertness[11] of the latter are extremely high.

We thank Dr. J. P. Kintzinger for stimulating discussions. The C.N.R.S. is gratefully acknowledged for financial support.

Received, 21st September 1984; Com. 1338

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