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Structure of a Synthetic Trefoil Knot Coordinated to Two Copper(I) Centers**

By Christiane O. Dietrich-Buchecker, Jean Guilhem, Claudine Pascard,* and Jean-Pierre Sauvage*

Although knotted forms of DNA are relatively common, as shown by recent results of molecular biology,^[1, 2] knotted compounds in chemistry have only been envisaged and discussed as hypothetical objects.^[3–5] A year ago, the first synthetic trefoil knot was reported.^[6] The preparation of this topologically novel molecular system was made possible by the use of a double three-dimensional template effect. Two coordinating molecular threads were interlaced on two copper(I) centers, forming a double helix, the precursor of a knotted system.

Although convincing evidence for the knotted topology of the molecule was obtained from mass and $^1\text{H-NMR}$ studies, in particular by taking advantage of the chirality of a trefoil knot, it was of utmost importance to obtain an X-ray structure of the molecule. In the meantime this has been achieved, and we now report the molecular structure of the compound. This study removes the last uncertainty regarding the knotted structure of the molecule obtained. It also provides interesting data on the fine structure and conformation. Moreover, it demonstrates that the knotted compound undergoes spontaneous resolution, which is very encouraging for a future separation into right- and left-knotted enantiomers.^[7]

The chemical representation of the molecule is given in Figure 1. The organic skeleton is made up of a single 86-membered molecular chain, whose ends are tied with formation of a trefoil knot. The molecule still contains the two copper(I) centers used as templating species during the synthesis.

[*] Dr. C. Pascard, Dr. J. Guilhem
Laboratoire de Cristallographie
Institut de Chimie des Substances Naturelles, CNRS
F-91198 Gif-sur-Yvette (France)

Dr. J. P. Sauvage, Dr. C. O. Dietrich-Buchecker
Laboratoire de Chimie Organo-Minérale, UA 422 du CNRS
Institut de Chimie, Université Louis Pasteur
F-67008 Strasbourg (France).

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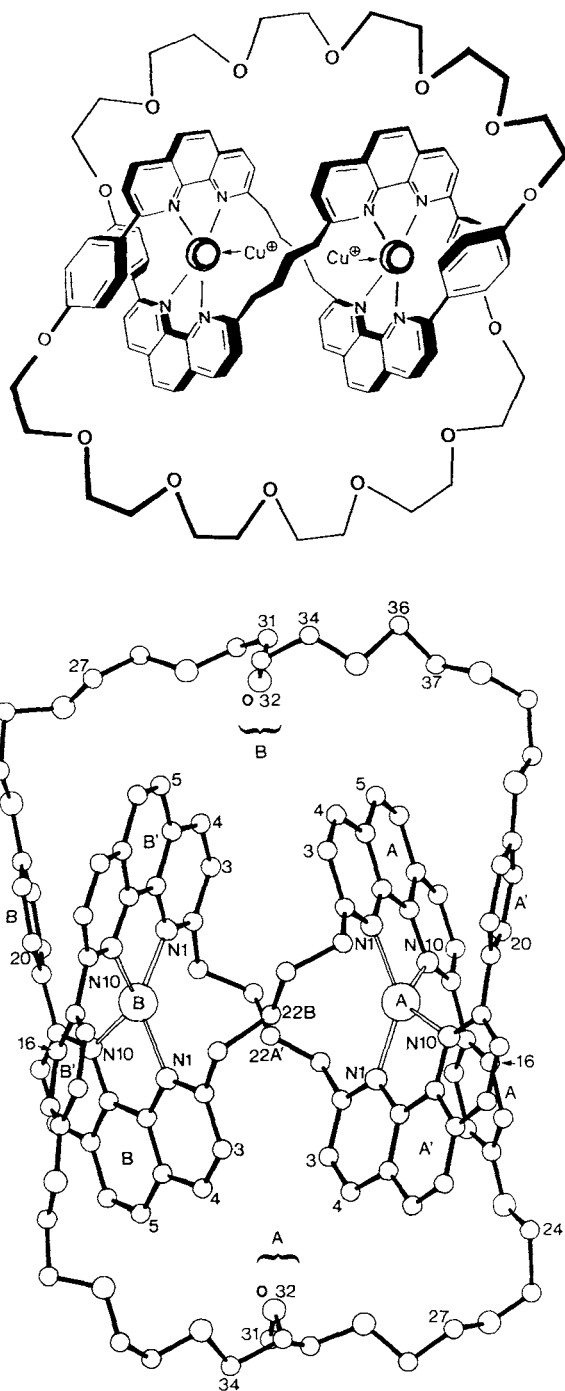


Fig. 1. Structural formula (top) and ORTEP of the knotted compound. For sake of clarity, the written symbols corresponding to the crystallographic numbering have all been omitted, those of O partly omitted. A denotes CuA and B denotes CuB.

The X-ray crystallographically determined molecular structure is shown in Figure 1 (bottom).^[8] The molecule has effective D_2 symmetry, with three mutually perpendicular pseudo-twofold axes, one joining the two copper cations, one passing through the middle of the two $(\text{CH}_2)_4$ bridges, and the third one passing through the central oxygens of the two polyoxyethylene chains. The symmetry places the two complexes around CuA and CuB, with their respective 1,10-phenanthroline rings (CuA with phen A and phen A' and CuB with phen B and phen B') in superimposed fashion: A over B', and A' over B. Starting from phen A, the molecular

ribbon goes along the $(\text{CH}_2)_4$ bridge joining phen A to phen B, turns around CuB with phen B, follows the long oxy chain B back to phen A', turns around CuA with phen A', goes along the second $(\text{CH}_2)_4$ bridge to phen B', and, following the oxy chain A, ends up at the starting point phen A.

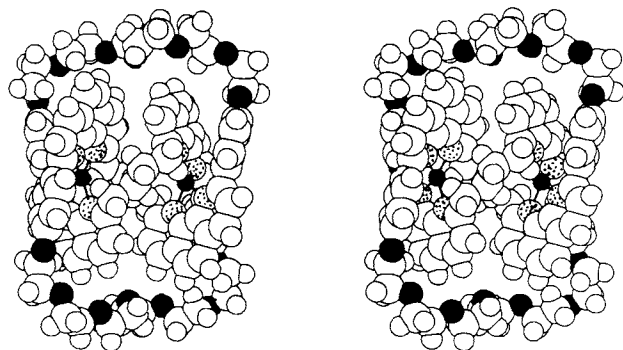


Fig. 2. Stereoview of the knotted compound.

The stereoview (Fig. 2) shows how the two metal atoms are located 6.3 Å apart inside a double helix. The two complexes, around CuA and CuB face each other with similar coordination angles (see Table 1), the wider angle (141° average) opening towards the center of the knot.

Table 1. Structural data of the Cu centers

Cu A environment		Cu B environment	
<i>Distances [Å]</i>			
Cu-N1A	2.00(3)	Cu-N1B	2.08(2)
Cu-N10A	2.14(2)	Cu-N10B	2.06(3)
Cu-N1A'	1.95(2)	Cu-N1B'	2.11(2)
Cu-N10A'	2.11(2)	CuN10B'	2.13(3)
<i>Angles [°] ($\sigma \approx 1^\circ$)</i>			
N1A-Cu-N10A	83	N1B-Cu-N10B	80
N1A'-Cu-N10A'	83	N1B'-Cu-N10B'	79
N10A-Cu-N10A'	128	N10B-Cu-N10B'	135
N10A-Cu-N1A'	113	N10B-Cu-N1B'	112
N1A-Cu-N10A'	114	N1B-Cu-N10B'	120
N1A-Cu-N1A'	143	N1B-Cu-N1B'	140

The general molecular shape of the knotted complex can be compared with that of the chemically related dicopper(I) [3]-catenate consisting of two peripheral 30-membered rings separately interlocked with a central 44-membered ring.^[9, 10] In the [3]-catenate, the Cu...Cu distance is noticeably longer than in the knot (8.0 Å instead of 6.3 Å), although better π -stacking is observed in the [3]-catenate than in the knot (see Table 2). In the [3]-catenate^[10] the superimposed

Table 2. Relevant dihedral angles [°] between aromatic rings.

	Phenyl A	phen A'	Phenyl A'	phen B	Phenyl B	phen B'	Phenyl B'
phen A	43	64	29	60	19	24	45
Phenyl A		25	37	16	26	52	23
phen A'			43	20	46	60	22
Phenyl A'				50	20	18	22
phen B					42	67	32
Phenyl B						28	38
phen B'							39

phenanthroline rings are roughly parallel (dihedral angle 7°), whereas in the knotted compound they are inclined toward each other (24° and 20°) with their tip ends in proximity: average distance between H3 and H4 of each pair of phenanthrolines (A-B' and A'-B): 3.5 Å. On the other hand, the coordination sphere of each copper(I) ion in the knotted compound is only very slightly distorted compared to that in the [3]-catenate.

Within the complex units of the knotted compound, the dihedral angle between the two phenanthroline rings is 64 and 67° respectively, which reflects the strong distortion of each coordination polyhedron from a tetrahedral geometry. Furthermore, each phenyl ring forms a dihedral angle of approximately 42° with its bonded phenanthroline.

All the oxygen atoms of the polyoxyethylene chains are turned inward, and the molecule has a rectangular hydrophobic feature. The chains are actually a little too long, as can be seen by the folded fragments around the central oxygens O32A and O32B.

The centers of the short $(\text{CH}_2)_4$ bridges are very close together, with short distances between the hydrogens of the methylenic carbon atoms C22B and C22A'. Many other short distances exist, in particular between the hydrogen atoms of the hexaethyleneoxy chains and the aromatic groups. The most important data have been collected in Table 3.

Table 3. Shortest intramolecular H-H distances [Å] ($\sigma \approx 0.1$ Å).

<i>Between superimposed phenanthroline rings</i>	<i>Between phenyl rings</i>
H4A-H4B' 3.5	H16A-H20A' 2.4
H4B-H4A' 3.4	H16B'-H20B 2.5
H4B-H3A' 3.4	
<i>Between phenanthroline rings and polyoxyethylene chains [a]</i>	<i>Between (CH₂)₄ bridges</i>
H5A-H _a 37B 2.8	H _a 22B-H _a 22A' 2.3
H4A'-H _a 27A 2.6	
H5B-H _a 31A 2.7	
H5B'-H _a 27B 2.4	
<i>Between the methylene groups in a chain [a]</i>	
H _a 24A-H _a 27A 2.4	
H _b 31A-H _b 34A 2.2	
H _a 31B-H _a 34B 2.2	
H _a 31B-H _b 36B 2.5	

[a] H_a and H_b are the two H atoms of a given CH₂ group.

Further, the X-ray structure analysis revealed that the chiral dicopper(I) knotted compound crystallizes as a conglomerate of enantiomers, i.e. a given crystal contains only one enantiomer: Figure 3 shows a stereoview of the unit cell with two left knotted enantiomers.

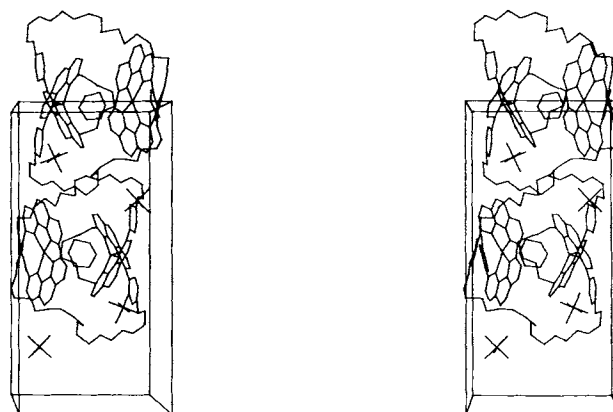


Fig. 3. Stereoview of the unit cell. Shown are two complexes, four anions (PF_6^-), and two solvent molecules (benzene).

Experimental

Crystals of $[C_{104}H_{104}N_8O_{14}Cu_2](PF_6)_2 \cdot C_6H_6$ were grown from CH_2Cl_2/C_6H_6 by vapor diffusion of benzene. The dark-red, well-shaped crystals obtained ($0.8 \times 0.3 \times 0.1$ mm) were sealed in a capillary tube. Intensity data were collected at 1.1 Å resolution ($\theta_{max} = 45^\circ$) with an automatic Philips PW1100 diffractometer, wavelength $Cu_{K\alpha}$ ($\lambda = 1.5418$ Å), graphite monochromator. From 7925 unique measured reflections, only 2967 independent reflections with $I \geq 2\sigma(I)$ were kept in the calculations. $M = 2183$, monoclinic, space group $P2_1$, $a = 13.462(6)$, $b = 27.841(14)$, $c = 13.912(7)$ Å $\beta = 93.66(4)^\circ$, $V = 5204$ Å³, $Z = 2$, $\rho_{calc} = 1.39$ g cm⁻³. Structure solved by direct methods [11]. High pseudo symmetry rendered the crystallographic study very difficult. Low resolution and thermal agitation led to rigid block refinement of the aromatic parts (except in the last refinement cycle) and constraints in the long chains. The final R factor is 12.8%. Further details of the crystal structure will be published elsewhere and will be available from the Director of the Cambridge Crystallographic Data center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (UK), on quoting the names of the authors and the journal citation.

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Synthesis, Structure, and Catalase-Type Activity of a Novel Oxo-Bridged Tetranuclear Manganese Aggregate Exhibiting Short O...O Interactions

By Robert T. Stibrany and Sergiu M. Gorun*

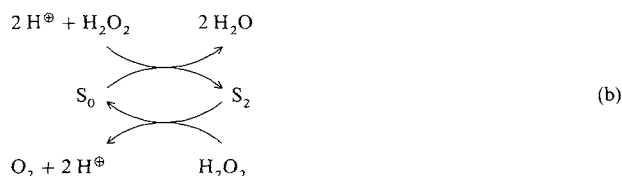
Dedicated to Professor Stephen J. Lippard on the occasion of his 50th birthday

Due to their relevance to the catalytic center of the photosynthetic water splitting apparatus of green plants and cyanobacteria, tetranuclear manganese aggregates have become a subject of intensive research.^[1] A Mn₄ unit is essential for the coupling of two water molecules and liberation of dioxygen [Eq. (a)] in photosystem II (PSII).^[2]



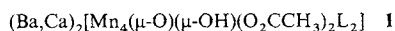
During this process the Mn₄ aggregate passes through five oxidation states, S₀ to S₄, S₀ representing the most reduced state.^[3] The S₀ state is believed to comprise one Mn^{II} and

three Mn^{III} centers.^[1] EXAFS and EPR spectroscopy suggest that the Mn ions are primarily ligated by O donor atoms.^[1, 2] Oxo, hydroxo or alkoxo groups are believed to bridge the metals. Two hydroxo groups (to be evolved as O₂ after deprotonation and coupling) have been postulated to be present in the S₀ state.^[4] Calcium has also been shown to be essential for activity but its function is not understood.^[5] Interestingly, in the absence of light the PSII reaction center can evolve O₂ when H₂O₂ is added as a substrate, a process believed to involve the S₀ and S₂ states [Eq. (b)].^[6]



Despite great efforts no structurally characterized model for the S₀ state exists.^[1c, 7] Furthermore, tetranuclear manganese aggregates associated with the biologically relevant calcium ions are not known, and, to our knowledge, biomimetic activity has not been reported thus far for the inorganic models.

We report here the synthesis and structural characterization of the mixed valence Mn^{II}Mn^{III} complex **1**,^[8] which contains an unprecedented (Mn₄O₂H)⁸⁺ core. We also report the catalytic biomimetic decomposition of H₂O₂ by **1**.



L = 1,3-Diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetic acid.

In the anion of **1**, shown in Figure 1, the four manganese ions describe a trapezoid. A crystallographically imposed

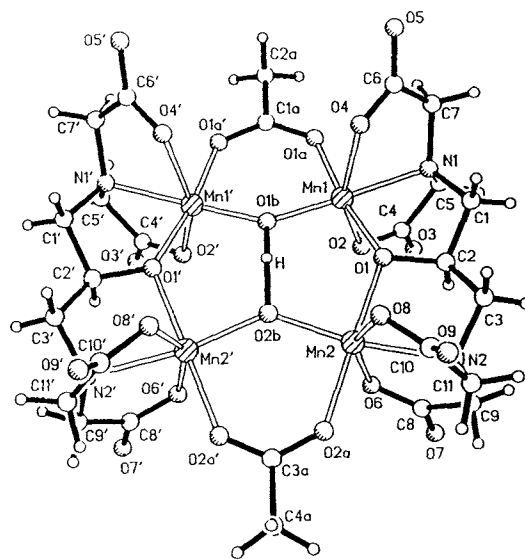


Fig. 1. Structure of the anion of **1** in the crystal. Selected bond lengths [Å] and angles [°]: Mn1–Mn1' 3.379(2), Mn2–Mn2' 3.584(2), Mn1–Mn2 3.718(1), Mn1–O1b 1.817(2), Mn1–O1a 1.961(4), Mn1–O4 2.217(4), Mn1–N1 2.120(4), Mn1–O2 2.152(4), Mn1–O1 1.954(3), Mn2–O2b 1.925(3), Mn2–O2a 2.078(5), Mn2–O8 2.169(5), Mn2–N2 2.190(4), Mn2–O6 2.140(4), O1b–H 1.2(2), O2b–H 1.3(1); Mn1–O1b–Mn1' 136.8(3), Mn2–O2b–Mn2' 137.2(4), Mn1–O1–Mn2 132.5(2), O1b–H–O2b 156(10).

[*] Dr. S. M. Gorun, R. T. Stibrany
Exxon Research & Engineering Company
Corporate Research Science Laboratories
Annandale, N. J. 08801 (USA)