Copper(I)-Assembled Pseudorotaxanes Bearing Bis(nitrile) Ligands: Selective Formation of Large Chelate Rings

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The syntheses of two novel Cu^I-bis(benzonitrile) complexes of the type $[Cu(dCN_n)_2][PF_6]$ {where $dCN_n = NCPhO(CH_2)_n$-OPhCN, $n = 3, 4$} are described. Both compounds have been characterized by X-ray crystallography. To our surprise, and although the two complexes were quite similar, two very distinct structures were obtained. For the $[Cu(dCN_4)_2][PF_6]$ complex, a tetrahedral geometry was observed whereas for $[Cu(dCN_3)_2][PF_6]$, a polymeric assembly was formed. A further extension of this work involved the syntheses of two threaded species bearing the M30 macrocycle, Cu metal and a dCN_n ligand. The formation of the desired complexes was confirmed by means of mass spectrometry as well as 1-D and 2-D ^1H NMR spectroscopy. Finally, the cyclic voltammograms of all 4 new species were recorded giving rise to redox potentials ranging from +0.88 to +1.25 V. These new threaded complexes are of particular interest since they can form the basis of novel rotaxane structures.

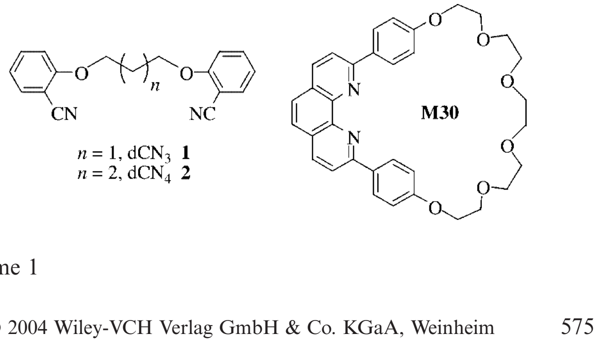
Introduction

Nowadays rotaxanes and catenanes constitute an important class of compounds[1] exhibiting interesting properties such as photoinduced electron transfer[2] and controlled molecular motion.[3] Due to the various synthetic strategies developed during the course of the last 20 years, interest in these multi-component systems has experienced a spectacular revival. However, as some of the synthetic approaches employed for their preparation are based on a metal-templated strategy,[4] the metallic species involved should be carefully chosen as it plays an essential role in the actual assembling of such complex structures. In addition, the electronic properties of the metal in question are important in order to control intramolecular electron transfer processes, in relation to the modeling of the photosynthetic reaction center, or to trigger electrochemically driven motions in artificial molecular machines and motors.[5] Traditionally, tetrahedral copper(I) has been the metal of choice in order to induce the formation of entangled structures from two coordinating molecular threads or to drive the formation of a pseudo-rotaxane from a ring and a molecular string.[4] Moreover, the use of octahedrally coordinated metal centers in order to assemble and pre-organize the various organic fragments to be incorporated in the desired catenanes and rotaxanes has also been described.[6,7] A further extension of this work involved the use of a five-coordinate Zn^{2+} center bearing terpyridine and phenanthroline as the coordinating ligands thus giving rise to novel catenane structures.[8]

Although the bidentate chelate of choice has mainly been the 1,10-phenanthroline (phen) unit and its derivatives, other ligands can be envisaged which should also lead to intertwined or threaded species, precursors of the catenanes and rotaxanes to be synthesized. Since copper(I) forms relatively stable complexes with π-accepting ligands and, in particular, with acetonitrile, the possibility of using bidentate chelates consisting of two terminal benzonitrile groups has been explored. In the present article the coordination chemistry between copper(I) and the aforementioned ligands as well as the formation of threaded complexes containing the traditional phen-incorporating 30-membered ring (M30),[9] copper(I) and a bis(nitrile) ligand is described.

Results and Discussion

The bis-nitrile ligands, as well as the 30-membered ring (M30) used in the preparation of the threaded complexes are represented in Scheme 1.



Scheme 1

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Surprisingly, chelates consisting of two or more nitrile groups as coordinating sites have been very scarcely used. Angelici and co-workers synthesized a series of interesting complexes with various metal centers in conjunction with such ligands or their isocyanide analogues.[10] Recently, our group also described the synthesis of ruthenium(II) benzonitrile complexes in relation to light-driven molecular machines and motors.[11]

1. Synthesis of [Cu(dCN$_n$)$_2$][PF$_6$] (n = 3, 4) Complexes

The synthesis of the two novel copper(I)–bis(benzonitrile) complexes is depicted in Equation (1).

$$[Cu(CH_3CN)_4][PF_6] \xrightarrow{2\ dCN_n} [Cu(dCN_n)_2][PF_6] + 4\ CH_3CN \qquad (1)$$

$n = 3$, $[Cu(dCN_3)_2][PF_6]$ **3**

$n = 4$, $[Cu(dCN_4)_2][PF_6]$ **4**

Reaction of $Cu(CH_3CN)_4{\cdot}PF_6$ with two equivalents of the corresponding dCN$_n$ (n = 3, 4) ligand in dichloromethane results in the quantitative formation of compounds **3** and **4**. The novel complexes were obtained as solids and were characterized by mass spectrometry and ^{1}H NMR spectroscopy. Moreover, reversible cyclic voltammograms were recorded for both Cu–dCN$_n$ complexes. In particular, $[Cu(dCN_3)_2]^{2+/+}$ showed a remarkably high redox potential of $E° = +1.20$ V vs. the SCE in CH_2Cl_2, similar to that of the tetrahedral complex $[Cu(dCN_4)_2]^{2+/+}$ ($E° = +1.25$ V vs. SCE) in the same solvent.

X-ray Structural Studies

In both cases, single crystals suitable for X-ray analysis were obtained by slow diffusion of n-hexane (for compound **3**) or diisopropyl ether (for compound **4**) into a degassed solution of the corresponding complex in dichloromethane. Although the only difference between the two Cu–dCN$_n$ complexes resides in the number of carbon atoms incorporated in the chain connecting the two benzonitrile rings, it is sufficient to give rise to two distinct structures as shown in Figures 1 and 2. Thus, although for the $Cu(dCN_3)_2{\cdot}PF_6$ complex a polymeric structure was obtained, for the $Cu(dCN_4)_2{\cdot}PF_6$ compound a monomeric tetrahedral structure was quantitatively formed. In the latter case, a bis-macrocyclization was achieved resulting in the formation of two 15-membered rings assembled around the copper center. The stability of this complex is remarkable confirming the preference of Cu^I in a tetra-coordinated geometry, as well as the "chelate" effect that the two dCN$_4$ ligands are exerting on the metal atom. Moreover, the high yielding reaction leading to this complex shows that very large metallacycles can be strongly stabilized over ill-defined oligomers or polymers. This is consistent with the observation that cyclic assemblies are very often formed quantitatively from multisite ligands and appropriate metal centers, one of the archetypical examples being that of Fujita's squares consisting of 4 Pd^{II} atoms at the corners and four 4,4′-bipyridine units as edges.[12]

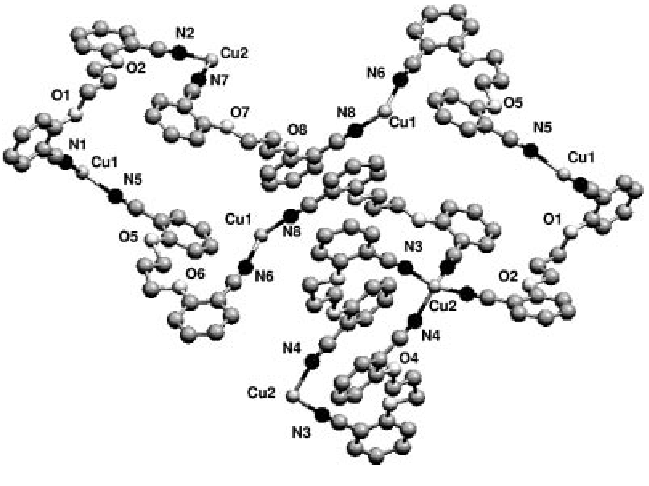


Figure 1. Repeating unit of the polymeric structure obtained for $[Cu(dCN_3)_2][PF_6]$. The assembly consists of 2 types of macrocycles of different size. Hence, the small cycle (28-membered ring) contains two Cu centers connected via two dCN$_3$ ligands whereas the larger cycle (84-membered ring) bears six Cu centers and the same number of dCN$_3$ ligands connected to each other in an alternating fashion (Cu-dCN$_3$–Cu-dCN$_3$···)

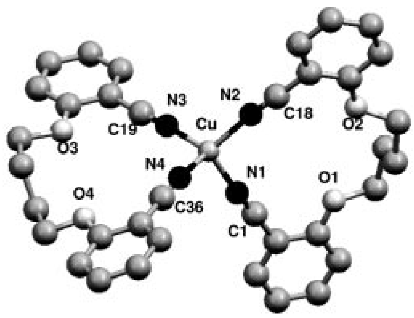


Figure 2. Crystal structure of $[Cu(dCN_4)_2][PF_6]$. A tetrahedral geometry around the Cu-center, can be observed with the average Cu–N distances being 1.97 Å. Hydrogen atoms are omitted for clarity. The average N–Cu–N bond angle is 109.4 deg

It should be noted, however, that in the case of the polymeric structure **3** the average Cu^I–N bond length was found to be 1.99 Å which is not significantly different from that of the monomeric complex **4** (1.97 Å) and of the same order of magnitude as the average bond length found in $[Cu(CH_3CN)_4][PF_6]$ (1.99 Å).[13] On the other hand, a slightly longer Cu^I–N distance was measured in the tetrakis benzonitrile Cu^I complex $[Cu(PhCN)_4][SbCl_6]$ (2.05 Å).[14] Selected bond lengths and bond angles are given for both complexes in Tables 1 and 2.

2. Synthesis of [Cu(M30)(dCN$_n$)][PF$_6$] (n = 3, 4) Threaded Complexes

Having successfully synthesized the two new Cu-dCN$_n$ complexes, the threading reaction incorporating a ring, namely M30, the Cu metal and a dCN$_n$ ligand was also attempted in order to see if the synthesis of pseudo-rotaxane structures based on such benzonitrile ligands was feasible.

Based on CPK models, the dCN ligand was found to fit comfortably within the cavity of the M30 ring which was therefore chosen as the macrocycle for the threading reac-

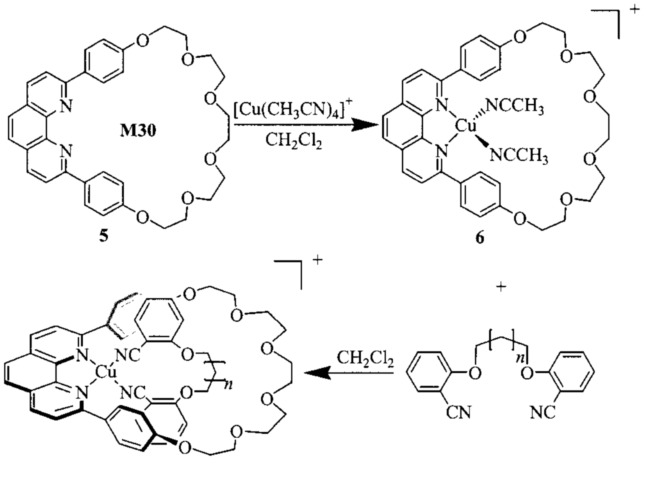
Table 1. Selected bond lengths [Å] and bond angles [deg] for **3**

3	Length (Å)	**3**	Angle (deg)
$Cu(1)-N_{dCN(1)}$	2.01	$N_{dCN(1)}-Cu(1)-N_{dCN(5)}$	114.2
$Cu(1)-N_{dCN(5)}$	2.00	$N_{dCN(1)}-Cu(1)-N_{dCN(6)}$	113.2
$Cu(1)-N_{dCN(6)}$	2.00	$N_{dCN(1)}-Cu(1)-N_{dCN(8)}$	103.9
$Cu(1)-N_{dCN(8)}$	1.989	$N_{dCN(5)}-Cu(1)-N_{dCN(6)}$	101.2
$Cu(2)-N_{dCN(2)}$	2.001	$N_{dCN(5)}-Cu(1)-N_{dCN(8)}$	110.6
$Cu(2)-N_{dCN(2)}$	2.001	$N_{dCN(6)}-Cu(1)-N_{dCN(8)}$	114.1
$Cu(2)-N_{dCN(3)}$	1.997	$N_{dCN(2)}-Cu(2)-N_{dCN(3)}$	110.7
$Cu(2)-N_{dCN(4)}$	2.009	$N_{dCN(2)}-Cu(2)-N_{dCN(7)}$	107.4
$Cu(2)-N_{dCN(7)}$	1.99	$N_{dCN(3)}-Cu(2)-N_{dCN(7)}$	115.6
		$Cu(1)-N_{dCN(1)}-C_{(1)}$	178.0

Table 2. Selected bond lengths [Å] and bond angles [deg] for **4**

4	Length (Å)	**4**	Angle (deg)
$Cu(1)-N_{dCN(1)}$	2.004	$N_{dCN(1)}-Cu(1)-N_{dCN(2)}$	107.8
$Cu(1)-N_{dCN(2)}$	1.955	$N_{dCN(2)}-Cu(1)-N_{dCN(3)}$	116.7
$Cu(1)-N_{dCN(3)}$	1.982	$N_{dCN(3)}-Cu(1)-N_{dCN(4)}$	107.6
$Cu(1)-N_{dCN(4)}$	1.963	$N_{dCN(1)}-Cu(1)-N_{dCN(4)}$	110.7
		$N_{dCN(1)}-Cu(1)-N_{dCN(3)}$	104.9
		$N_{dCN(2)}-Cu(1)-N_{dCN(4)}$	109.0
		$Cu(1)-N_{dCN(1)}-C(1)$	173.7

tion. The synthetic strategy employed in order to prepare the desired threaded species is shown in Scheme 2.



$n = 1$, [Cu(M30)(dCN$_3$)][PF$_6$] **7**
$n = 2$, [Cu(M30)(dCN$_4$)][PF$_6$] **8**

Scheme 2. Synthesis of the threaded complexes **7** and **8**

Thus, to a degassed solution of M30 in dichloromethane, a solution of the $Cu(CH_3CN)_4{\cdot}PF_6$ salt in the same solvent was added. Upon addition, a drastic change in color was observed from yellow to orange confirming the formation of complex **6**. To this complex, a solution of the corresponding dCN$_n$ ligand was added and the reaction stirred overnight at ambient temperature under argon. The formation of the desired complexes **7** and **8** was confirmed by means of mass spectrometry and 1-D and 2-D ^1H NMR spectroscopy. In particular the 2-D NMR spectra were very informative, well-resolved and corresponded to the desired compounds. As shown in Figure 3, ^1H NMR spectroscopy confirmed the threaded structure of **8** and the entwining of the phen and dCN$_4$ units around the metal center. A similar spectrum was also obtained for compound **7**.

Hence, due to the intense ring current effect of the C_6H_4CN units, the resonance signals corresponding to the H_o and H_m protons of the phenoxy moieties in the threaded complex move to higher field compared with the free ligand M30. The same pattern was also observed for the $H_{1'}$ protons of the dCN$_4$ ligand which, upon threading, experience the ring current of the macrocycle and thus move to lower ppm values. This NMR behavior is in accord with previously described systems.[15] 2-D ^1H NMR spectroscopy was also employed in order to further elucidate both structures. The ROESY spectrum of complex **8** is given as a representative example in Figure 4. As expected, signals in the aromatic region showing the through space coupling of protons $H_{5,6}$ with $H_{4,7}$ and H_o with $H_{3,8}$ were observed. Moreover, interactions between the H_α protons of the dCN$_4$ ligand with $H_{4'}$ as well as coupling of the H_a protons of the M30 chain with H_m were present.

However, the threading reaction was mainly confirmed by the ROESY signals such as those between the $H_{4'}$ protons of dCN$_4$ and the $H_{b,c,d}$ protons of the M30 ring, as well as the signals between the H_α and H_β protons of dCN$_4$ and the H_a and $H_{b,c,d}$ protons of the macrocyclic chain. Two equally important signals stem from the interactions of both H_α and H_β protons of the dCN$_4$ ligand with the H_m protons of the phenoxy rings. All these observations are consistent with the interactions predicted based on the CPK model of the threaded structure in question.

Finally, the cyclic voltammograms of the pseudorotaxane structures **7** and **8** were also obtained. Hence, for the threaded complexes the *E*° values were found to be +0.95 V and +0.88 V for $[Cu(M30)(dCN_3)]^{2+/+}$ and $[Cu(M30)(dCN_4)]^{2+/+}$, respectively. The less positive *E*° values of compounds **7** and **8**, when compared with the *E*° values of **3** and **4**, indicate a slight destabilization of the Cu^I oxidation state versus Cu^{II} upon formation of the pseudorotaxane structures. Unfortunately, all attempts to grow crystals suitable for X-ray analysis were unsuccessful for either of the two complexes.

However, both compounds are of particular interest since they could form the basis of novel rotaxane structures. Forming derivatives of the benzene rings could be envisaged in order to attach "stoppers" at each of the dCN fragments thus leading to the final rotaxanes.

Experimental Section

General: ^1H NMR spectra were acquired on either a Bruker AM 300 (300 MHz) or a Bruker AM 400 (400 MHz) spectrometer using the deuterated solvent as the lock and the residual solvent as the internal reference. Mass spectra were obtained using a VG ZAB-HF (FAB) spectrometer or a VG-BIOQ triple quadrupole, positive mode (ES-MS). Electrochemical experiments were performed using an EG&G PAR model 273A potentiostat with a standard three-

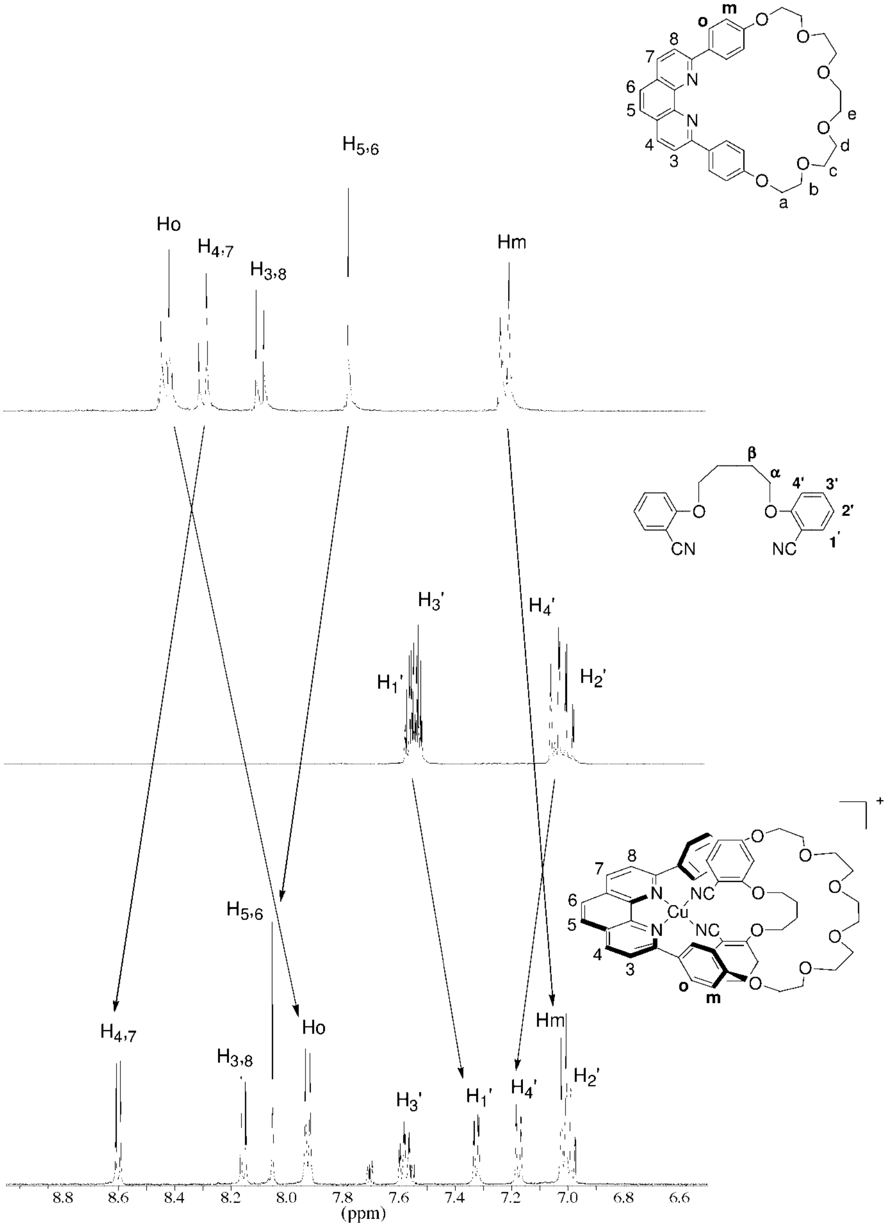


Figure 3. ^{1}H NMR spectra showing the aromatic regions of the macrocyclic ring **5**, the free ligand **3** and the corresponding threaded complex **8** in CD_2Cl_2

electrode configuration. Cyclic voltammetry was carried out in CH_2Cl_2, using as supporting electrolyte a Pt working electrode, a Pt counter-electrode, and an SCE as the reference electrode. The typical sweep rate was 100 mV/s, and the window used was from −2.0 V to +1.4 V. The following chemicals were prepared according to literature procedures: M30,[9] dCN$_3$,[11] dCN$_4$.[11] CH_2Cl_2 was dried by heating to reflux over CaH_2 followed by distillation.

[Cu(dCN$_3$)$_2$][PF$_6$] (3): To a degassed solution of $Cu(CH_3CN)_4{\cdot}PF_6$ (36.2 mg, 0.09 mmol) in CH_2Cl_2 (4 mL) was added a solution of dCN$_3$ (54.3 mg, 0.19 mmol) in the same solvent (4 mL) and the resultant reaction mixture was left stirring at 20 °C under argon for 24 h. Evaporation of the solvent gave complex **3** as a yellowish solid (69 mg). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta = 7.73-7.60$ (m, 4 H), 7.18−7.06 (m, 4 H), 4.38 (t, $J = 5.5$ Hz, 4 H), 2.45 (q, $J = 5.5$ Hz, 2 H) ppm. MS: (ES-MS): m/z (%) = 619 (100) [M − H − PF_6^-], 341 (100) [M − dCN$_3$ − H − PF_6^-]. Redox potential (V vs. SCE): $E°$ ($Cu^{II/I}$) = 1.20 V.

[Cu(dCN$_4$)$_2$][PF$_6$] (4): To a degassed solution of $Cu(CH_3CN)_4{\cdot}PF_6$ (88.9 mg, 0.24 mmol) in CH_2Cl_2 (10 mL) was added a solution of dCN$_4$ (0.14 g, 0.48 mmol) in the same solvent (10 mL) and the resultant reaction mixture was left stirring at 20 °C under argon for 12 h. Evaporation of the solvent gave complex **4** as a white solid (187 mg, 98%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta = 7.71-7.59$ (m, 4 H), 7.11−7.01 (m, 4 H), 4.18 (br. s, 4 H), 2.13 (br. s, 4 H) ppm. MS: (ES-MS): m/z (%) = 647 (86) [M − H − PF_6^-], 355 (100) [M − dCN$_4$ − H − PF_6^-]. Redox potential (V vs. SCE): $E°$ ($Cu^{II/I}$) = 1.25 V.

[Cu(M30)(dCN$_3$)][PF$_6$] (7): A solution of $Cu(CH_3CN)_4{\cdot}PF_6$ (17 mg, 0.04 mmol) in degassed CH_2Cl_2 (6 mL) was added under argon and

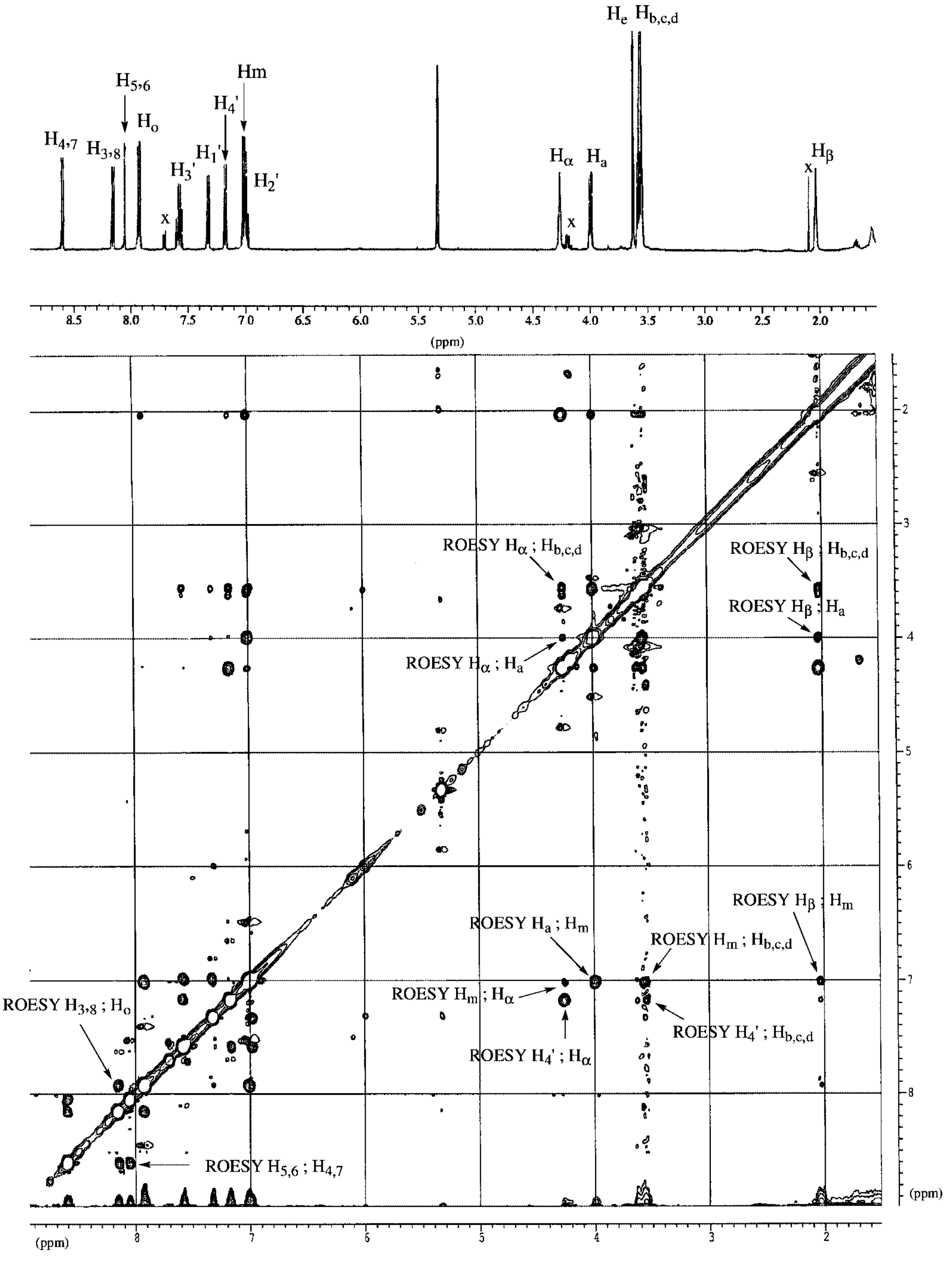


Figure 4. ROESY spectrum of the threaded complex **8** in CD_2Cl_2, (X denotes a small amount of impurity)

at 20 °C to a stirred degassed solution of M30 (25.8 mg, 0.04 mmol) in CH_2Cl_2 (5 mL) via a cannula. The instantaneous appearance of a deep orange color was ascribed to the formation of **6**. After 1 h at room temperature a solution of dCN_3 (12.7 mg, 0.04 mmol) in CH_2Cl_2 (5 mL) was added to **6**. The resultant reaction mixture was stirred for a further 2.5 h under argon. Evaporation of the solvent gave **7** as a brown solid (47 mg, 99.2%). ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 8.63 (d, J = 8.2 Hz, 2 H), 8.19 (d, J = 8.4 Hz, 2 H), 8.07 (s, 2 H), 7.92 (d, J = 8.5 Hz, 4 H), 7.56 (ddd, J = 8.0, J = 1.7, J = 1.4 Hz, 2 H), 7.47 (dd, J = 7.8, J = 1.7 Hz, 2 H), 7.11 (d, J = 8.5 Hz, 2 H), 7.05 (d, J = 7.8 Hz, 4 H), 7.03 (dt, J = 7.5, J = 0.7 Hz, 2 H), 4.34 (t, J = 5.8 Hz, 4 H), 4.06 (t, J = 5.6 Hz, 4 H), 3.62 (t, J = 5.6 Hz, 8 H), 3.59 (s, 4 H), 3.54 (s, 4 H), 2.36 (q, J = 5.8 Hz, 2 H) ppm. MS: (ES-MS): m/z (%) = 907 (79) [M − H − PF_6^-], 629 (74) [M − dCN_3 − PF_6^-]. Redox potential (V vs. SCE): $E°$ ($Cu^{II/I}$) 0.95 V.

[Cu(M30)(dCN$_4$)][PF$_6$] (8): A solution of $Cu(CH_3CN)_4{\cdot}PF_6$ (62.9 mg, 0.17 mmol) in degassed CH_2Cl_2 (15 mL) was added under argon and at 20 °C to a stirred degassed solution of M30 (96.1 mg, 0.17 mmol) in CH_2Cl_2 (15 mL) via a cannula. The instantaneous appearance of a deep orange color was ascribed to the formation of **6**. After 1 h at room temperature a solution of dCN_4 (49.6 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) was added to **6**. The resultant reaction mixture was stirred for a further 2.5 h under argon. Evaporation of the solvent gave **8** as a brown solid (176 mg, 99%).

^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): δ = 8.60 (d, J = 8.4 Hz, 2 H), 8.15 (d, J = 8.2 Hz, 2 H), 8.05 (s, 2 H), 7.92 (d, J = 8.7 Hz, 4 H), 7.58 (ddd, J = 8.0, J = 1.7, J = 1.4 Hz, 2 H), 7.32 (dd, J = 7.8, J = 1.7 Hz, 2 H), 7.17 (d, J = 8.5 Hz, 2 H), 7.01 (d, J = 8.8 Hz, 4 H), 6.98 (dt, J = 7.5, J = 0.9 Hz, 2 H), 4.26 (s, 4 H), 3.99 (t, J = 6.0 Hz, 4 H), 3.62 (s, 4 H), 3.54−3.60 (m, 12 H), 2.03 (s, 4 H) ppm. MS: (FAB-MS): m/z (%) = 921 (60) [M − H − PF$_6^-$], 629 (100) [M − dCN$_4$ − PF$_6^-$]. Redox potential (V vs. SCE): $E°$ (Cu$^{II/I}$) = 0.88 V.

X-ray Data Collection: Crystal data and details of data collection for both **3** and **4** are given in Table 3. The Mo1EN package was used for all computations.[16]

Table 3. Crystallographic data for **3** and **4**

	3	4
Empirical formula	$C_{68}H_{58}Cu_2F_{12}N_8O_9P_2$	$C_{72}H_{64}Cu_2N_8O_8{\cdot}2PF_6$
Formula mass	1548.28	1586.37
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P1\ 2_1/c1$
a (Å)	15.3889(3)	15.7347(2)
b (Å)	16.1548(3)	14.2188(2)
c (Å)	16.9597(3)	32.8202(4)
α (deg)	62.249(5)	90
β (deg)	75.535(5)	91.868(5)
γ (deg)	73.918(5)	90
V (Å^3)	3548.9(1)	7338.9(2)
Z	2	4
Color	colorless	colorless
$D_{calcd.}$ (g cm^{-3})	1.45	1.44
μ (mm^{-1})	0.736	0.713
Temp. (K)	173	173
λ (Å)	0.71073	0.71073
R[a]	0.096	0.083
R_w[b]	0.113	0.097

CCDC-215999 and -216000 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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