Self assembly of a diphenanthrolinylpyrene-bridged Cu^{I} trimer

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The ligand 1,8-di(1,10-phenanthrolin-2-yl)pyrene has been prepared and complexed with Cu^{I} such that three ligands bridge a triangular arrangement of three metals resulting in a symmetrical helical assembly with each pyrene layered between two phenanthrolines at optimum π-stacking distance.

The use of metals and appropriate bridging ligands has become a dominant theme in the construction of some interesting three dimensional arrays.[1] Cu^{I} is particularly useful in this regard since many of its diimine complexes are labile, allowing ligand interchange to occur until the most thermodynamically stable assembly has been attained.[2] This report will focus on a Cu^{I} trimer of a diphenanthrolinylpyrene ligand **3**.

The Friedel–Crafts diacetylation of pyrene affords a mixture of the 1,3-, 1,6- and 1,8-diacetyl derivatives from which the pure 1,8-isomer **1** can be isolated.[3] When this material is treated with 2 equiv. of 8-aminoquinoline-7-carbaldehyde,[4] a 93% yield of 1,8-di(1,10-phenanthrolin-2-yl)pyrene **3** was obtained (Scheme 1). Treatment of this ligand in MeCN–CH_2Cl_2 (3 : 4) with 1 equiv. of [Cu(MeCN)$_4$]ClO$_4$ afforded a crude material which upon extraction with MeCN provided a 36% yield of the complex [(Cu**3**)$_3$](ClO$_4$)$_3$.

Constable and co-workers[5] have reported a system where two 6-substituted 2,2′-bipyridines joined by a 1,3-phenylene spacer bridged two metals while Sauvage and co-workers[6] have prepared a related di-1,10-phenanthrolinyl analogue. We expected a similar 2 : 2 combination of metal and ligand, which would afford a complex where the bridging pyrene moieties would be held co-facial to one another. This premise appeared to be supported by the high symmetry of the ^{1}H NMR spectrum (Fig. 1).

At 300 MHz the free ligand shows eleven well resolved signals between δ 7.75 and 9.05: three AB quartets for $H_{2,3}$, $H_{3',4'}$ and $H_{5',6'}$; singlets at δ 8.59 (H_9) and 8.40 (H_4); and a typical three proton pattern for H_7, $H_{8'}$ and $H_{9'}$. The complex also shows eleven well resolved signals with some shifted substantially upfield. The electrospray mass spectrum showed two major peaks at high mass. The peak at *m/z* 622, corresponding to [(Cu**3**)$_n$]$^{n+}$, established the 1 : 1 relationship of ligand and metal while the peak at *m/z* 983, corresponding to [(Cu**3**)$_3$(ClO$_4$)]$^{2+}$, indicated the trinuclear nature of the system.

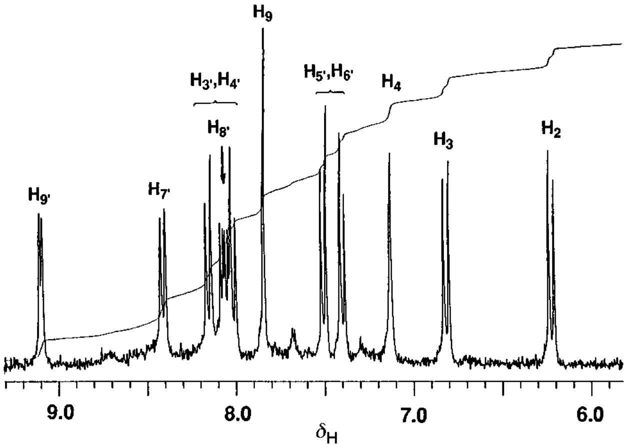
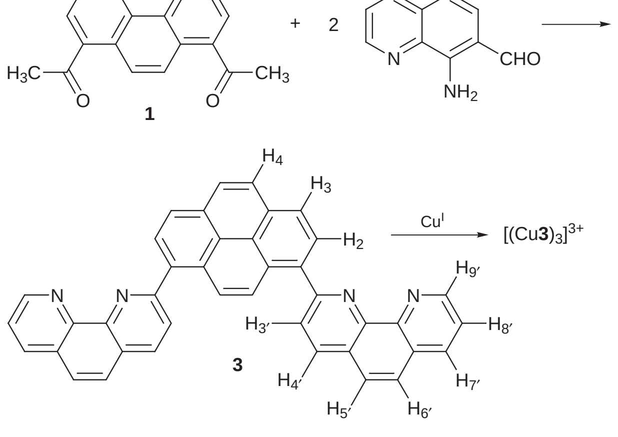


Fig. 1 300 MHz ^{1}H NMR spectrum of [(Cu**3**)$_3$](ClO$_4$)$_3$ at 25 °C in DMSO-*d*$_6$.



Scheme 1

The structure of the complex was revealed by an X-ray analysis of a crystal grown from DMSO solution. Unfortunately the crystal quality was poor so that only a preliminary structure of the cation could be obtained. An ORTEP drawing of the cation is shown in Fig. 2 and Table 1 provides a summary of selected structural features. The geometry around copper is quite distorted. Each 1,10-phenanthroline unit binds to the metal through a short bond (1.96–1.99 Å) using the distal nitrogen N_{10}. The internal nitrogen N_1 forms a much longer bond to the metal (2.10–2.16 Å). We have seen similar bond distortions in the Cu^{I} complex of a highly twisted 2,2′-biquinoline derivative.[7] The tetrahedral geometry is also distorted. The N1–Cu–N10 chelation angles are relatively normal (80.9–81.5°) but the

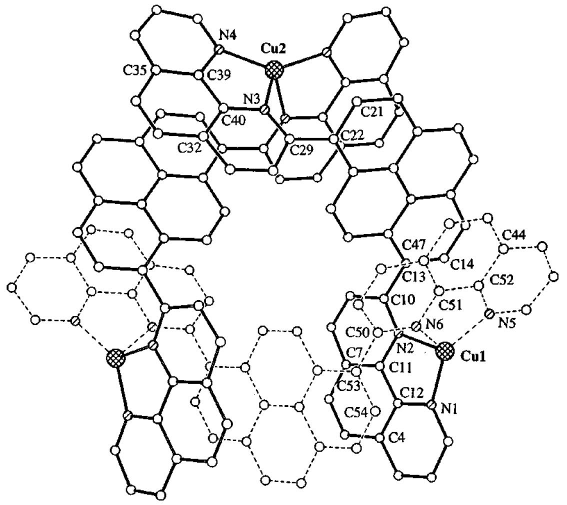


Fig. 2 ORTEP diagram of the cation of [(Cu**3**)$_3$](ClO$_4$)$_3$ with atomic numbering for key atoms.

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Table 1 Selected geometric parameters for $[(Cu\mathbf{3})_3]^{3+}$ according to the numbering scheme in Fig. 2

Bond lengths (Å)		Bond angles (°)	
Cu1–N1	1.96 (0.0139)	N1–Cu1–N2	81.47 (0.59)
Cu1–N2	2.16 (0.0130)	N5–Cu1–N6	81.37 (0.54)
Cu1–N5	1.98 (0.0141)	N3–Cu2–N4	80.89 (0.47)
Cu1–N6	2.10 (0.0118)	N1–Cu1–N5	146.05 (0.63)
Cu–N3	2.14 (0.0113)	N1–Cu1–N6	121.94 (0.52)
Cu2–N4	1.99 (0.0108)	N2–Cu1–N5	123.12 (0.52)
		N2–Cu1–N6	96.52 (0.44)
Dihedral angles (°)			
N4–C39–C40–N3	1.65 (1.79)	Cu1–N1–C12–C4	170.65 (1.14)
N6–C51–C52–N5	2.67 (2.11)	Cu1–N2–C11–C7	168.04 (1.14)
N2–C11–C12–N1	4.59 (2.08)	Cu1–N5–C52–C44	167.98 (1.16)
N2–C10–C13–C14	59.73 (1.90)	Cu1–N6–C51–C4	168.13 (1.22)
N6–C50–C53–C54	57.75 (2.95)	Cu2–N3–C40–C32	168.63 (1.11)
N3–C29–C22–C21	58.34 (1.80)	Cu2–N4–C39–C35	170.75 (1.09)

N–Cu–N angles involving two different ligands are less regular with N1–Cu–N6 and N2–Cu–N5 being 122 and 123°, respectively, while N1–Cu–N5 is about 24° larger and N2–Cu–N6 is about 26° smaller. The planes of the two phenanthrolines are not orthogonal to one another. The extent to which the Cu lies out of the plane of the phenanthroline ring can be assessed by examining the C_a–C_b–N–Cu dihedral angle where C_a and C_b denote the two carbons common to pyridine and the central benzo-ring of phenanthroline. These angles range from 168–171°, where the ideal angle would be 180°, again indicating some distortion of tetrahedral geometry,

This cation has D_3 symmetry so that all three ligands are identical having the same helical twist about the phen–pyrene–phen bonds (57.8–59.7°). The phenanthroline rings are fairly planar with N_1–C–C–N_{10} dihedral angles of 1.7–4.6°. What is truly remarkable about the cation structure is the manner in which the aromatic rings π-stack, a pyrene being layered between two phenanthrolines to form three triple decked stacks which define a donut-shaped assembly (see Fig. 3 for stereoview). The stacking of the three rings is well organized and the average distance of any atom in a phenanthroline ring to the mean plane of the layered pyrene ring is 3.6 Å, which is approximately the optimal π-stacking distance. The increased surface area of pyrene as well as its ability to form well organized π-stacked arrays apparently dictates the nuclearity of the complex. A similar effect for an Ag^+ trimer has recently been reported by Williams and co-workers.[8]

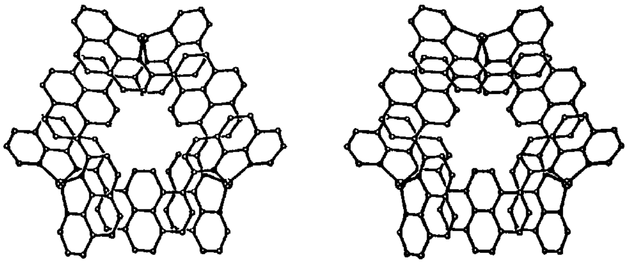

Fig. 3 Stereoview of the cation of $[(Cu\mathbf{3})_3](ClO_4)_3$.

From the stereodrawing, we notice that the hydrophobic cavity of the molecule consists of eighteen methine units. At the interior of the cavity are the C_9 and C_{10} hydrogens of the three pyrene units. On one face of the cavity are the C_3 and C_4 hydrogens of one set of three phens and on the other face are the C_3 and C_4 hydrogens of the other set of phens. The approximate diameter of the cavity is estimated to be about 3 Å by measuring the distance between opposing sets of atoms. If the van der Waals radii of the atoms are taken into account, the cavity size shrinks to about 1.8 Å. To verify that this cavity is indeed too small to accommodate a hydrophobic guest, we added Bu_2O to an NMR sample of $[(Cu\mathbf{3})_3](ClO_4)_3$ in DMSO-d_6 but no change was observed from the chemical shift values of the uncomplexed species.

Knowing the three dimensional structure, we can now more confidently assign the proton resonances in Fig. 1. The singlet for H_9 on the interior of the donut is downfield from the singlet for H_4 on the exterior. Similarly $H_{3'}$ and $H_{4'}$ are assigned as the downfield AB quartet. Due to the twist about the pyrene–phen bond, H_2 is held over the shielding region of the neighboring phen and found at higher field (δ 6.22).

To evaluate other features of the trimer, it became useful to prepare a monomeric analogue and hence the ligand 2-(pyren-1-yl)-1,10-phenanthroline **4**[9] was complexed in a 2:1 fashion with Cu^I. An NMR spectrum of the crude reaction product showed two sets of peaks in a 2:1 ratio which were attributed to conformational differences about the 2,1′-bond of ligand **4** in the complex.

The electronic absorption spectra (MeCN) of the ligands show long wavelength absorptions at 374 (log ε 4.53) for **3** and 342 nm (log ε 4.44) for **4**. The lower energy absorption of **3** is attributed to the presence of two phen substituents. The complexes show absorptions at 379 (log ε 4.76) and 473 nm (log ε 4.00) for $[(Cu\mathbf{3})_3]^{3+}$ and 346 (log ε 4.61) and 453 nm (log ε 3.50) for $[Cu(\mathbf{4})_2]^+$. The more intense, shorter wavelength band relates to the corresponding ligand absorption. The weak longer wavelength band is assigned to a characteristic metal to ligand charge transfer (MLCT) which gives the complexes their red color. The absorbance of the trimer appears at lower energy and is approximately 50% more intense than the monomer due to the 3:2 ratio of pyrene found in these two complexes.

Upon excitation into their lowest energy bands, the ligands exhibit strong pyrene-based emissions at 434 (**4**) and 450 nm (**3**). For the corresponding complexes these bands are greatly reduced in intensity possibly due to quenching by the copper center. Excitation into the MLCT bands of the complexes revealed only very weak luminescence.

The half-wave oxidation potentials for the two Cu^I complexes were determined by cyclic voltammetry and found to be virtually identical at +0.31 V (*vs.* SCE). This value compares with +0.67 V for $[Cu(dmp)_2]$+ (dmp = 2,9-dimethylphen).[10] It is noteworthy that the monomeric system is considerably more reversible than the trimer. The question of whether one or more electrons was being transferred in the oxidation of $[(Cu\mathbf{3})_3]^{3+}$ was addressed by controlled potential coulometry at 0.8 V, which indicated that only one copper in the trimer is being oxidized to Cu^{II}.

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