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Self-Assembly and X-ray Structure of a Dimetalloparacyclophane Incorporating a $\pi-\pi$ Stacked Subunit

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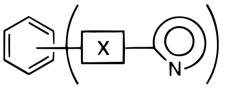
Introduction

The controlled self-assembly of supramolecular coordination compounds is a subject of much current investigation.[1] Ligands containing multiple donor atoms can act in a chelating mode or as bridging ligands for the formation of either chain or ring compounds (Scheme 1).[2] We are currently engaged in a detailed study of the coordination chemistry of a series of polyheteroaryl-substituted arenes (**1**), which consist of various heterocyclic rings attached via spacer groups, X, to a central arene core, and have recently reported the syntheses of a number of polypyrazolylmethylbenzenes.[3] Such compounds exhibit a variety of coordination modes, including those shown in Scheme 1, depending on the nature of the heterocycle, the spacer group, the specific metal used, and the reaction conditions.[4] Other workers have recently used other polyheteroaryl-substituted arenes to study metal-metal interactions in bi- and multinuclear complexes[5] and to construct supramolecular species with novel topological structures, such as cages, ladders, bricks, helicates and polycatenates, some of which contain interlocking rings and interpenetrating 3D networks.[6] We now report the synthesis of the new ligand **2** and its reaction with silver nitrate to produce a novel [2 + 2] ring compound that contains a $\pi-\pi$ stacked subunit.



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Scheme 1

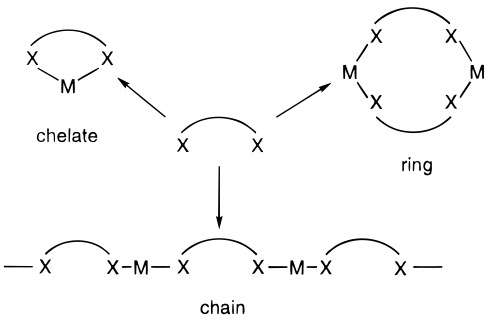

Table 1. Crystallographic Data for **3**

$C_{32}H_{28}Ag_2N_6O_{12}$	fw = 904.34 g mol^{-1}
$a = 11.111(1)$ Å	space group: $P2_1/n$
$b = 10.964(1)$ Å	$D_c = 1.880$ g cm^{-3}
$c = 13.128(1)$ Å	$\mu = 1.30$ mm^{-1}
$\beta = 92.324(6)°$	$F(000) = 904$
$V = 1598.0(2)$ Å^3	$T = -140$ °C
$Z = 2$	$R^a = 0.0257$
$\lambda = 0.71073$ Å	$R_w{}^b = 0.0632$ (all 3141 data)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ for 2586 data with $I > 2\sigma(I)$. [b] $R_w = (\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2])^{1/2}$.

Experimental Section

Preparation of 1,4-Bis(2-pyridoxy)benzene (2). Hydroquinone (5.24 mmol) and 2-bromopyridine (10.5 mmol) were heated to 180 °C, potassium carbonate (10.5 mmol) was added, and the mixture was stirred and heated at 210-220 °C for 5 h. The resulting tar was extracted several times with diethyl ether and the extracts combined and concentrated to give crude **2** (33% yield), which was recrystallized from ethyl acetate. Mp: 157−158 °C. ^{1}H NMR ($CDCl_3$, δ): 6.94, 2H, d, H3′; 7.00, 2H, t, H5′; 7.17, 4H, s, H2,3,5,6; 7.69, 2H, t, H4′; 8.21, 2H, d, H6′. ^{13}C NMR ($CDCl_3$): 111.38, C3′; 118.44, C5′; 122.32, C2,3,5,6; 139.41, C4′; 147.63, C6′; 150.58, C1,4; 163.73, C2′. Anal. Calcd for $C_{16}H_{12}N_2O_2\cdot{}^1/_4H_2O$: C, 71.50; H, 4.69; N, 10.42. Found: C, 71.47; H, 4.63; N, 10.29.

Preparation of Silver Complex 3. A solution of silver nitrate (0.59 mmol) in water (5 mL) was added to a solution of **2** (0.57 mmol) in acetone (10 mL). The resulting precipitate was filtered and washed with acetone (yield 43%). Crystals suitable for X-ray structure determination were obtained by slow evaporation of an acetonitrile solution of the above product. Mp: 221−222 °C. Anal. Calcd for $C_{32}H_{28}N_6O_{12}Ag_2$: C, 42.50; H, 3.12; N, 9.29. Found: C, 42.74; H, 3.10; N, 9.58.

X-ray Crystallography. Table 1 lists the crystallographic data. Cell parameters were determined by least-squares refinement of the angles of 41 accurately centred reflections with $2\theta > 29°$. A brown block (0.50 × 0.36 × 0.30 mm) was used to collect (Siemens P4s diffractometer, Mo Kα radiation, ω scans) 3141 independent reflections with $4° < 2\theta < 52°$. The structure was solved by direct methods and refined (all non-hydrogen atoms anisotropic) on F^2, using all data. C−H hydrogen atoms were included in calculated positions; the two water hydrogens were located from a difference map and their positions refined. Selected interatomic distances and angles are given in Table 2.

Results and Discussion

Reaction of hydroquinone with 2 equiv of 2-bromopyridine, in the presence of potassium carbonate at 210 °C, gave 1,4-bis(2-pyridoxy)benzene (**2**), which was characterized by spectroscopic and analytical techniques (Scheme 2). Reaction of an acetone solution of **2** with a stoichiometric amount of an aqueous solution of silver nitrate gave immediate precipitation of a product (**3**) that analyzed as [$\mathbf{2}\cdot AgNO_3\cdot H_2O$] and which, on slow evaporation of an acetonitrile solution, furnished crystals

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **3**[a]

Ag(1)−N(1′)	2.212(2)	Ag(1)−N(1″A)	2.211(2)
Ag(1)−O(10)	2.528(2)	Ag(1)−O(1)	2.973(2)
Ag(1)−O(4A)	2.942(2)	C(1)−O(1)	1.402(3)
C(4)−O(4)	1.400(3)	O(1)−C(2′)	1.362(3)
O(4)−C(2″)	1.361(3)	N(10)−O(11)	1.237(3)
N(10)−O(12)	1.252(3)	N(10)−O(13)	1.251(3)
N(1′)−Ag(1)−N(1″A)	157.11(7)	O(10)−Ag(1)−N(1′)	101.23(8)
O(10)−Ag(1)−N(1″A)	101.18(8)	C(1)−O(1)−C(2′)	118.1(2)
C(2′)−N(1′)−Ag(1)	118.0(2)	C(6′)−N(1′)−Ag(1)	124.3(2)
N(1′)−C(2′)−O(1)	112.1(2)	C(2″)−O(4)−C(4)	118.6(2)
N(1″)−C(2″)−O(4)	111.8(2)	O(11)−N(10)−O(12)	119.5(2)
O(11)−N(10)−O(13)	120.7(2)	O(12)−N(10)−O(13)	119.8(2)

[a] N(1″A) and O(4A) are related to N(1″) and O(4), repectively, by the following symmetry transformation: $1 - x, -y, 1 - z$.

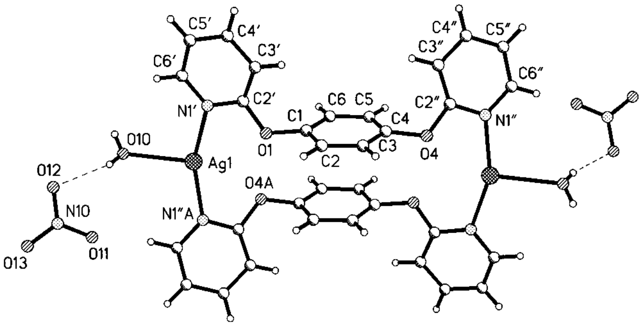


Figure 1. Side view and atom labeling of the structure of **3**.

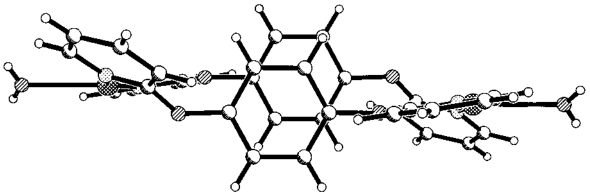
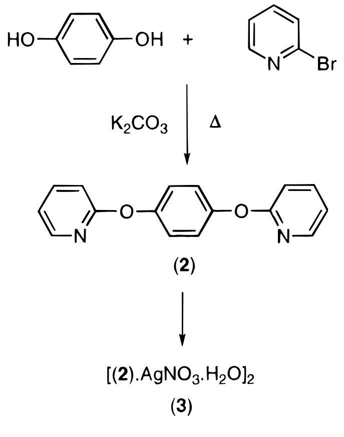


Figure 2. Top view of the structure of **3**.

Scheme 2



suitable for a single-crystal X-ray structure determination. Figure 1 shows a side view and atom labeling of this structure, which is a centrosymmetric [2 + 2] dimeric dimetalloparacyclophane which has an Ag−Ag separation of 10.384(1) Å. A top view of **3** is shown in Figure 2.

Each silver atom is coordinated to two pyridine nitrogens and, less strongly, to a water oxygen atom which, in turn, acts as a hydrogen bonding bridge to the noncoordinating nitrate counterion.[7] As has been observed in other dimeric silver complexes,[8,9] the geometry at the silver atom is distorted T-shaped. However, it has previously been noted[8] that axial coordination by water molecules is rare in such compounds. Furthermore, there is evidence for additional weak coordination of the silver by the ether oxygens (O(1)/O(4)) of the ligands (see interatomic distances listed in Table 2).

The most interesting feature of the structure is the close $\pi-\pi$ stacking of the two benzene rings, which are coplanar and separated by only 3.33(1) Å, similar to the value in graphite (3.35 Å). The most closely related structures in the literature are a series of copper and cobalt complexes of a tetrakis(2-imidazolinyl)benzene, which have parallel benzene rings, but separated by 3.9−4.4 Å.[10] In the complex **3** the $\pi-\pi$ interaction is clearly much stronger. There has been considerable discussion in the recent literature about the nature of $\pi-\pi$ interactions between arene rings, with much of the work focused on determining the most favorable relative orientation of the two rings.[11] As shown in the top view of the structure (Figure 2), in the complex **3** the two benzene rings are displaced from one another in such a way that the centroid of each ring lies above an atom of the other ring. This has the effect of reducing the potential D_{2h} symmetry of the dimetallocyclophane component by means of torsional adjustments.[12]

It is interesting to speculate as to the extent to which this interaction is responsible for the self-assembly of this structure and whether, or not, the ether oxygens are necessary for such assembly.[13] To this end we are currently studying the reactions of silver nitrate with various structurally related ligands. Thusfar we have been able to establish that a similar structure is obtained from the *meta*-isomer of **2**, but that polymeric chain structures result from introduction of methylene groups on either side of the oxygen atoms in **2** or by replacement of the 2-pyridoxy groups with *N*-pyrazolylmethyl groups. These investigations are continuing.

Supporting Information Available: Tables of information on data collection, structure solution and refinement, atom coordinates, anisotropic displacement parameters, and a complete list of bond distances and angles for **3** (6 pages). An X-ray crystallographic file in CIF format is also available on the Internet. Access and ordering information is given on any current masthead page.

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(7) In fact, each of the water hydrogen atoms is involved in an approximately linear hydogen bond to a nitrate oxygen; in addition to the hydrogen bond shown [O(10)···O(12) = 2.928(3) Å], the other hydrogen arom is bonded to an oxygen atom (not shown) of an adjacent nitrate anion related by a crystallographic glide plane [O(10)···O(13) = 2.839(3) Å].

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(12) In the structure of **3**, the meanplane of the benzene ring is inclined to the plane of the appended pyridine rings at angles of 89.4(1) and 109.2(1)°, while the two pyridine ring meanplanes at each silver atom are inclined to one another at an angle of 35.9(1)°.

(13) The dimetallocyclophane structure appears not to remain intact in solution; dissolution of the complex **3** in CD_3CN leads to NMR spectra identical with those of the free ligand **2**.