A Thirty-Membered Macrocyclic Binuclear Metal Complex: Synthesis and Structural Characterization of $[Ag_2(psb)_2]^{2+}$ {psb = 1,2-Bis[(4-pyridyl)sulfanylmethyl]benzene}

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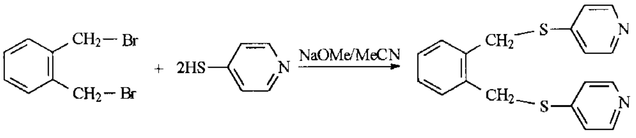
A neutral exo-pyridino-bidentate ligand, 1,2-bis[(4-pyridyl)sulfanylmethyl]benzene (psb), was prepared from the reaction of 1,2-bis(bromomethyl)benzene and sodium pyridine-4-thiolate for metal complex syntheses. The reaction of silver salt and psb resulted in binuclear complex $[Ag_2(psb)_2](ClO_4)_2$ with a thirty-membered macrocycle, in which the length is 2.0 nm.

Design and research of discrete macrocycles and cages are a subject of great interest in the supramolecular chemistry.[1-3] The potential use of this kind of compound largely depends on their cavity size and type, which are controlled by the ligands. Therefore, the design of ligands is crucial to the constructions of specific supramolecular architectures.[4-6] For instances, triple helicate tetrahedral cluster cage can be obtained by the self-assembly reaction of bis(bidentate)catecholamide and metal ions.[7] The treatment of $[Pd(NO_3)_2(en)]$ with 2,4,6-tri(4-pyridyl)-1,3,5-triazine resulted in a molecular cage,[1] while the similar reaction with 2,4,6-tri(3-pyridyl)-1,3,5-triazine in place of 2,4,6-tri(4-pyridyl)-1,3,5-triazine led to a bowl-like macrotricycle.[3a 3b]

In our previous studies, we used some simple ligands containing both sulfur and nitrogen donors, such as pyridine-2-thiolate, pyrimidine-2-thiolate, pyridine-2-thione, and 2-mercaptoethylamine, and obtained a series of complex polymers with linear chain or 3-D network structures.[8] Considering the fact that a little information is contained in the ligands we used, we carefully examined the geometric requirements of particular symmetry and stereochemitry, and began to design ligands containing more information, expecting to obtain metal complexes with novel structures.[9] Herein, we report a neutral exo-pyridino-bidentate ligand 1,2-bis[(4-pyridinyl) sulfanylmethyl]benzene(psb), which contains two 4-thiopyrimidine groups separated by an *o*-xylyl spacer, and metal complex with a thirty-membered macrocycle $[Ag_2(psb)_2](ClO_4)_2$ prepared from silver salt with the ligand psb.

The ligand psb was prepared frorn the reaction of 1,2-bis(bromomethyl)benzene and sodium pyridine-4-thiolate. A solution of 1,2-bis(bromomethyl)benzene (1.32 g, 5 mmol) and sodium pyridine-4-thiolate (1.33 g, 10 mmol) in MeCN (50 cm^3) was heated to 60 °C for 3 h with vigorously stirring. After cooling, the pale yellow solution was filtered. Removal of the solvent gave an oil, which afforded a light yellow powder (psb) on recrystallization from CH_2Cl_2/Et_2O/hexane (yield 1.41 g, 84%).

The psb ligand possesses four possible bonding sites, i.e., two sulfur and two nitrogen atoms. Owing to the poor metal-complexing ability,[10] the sulfur atom of the thioether may act as no coordination donor. Due to the behavior of the exo-bidentate ligand of pyridine group[11] along with the *o*-xylyl spacer, the N atoms of the two 2-thiopyridine groups can only bond to different metal atoms. Therefore, psb may be a bidentate but nonchelating ligand, and able to bridge two metal atoms in specific directions.



psb

The complex $[Ag_2(psb)_2](ClO_4)_2$ was obtained from the reaction of $AgClO_4$ with psb in a metal-to-ligand ratio of 1 : 1 in DMF/MeCN, respectively. To a solution of $AgClO_4$ (0.11 g, 0.5 mmol) in DMF a solution of the ligand psb (0.32 g, 1 mmol) in acetonitrile (10 ml) was added. The reaction mixture was stirred for 3 h. The resulting solution is filtered and the filtrate was slowly diffused by ether to give a large amount of colorless block crystals of the complex.

Single-crystal X-ray diffraction analyses of the complex were carried out.[12] Crystal data: Crystal dimensions 0.16 x 0.14 x 0.10 mm, Formula $C_{36}H_{32}N_4Ag_2Cl_2S_4O_8$, Fw 1063.54, triclinic, space group $P1$, a = 8.1587(14) Å, b = 8.4447(14) Å, c = 14.745(3) Å, α = 87.307(3)°, β = 82.638(3)°, γ = 72.716(3)°, V= 962.0(3) Å^3, Z= 1, $R(wR)$=0.0347(0.0961) for 5229 reflections with $F \geq 2.0\ \sigma(Fo)$. The crystallographic analyses revealed that the cation is a binuclear complex with a thirty-membered macrocycle, as shown in Figure 1. The macrocycles are linked by ClO_4^{2-} through weak Ag-O interactions (Ag-O distances range from 2.944 to 4.000 Å) to form

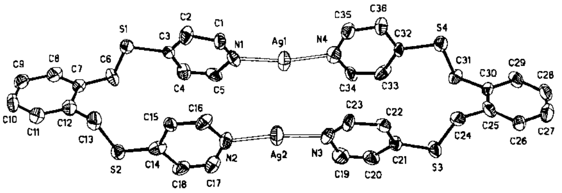


Figure 1. View of the cation binuclear unit $[Ag_2(psb)_2]^{2+}$. Important bond lengths (Å) and angles (°): Ag(1)-N(4)2.142(2), Ag(1)-N(1) 2.148(2), Ag(2)-N(3) 2.120(2), Ag(2)-N(2) 2.123(2), S(1)-C(3) 1.783(2), S(1)-C(6) 1.815(2), S(2)-C(14) 1.713(2), S(2)-C(13) 1.808(3), S(3)-C(21) 1.712(2), S(3)-C(24) 1.840(3), S(4)-C(32) 1.783(2), S(4)-C(31) 1.838(2), N(4)-Ag(1)-N(1) 169.81(9), N(3)-Ag(2)-N(2) 172.92(9).

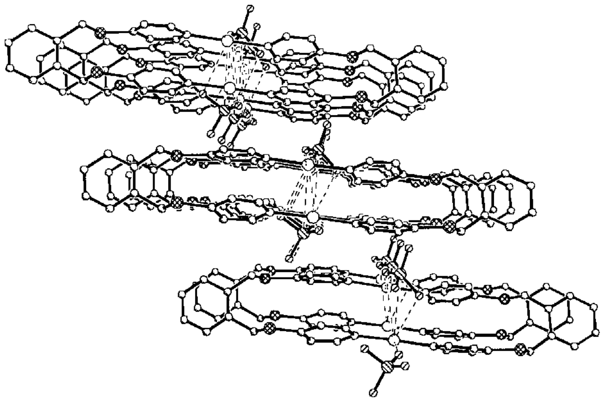


Figure 2. Packing diagram along *c* axis.

layer structure, Figure 2 represents the packing diagram along c axis. As expected, each psb acts as bidentate ligand, in which two nitrogen atoms from different pyridine groups coordinate to two Ag atoms, respectively. The other psb coordinates to same two silver atoms in the opposite direction to meet linear coordination of the silver atoms. Therefore, two psb ligands are linked by two silver atoms forming a thirty-membered macrocycle with the length of 2.0 nm, the Ag-Ag distance in the macrocycle is 3.411 Å. Each silver atom is two-coordinated in a slightly distorted linear fashion of AgN_2. The Ag-N bond distances fall in the range of 2.142(2) to 2.148(2) Å, which are much shorter than those found in the silver(I)-pyridine complexes.[8,9,11,13] The average bond angle of N-Ag-N, is 171.34(9)°.

Further studies, such as, anion-exchange properties of complexes with other weakly coordinating anions, which may result in the insertion of the anion into the macrocycle or structural change, and self-assembly of the ligand bsp and its derivation with other metal ions will be reported in full paper.

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12 The intensity data were collected on a SIMENS SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation at room-temperature. The crystal structure was soloved by directed methods. All of the calculations were performed by using the SHELXTL-PL version 5.5 package on an HP 5/75 computer. Crystallographic details and complete listings have been deposited at the Cambridge Crystallographic.

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