A Silver(I) Coordination Polymer Chain Containing Nanosized Tubes with Anionic and Solvent Molecule Guests**

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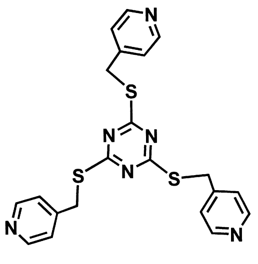
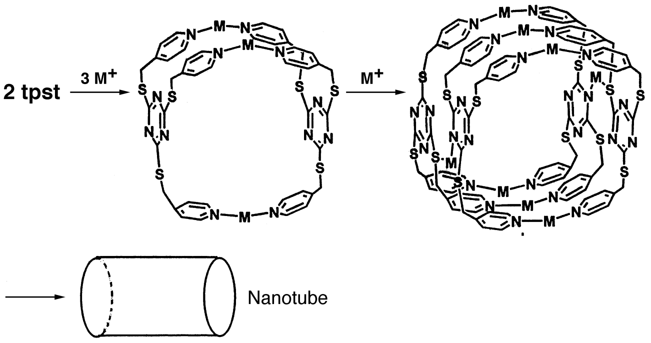
Design of and research on supramolecular architectures with inner cavities have attracted considerable current interest because of their ability to selectively include ions and molecules and catalyze specific chemical transformations.[1–6] The potential uses of such architectures, which include molecular cages, two- and three-dimensional synthetic receptors, and extended porous frameworks, largely depend on their cavity size and type, which are mainly controlled by the ligands and appropriate metal ions.[3, 7, 8] For instance, a triple-helicate (M_2L_3) or a tetrahedral (M_4L_6) cluster was obtained from the self-assembly reaction of a bis-bidentate catecholamide and metal ions in the absence or presence of Me_4N^+ ions.[8] Robson et al. reported a very large $Cu_{12}L_8$ enclosure with a cubelike cage, which was derived from the self-assembly of the tris-bidentate ligand 2,4,6-triazophenyl-1,3,5-trihydroxybenzene (H_3tapp) and copper(II) ions.[9] By using the self-assembly of molecular units driven by coordination to transition-metal ions, Stang et al. have presented NMR and MS evidence for the formation of cuboctahedral and dodecaheral cations from tridentate and bidentate subunits.[10]

A number of infinite two- and three-dimensional coordination polymers possessing a variety of cavities capable of accommodating guests have been developed.[11] Zn/tpt and Cu/tpt (tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine) coordination polymers containing infinite two- and three-dimensional networks were generated by the assembly reaction of tpt and metal ions.[12] Recently, Goodgame et al. reported a new type of metal-organic large-pore zeotype, namely, $[Zn(dimto)_2]_n \cdot m$DMF (Hdimto = 4,6-di(1-imidazolyl)-1,3,5-triazin-2-one), which was generated from zinc bromide and 2,4,6-tri(1-imidazolyl)-1,3,5-triazine (timt).[13]



tpst

We have designed two multidentate ligands, 1,2-bis-[(2-pyrimidinyl)methylsulfanyl]benzene (bpsb) and 2,4,6-tris[(4-pyridyl)methylsulfanyl]-1,3,5-triazine (tpst), and obtained the two-dimensional lamellar network polymer $[Ag_2(bpsb)_3(ClO_4)_2]_n$ and the metallosupramolecular cube $[Ni_6(tpst)_8Cl_{12}]$.[14] Examining the geometric requirements of symmetry and sterochemistry, we expected to prepare coordination polymers with nanosized tubes of different lengths. As tpst is an exo-tridentate ligand, the N atoms of the three pyridyl groups can only bind to three different metal atoms (Scheme 1). By using metal ions with linear coordination geometry, such as gold(I), silver(I), and copper(I), to link tpst ligands, nanosized tubes with different lengths can be obtained. Here we report on the preparation and the structural characterization of a single-stranded one-dimensional coordination polymer, namely, compound **1**, which contains nanosized tubes.



Scheme 1. Reaction of tpst with silver(I) salts leads to $[Ag_3(tpst)_2]^{3+}$ nanosized rings, which are linked by other silver(I) centers to form a nanosized tube. M = Ag.

$[Ag_7(tpst)_4(ClO_4)_2(NO_3)_5(dmf)_2]_n$ (**1**)

The reaction of $AgNO_3$ with tpst was carried out with a metal-to-ligand ratio of 2:1 in DMF/MeOH followed by addition of $AgClO_4$. Slowly diffusing diethyl ether into the reaction solution produced crystals suitable for single-crystal X-ray diffraction. The crystallographic analysis of the complex [15] revealed that its crystal structure is a one-dimensional chain polymer containing a basic nanosized tube unit, $[Ag_7(tpst)_4]$. As can be seen in Figure 1, each ligand binds to three silver(I) centers through the N atoms of the three pyridyl groups, and each silver(I) ion is in turn coordinated by the pyridyl group of another tpst ligand to form an $[Ag_3(tpst)_2]$ nanosized ring. Two such rings are linked by Ag–N and Ag–S bonds from one N and one S atom of the trithiocyanuric spacer to form the basic nanosized tube unit with the dimensions of 1.34 × 0.96 × 0.89 nm, which accommodates two DMF molecules and two perchlorate ions. Figure 2 shows a space-filling representation. The tube units share Ag(1) by

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[**] This work was supported by the National Nature Science Foundation of China. M.C.H. thanks the Croucher Foundation of Hong Kong for financial support.

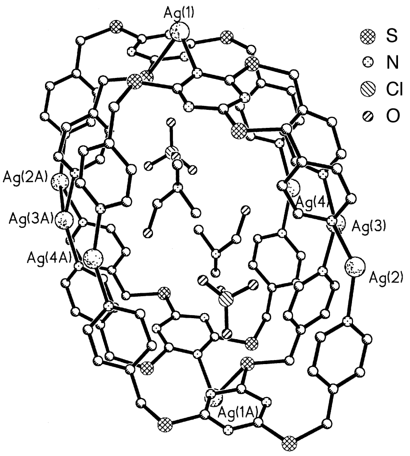

Figure 1. View of the basic nanosized tube unit in **1**.

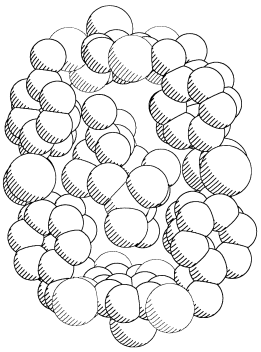

Figure 2. Space-filling representation of the nanosized tube unit in **1**.

Ag–N and Ag–S bonds to form an infinite chain (Figure 3). Such a single-stranded polymer chain with open nanosized tubes differs greatly from the usual polymer chain structures.[1] To our knowledge, the structure of **1** is a unique chain-structural motif in supramolecular coordination chemistry. The only example known to us of a larger coordinative cage that provides open framework is that in the infinite three-dimensional coordination polymer of composition $[Zn(dimto)_2]_n \cdot m\,DMF$ mentioned above.[13] Five NO_3^- ions in **1** are each located near the silver(I) centers and embedded in the polymer chain regions. The Ag···O distances are in the range of 2.65–3.10 Å.

All tpst moieties in **1** act as tetradentate ligands but with two kinds of coordination mode: one type coordinates to four silver atoms through three nitrogen atoms of different pyridyl groups and a sulfur atom of the thioether moiety, and the other through three pyridyl nitrogen atoms and one nitrogen atom of the triazine ring. The silver centers exhibit two kinds of coordination environment: one is the normal linear coordination mode of AgN_2 and the other is tetracoordinate with a slightly distorted square-planar AgS_2N_2 unit, which is seldom found in silver(I) compounds.

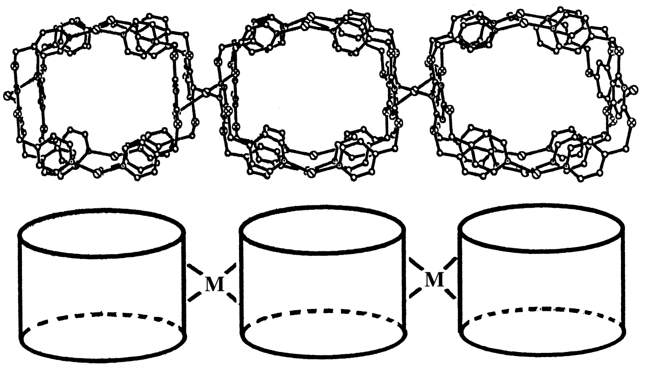

Figure 3. View of the one-dimensional polymer chain in **1** along the *b* axis.

Further studies, such as on tubes consisting of more than two $[Ag_3(tpst)_2]$ rings, solvent- and anion-exchange properties of the polymer, and self-assembly of the ligands with other metal ions, will be reported elsewhere.

Experimental Section

1: To a solution of tpst (1.5 mmol), prepared by heating a solution of 4-picolyl chloride hydrochloride (4.5 mmol), sodium trithiocyanurate (1.5 mmol), and NaOMe (4.5 mmol) in MeOH (25 mL) at 50 °C, a solution of $AgNO_3$ (3.0 mmol) in DMF (15 mL) was added. After the reaction mixture was stirred for 2 h, a solution of $AgClO_4$ (1.0 mmol) in DMF (10 mL) was added dropwise. The mixture was stirred for a further 2 h to give a colorless solution, which was filtered. Diffusion of diethyl ether into the resulting solution yielded a large amount of colorless needles of **1** with two water molecules per formula unit (0.76 g, 61 %). C,H,N analysis calcd for $C_{90}H_{90}N_{31}O_{27}Ag_7S_{12}Cl_2$: C 33.3, H 2.80, N 13.3; found: C 33.0, H 2.72, N 13.1; IR (KBr pellet): $\tilde{\nu} = 3450$ (m), 2929 (w), 2906 (w), 1676 (s), 1616 (s), 1479 (s), 1429 (m), 1261 (s), 1090 (s), 1028(s), 802 (s), 704 (m), 621 (m), 584 (w), 494 cm^{-1} (m).

Received: January 24, 2000 [Z14589]

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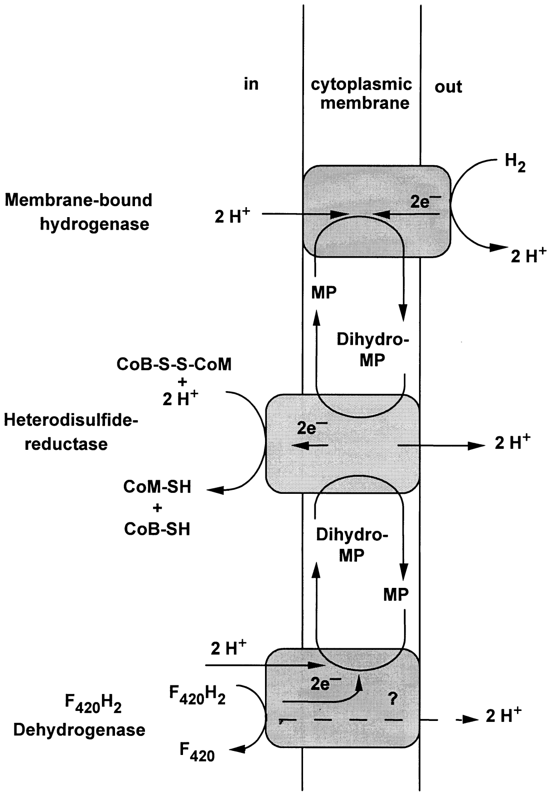
[15] Crystallography: The intensity data were collected on a Bruker CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) at room temperature. All calculations were performed by using the SHELXTL-PL version 5.10 package on an HP computer. The structure was solved by direct methods and refined by full-matrix least-squares methods. Crystal data for **1** with two water molecules per formula unit: colorless needle, dimensions 0.24 × 0.18 × 0.16 mm, $C_{90}H_{90}N_{31}O_{27}Ag_7S_{12}Cl_2$, $M_r = 3248.64$, monoclinic, space group $C2/c$; $a = 28.1019(20)$, $b = 16.8556(11)$, $c = 27.9278(21)$ Å, $\beta = 117.9154(15)°$, $V = 11689.3(25)$ Å^3; $\rho_{calcd} = 1.846$ g cm^{-3}, $Z = 4$; $F(000) = 6472$; $\mu(Mo_{K\alpha}) = 1.493$ mm^{-1}; 38967 reflections were collected, of which 7252 with $|F_o| \geq 2.0\sigma(|F_o|)$ were observed; $R_1 = 0.057$; $wR_2 = 0.184$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139799. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Methanophenazine: Structure, Total Synthesis, and Function of a New Cofactor from Methanogenic Archaea[**]

Uwe Beifuss,* Mario Tietze, Sebastian Bäumer, and Uwe Deppenmeier

Dedicated to Professor Sir Alan R. Battersby on the occasion of his 75th birthday

Methanogenic organisms belong to the kingdom of archaea and differ significantly from eukarya and bacteria.[1] Methanogenic archaea are widespread in anaerobic environments such as the sediments of lakes and rivers as well as the intestinal tract of ruminants. They form the end of the anaerobic food chain and transform simple substrates such as hydrogen/carbon dioxide, formic acid, methanol, methylamines, and acetic acid into methane. The latter subsequently is oxidized under aerobic conditions and is thus able to reenter the carbon cycle. Owing to the influences of civilization the amount of methane, one of the greenhouse gases, in the atmosphere has continuously increased during the last century.[2] A variety of unique enzymes and unusual cofactors contribute to its formation by methanogenic archaea. The central intermediate of all metabolic pathways of methanogens is methyl-S-CoM, which is reductively demethylated to methane under the catalytic influence of methyl-CoM-reductase.[3] The two electrons required in this process are derived from CoB-SH and lead to the formation of a heterodisulfide (CoB-S-S-CoM) from CoB-SH and CoM-SH.[4] The reduction of CoB-S-S-CoM is an energy-conserving step in the metabolism of methylotrophic methanogens (Scheme 1).[5] Two recently detected proton-translocating enzyme systems, the H_2:heterodisulfide oxidoreductase and the $F_{420}H_2$:heterodisulfide oxidoreductase, are involved in the membrane-bound electron transfer of *Methanosarcina mazei* Gö1.[6] The electron transport of $F_{420}H_2$ to CoB-S-S-CoM is catalyzed by an $F_{420}H_2$ dehydrogenase transferring the electrons to the heterodisulfide reductase. In the presence of molecular hydrogen a membrane-bound hydrogenase serves as an electron-feeding component to the heterodisulfide reductase (Scheme 1).



Scheme 1. Model of the membrane-bound electron transfer of *Methanosarcina mazei* Gö1. CoM-SH = coenzyme M; CoB-SH = coenzyme B; F_{420} = coenzyme F_{420}; $F_{420}H_2$ = reduced form of the coenzyme F_{420}; MP = methanophenazine; dihydro-MP = reduced form of methanophenazine.

The structure of the electron carrier was not known. Recently, we have been able to isolate a phenazine ether from membranes of *Methanosarcina mazei* Gö1.[7] Detailed

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[**] This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 416; grants De 488/6-1 and De 488/4-2) and the Fonds der Chemischen Industrie. We are grateful to Drs. J. Paust and H. Jaedicke (BASF AG, Ludwigshafen) and Dr. R. K. Müller (Hoffmann-La Roche Ltd., Basel) for generously providing chemicals.