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Synthesis and Structure of a One-Dimensional Coordination Polymer Based Upon Tetracyanocalix[4]arene in the Cone Conformation

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Tetracyanocalix[4]arene has been synthesized in a cone conformation and crystallized from solution in an orthorhombic system, space group $P2_12_12_1$, with $a = 13.7999(9)$ Å, $b = 16.820(1)$ Å, $c = 21.754(1)$ Å, $D_c = 1.218\ g/cm^3$, Z = 4 ($C_{62}H_{47}N_5O_4$). Refinement based on 11008 observed reflections yielded R1 = 0.042. Further crystallographic studies have revealed that this compound self-assembles into a one-dimensional coordination polymer in the presence of Ag^+ cation. This extended structure also crystallizes in an orthorhombic system, space group Cmca, with $a = 17.770(1)$ Å, $b = 31.498(2)$ Å, $c = 23.107(2)$ Å, $D_c = 1.319\ g/cm^3$, Z = 8 ($C_{63}H_{52}AgCl_2F_6N_4O_6P$). Refinement based on 7391 observed reflections yielded R1 = 0.109.

INTRODUCTION

Over the last decade the construction of coordination polymers has been an emerging field[1] because of its implications in material science for the rational design of functional solids with inclusion or catalytic properties.[2] The general principle is to apply the structural diversity provided by coordination chemistry to generate molecular networks by linking together metal centers and building blocks carrying suitable functionality. This approach has generated a large number of extended networks[1,3]. Our own efforts using this strategy have resulted in the formation of cavity-containing rectangular grids [Co(pyz)-(terph)(H_2O)$_2$] (where pyz = pyrazine, terph = 1,4-benzene dicarboxylate) able to include aromatic guests.[4]

For the construction of a framework generating cavities or channels, the building block needs to have an element of rigidity so that the loss of conformational entropy in the self-assembly process is minimized. Regarding this aspect, it seems that the chemically versatile calix[4]arene offers a preorganized backbone on which covalent modifications can easily be achieved for the introduction of four coordination sites in either the lower or upper rim. In general, calix[4]arene is able to assume four primary conformational arrangements[5] and, it has been showed that in the solid state the cone conformation of *p-tert*-butylcalix[4]arene forms complexes with guest such as toluene,[6] benzene,[7] xylene,[7] and anisole.[8] In this contribution, we describe the solid state structure of free tetracyanoca-

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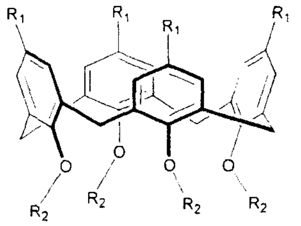
lix[4]arene and the Ag(I) 1-D polymeric structure where the calixarene serves as the bridging ligand and is in a pinched-cone conformation. Hosseini et al reported a 1D coordination polymer using similar material but the bridging calix[4]arene was in the 1,3-alternate conformation.[9]

EXPERIMENTAL

Compound **5** was prepared according to a procedure first reported by Gutsche.[10] The synthetic route is outlined in Scheme 1.



1 R_1 = *t*-Bu, R_2 = H
2 R_1 = H, R_2 = H
3 R_1 = H, R_2 = OBn
4 R_1 = Br, R_2 = OBn
5 R_1 = CN, R_2 = OBn

SCHEME 1

p-tert-Butylcalix[4]arene **1** was used as starting material to synthesize the ligand. Aluminum chloride catalyzed the removal of the *tert*-butyl group in toluene in the presence of phenol to provide **2** in high yield. The benzyl groups were introduced at the lower rim to prevent internal rotation by reacting **2** with benzyl bromide in the presence of NaH in THF/DMF to afford **3**. When **3** is treated with N-bromosuccinimide in butanone, the benzyl ether of p-bromocalix[4]arene **4** is obtained. The ^{1}H NMR spectrum shows that **4**adopts a cone conformation. The final compound was obtained by treating **4** with CuCN in refluxing *N*-methylpyrrolidinone under Argon atmosphere. The ^{1}H NMR spectrum of **5** displays the characteristics of a cone conformation.[11]

Crystals of **5** suitable for X-ray crystallographic analysis were grown by slow evaporation of an acetonitrile solution. A solution of **5** was added to a solution of $AgPF_6$ (both in nitromethane) at room temperature whereupon a colorless solid precipitated. The precipitate was filtered and dissolved in dichloromethane. Slow diffusion of a mixture of ethanol/methanol yielded single crystals (compound **6**) suitable for X-ray analysis. Data were collected at 173K on a Brucker SMART CCD diffractometer using Mo K_α radiation (λ = 0.7107Å). Both structures were solved and refined using SHELX-97[12]and the X-Seed[13] interface. The latter was also used to prepare Figs 1 and 2. Direct methods revealed all non-hydrogen atoms which were subsequently refined (on F^2) with anisotropic thermal parameters. All hydrogen atoms were placed in calculated positions with thermal parameters riding on those of their parent atoms. Residual electron density peaks in the structure of **6** indicated the presence of additional solvent which could not be modeled feasibly.

RESULTS AND DISCUSSION

The molecular structure of **5** is shown in Fig. 1a. As observed in most of the symmetrically substituted calix[4]arenes in the solid state[14] the compound adopts a pinched-cone conformation with C_{2v} symmetry. The asymmetric unit consists of one complete calixarene molecule in addition to a solvent acetonitrile molecule. Two opposite rings bearing the nitrile groups on the calixarene are parallel to each other while the remaining rings are flattened and pushed away from the cavity. The dihedral angles (Table I) between the phenyl rings and the plane of the four methylene groups are 78.6° and 80.0° for the upright rings and 141.4° and 143.3° for the angled rings[15]. Consequently two of the four coordination sites are diverging, leading to a situation favorable to the formation of a linear coordination polymer. All the benzyl groups are pointing outwards in a clockwise fashion as viewed from the upper rim side of the calixarene.

TABLE I Dihedral angles (°) between the phenyl groups and plane of the four methylene groups of tetracyanocalix[4]arene in **5** and **6**

	5	*6*
upright rings	78.6, 80.0	79.5, 79.0
angled rings	141.4, 143.3	142.2[a]

a. Only one ring is unique in this case.

The molecular structure of the calixarene molecule in **6** is shown in Fig 1b. The asymmetric unit consists of half a calixarene molecule situated on a mirror plane at (100), one silver(I) cation, one PF_6^- anion, one half of a dichloromethane molecule on a 2-fold rotation axis at (0.25, y, 0.25) and two complete methanol molecules (additional disordered solvent was not modeled). Analysis of the extended structure reveals the formation of a linear coordination polymer (Fig. 2) with a 1:1 ligand:metal stoichiometry. The 1-D chain consists of a wave-like ribbon structure in which the tetracyanocalix[4]arenes assemble in a head-to-tail fashion. This packing mode is reminiscent of the structure adopted by the water soluble *p*-sulfonatocalix[4]arene.[16] The silver(I) cation, surrounded by four nitrile groups in a tetrahedral arrangement, binds the calix[4]arene units together. As a result, this molecular network generates rectangular windows parallel to the *ab*-plane. The distance between the two Ag(I) cations located at opposite corners of the window is approximately 9.3 Å. The angle N-Ag-N between two adjacent calix[4]arenes is 112.0°. The 1-D polymers are aligned parallel to [100] (Fig. 2a) and the cross-section of the strand is approximately C-shaped (Fig. 2b). Adjacent polymers face one another and interlock as shown in Fig. 2c.

The distance between the nitrogen atoms of the two nitrile groups on the rings directed towards the cavity is remarkably similar in both the free and coordinated calix[4]arene structures (3.312Å and 3.314Å respectively). Table I also shows that the dihedral angles formed by phenyl rings and the plane of the calix[4]arene are relatively unchanged. This indicates that the preorganized backbone of calix[4]arene is a suitable building block for the formation of coordination polymers. As expected, the PF_6^- anion does not coordinate to the metal center. A further analysis shows that the PF_6^- anions are organized in columns parallel to the *c* axis.

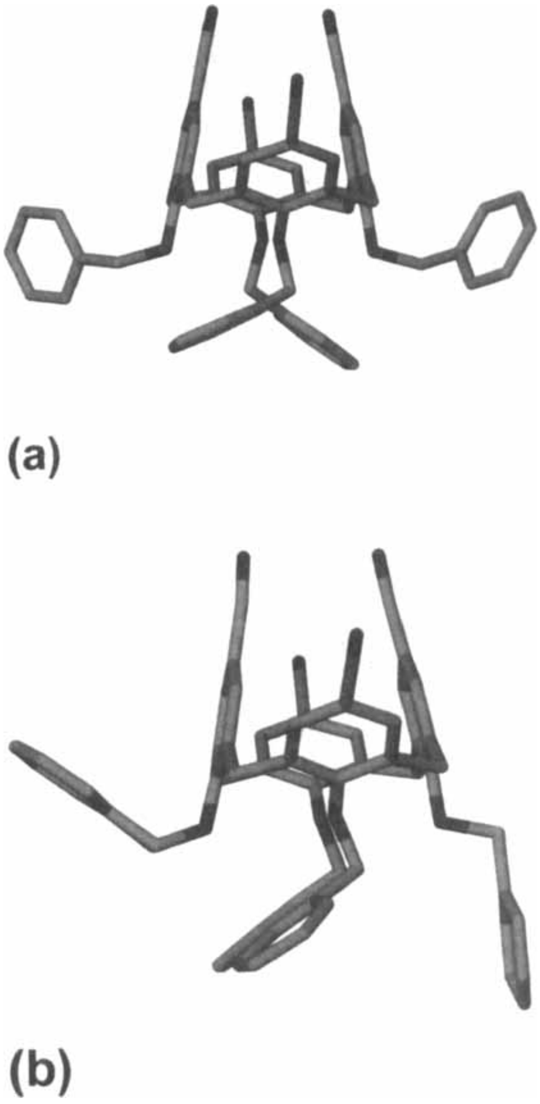


FIGURE 1 Molecular structure of tetracyanocalix[4]arene in the solid-state structures of (a) the free ligand and, (b) **6**

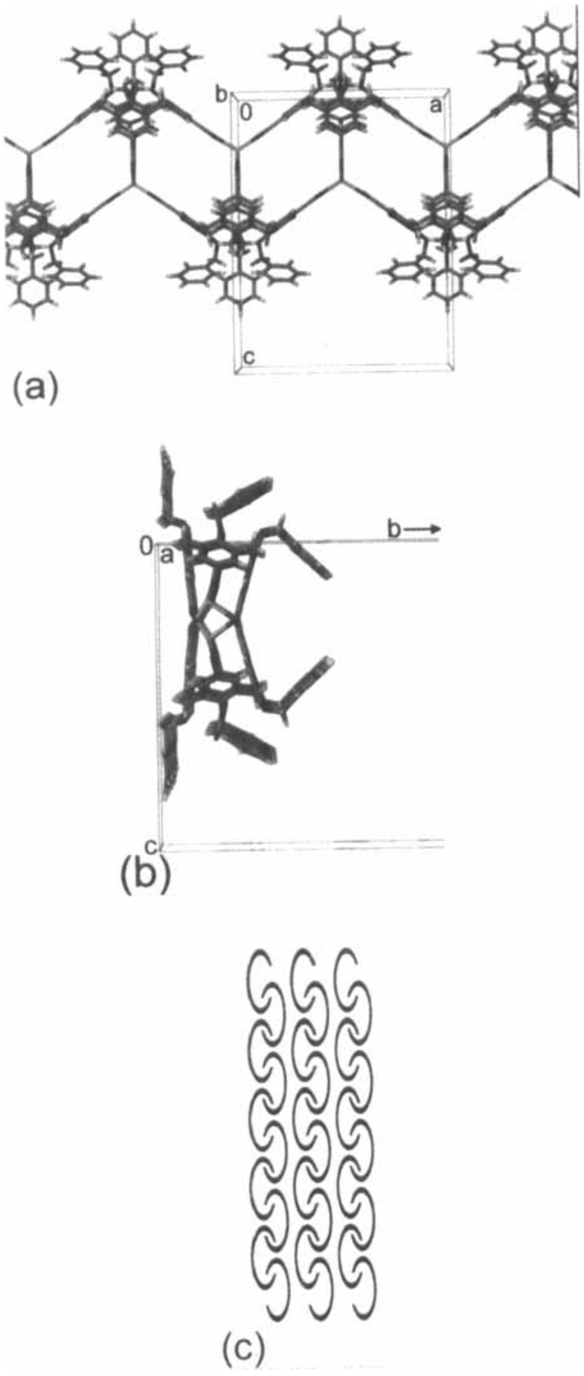


FIGURE 2 View of **6** along (a) [010] and, (b) [-100] showing the ribbon-like one-dimensional coordination polymer aligned parallel to the crystallographic *a* axis. The cross-section of the strand is approximately C-shaped and adjacent strands face one another with their cupped phenyl groups interlocked, (c)

In summary, this investigation illustrates that metal-ligand interaction for the formation of infinite networks can be applied to *p*-tetracyanocalix[4]arene. In addition to being a good host molecule for inclusion phenomena, we have shown that calix[4]arene with four nitrile groups covalently attached to the upper rim of the cone conformer can be a good candidate for the formation of coordination polymers.

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[11] ^{1}H-NMR (250MHz), (CDCL$_3$) 7.60 (br m, 7H, Ar**H**), 5.32 (s, 2H, benzyl**CH2**), 4.40 (d, 1H, methylene **CH2**), 3.19 (d, 1H, methylene **CH2**).

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