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Self-Assembly of a Tetranuclear Co^{III}-Metallacycle from the Reaction of a Bis(benzene-*o*-dithiolato) Ligand with Co^{II} and Subsequent Aerial Oxidation

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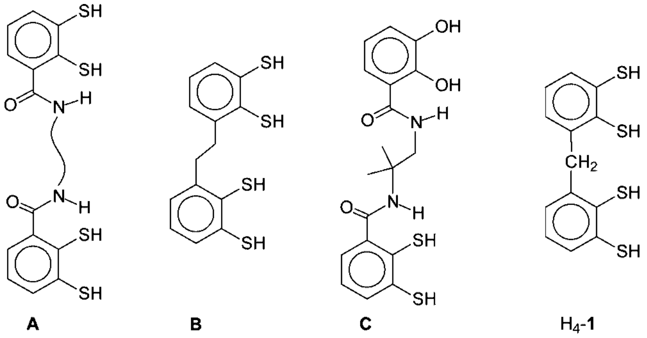
The bis(benzene-*o*-dithiol) ligand $[(HS)_2\text{-}2,3\text{-}C_6H_3\text{–}CH_2\text{–}C_6H_3\text{-}2,3\text{-}(SH)_2]$ (H_4-**1**) reacts, after deprotonation with Li_2CO_3, with $CoCl_2·6H_2O$. Aerial oxidation in methanol gives the tetranuclear metallacycle $Li_4[Co_4(\mathbf{1})_4]$. The X-ray structure analysis of $(PNP)_4[Co_4(\mathbf{1})_4]$ (**7**) reveals a cyclic structure in which each of the bis(benzene-*o*-dithiolato) ligands forms a bridge between two cobalt centers. Two differently coordinated cobalt atoms (*syn* and *anti*) are observed in the tetranuclear complex.

Introduction

The combination of polydentate organic ligands and transition metals has led to supramolecular complexes.[1] Metal-directed self-assembly has been used to form different supramolecular architectures like helicates,[2] boxes,[3] squares,[4] molecular containers,[5] and other structural motifs.[6] Among those, metal helicates have attracted special interest owing to their presence in nature.[2] The first triple-stranded helicate $[Fe_2(RA)_3]$ (RA = rhodotorulic acid), containing exclusively oxygen donor functions from hydroxamate groups, was isolated and characterized by Raymond et al.[7] The early helicate chemistry, however, was dominated by nitrogen donor ligands like oligobipyridines.[2,8] Later, triple-stranded helical complexes with catecholato donor groups were prepared.[2,9] The coordination chemistry of dicatechol ligands has been reviewed.[10] Double-stranded helical structures built from ligands with an unsymmetrical spacer (directional ligands) have been reported.[11] Even the triple-stranded helicate of a catecholato/aminophenolato ligand has been described.[12]

Much less is known about helicates containing benzene-*o*-dithiolato or other dithiolene donor groups. We have described a method for the *o*-functionalization of benzene-1,2-dithiol, which gives 2,3-dimercaptobenzoic acid[13] or 2,3-dimercaptobenzyl alcohol.[14] These building blocks were used to synthesize bis(benzene-*o*-dithiol) ligands of type **A**,[15,16] **B**,[16] and the benzene-*o*-dithiol/catechol ligand **C**[17] (Scheme 1). Non-helical mono- and dinuclear complexes have been obtained with ligands **A** and **B**, while ligand **C** reacts with Ti^{IV} to give a triple-stranded helicate with a parallel ligand orientation.



Scheme 1. Ligands containing the benzene-*o*-dithiol donor group.

However, no dinuclear triple-stranded helicates have been obtained so far from bis(benzene-*o*-dithiol) ligands such as **A** and **B**. Albrecht et al. have shown that methylene-bridged dicatecholato[18] and catecholato/aminophenolato[12] ligands are capable of forming triple-stranded helicates with Ti^{IV} and Ga^{III}. In our search for helicates built exclusively from sulfur donors, we have therefore prepared the novel methylene-bridged bis(benzene-*o*-dithiol) ligand H_4-**1** (Scheme 1). Here we present the preparation of ligand H_4-**1** and its coordination chemistry with Co^{III}.

Results and Discussion

Ligand H_4-**1** was prepared as depicted in Scheme 2. 1,2-Bis(isopropylmercapto)benzene (**2**) was synthesized as described previously.[14,16] Deprotonation of **2** with *n*BuLi/TMEDA in hexane yielded the organolithium compound **3**. Compound **3** was not isolated but immediately transformed into 2,3-bis(isopropylmercapto)benzaldehyde (**4**) by reaction with *N*,*N*-dimethylformamide followed by an acidic

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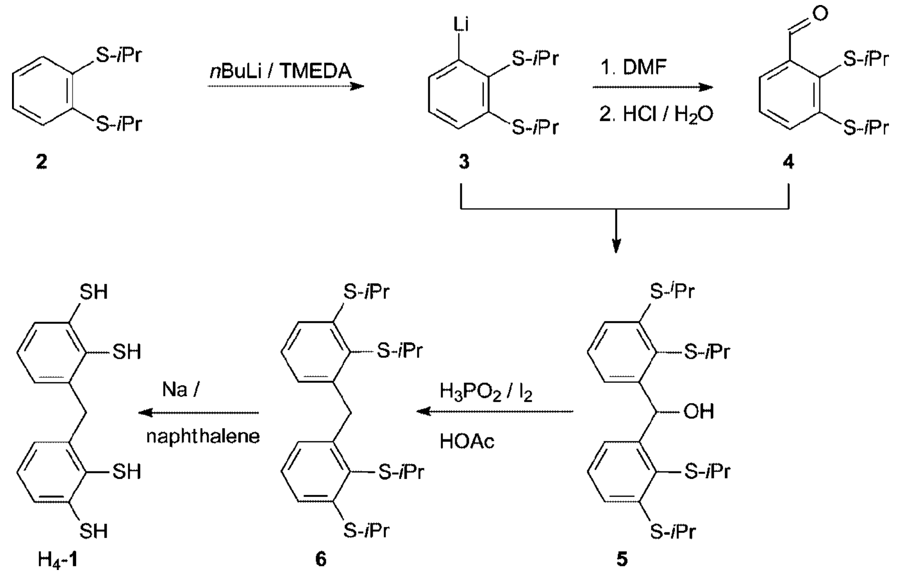


Scheme 2. Synthesis of the bis(benzene-*o*-dithiol) ligand H_4-**1**.

workup. Reaction of equimolar amounts of **3** and **4** in hexane yielded the alcohol **5** after acidification. Alcohol **5** was deoxygenated with hypophosphorous acid in the presence of a catalytic amount of iodine in acetic acid.[19] Removal of the *S*-protection groups in ligand precursor **6** with sodium/naphthalene in THF liberated ligand H_4-**1**, which was isolated after hydrolysis in approximately 85% yield (relative to **2**).

Reaction of equimolar amounts of H_4-**1** and $CoCl_2\cdot 6H_2O$ in methanol at ambient temperature in the presence of two equivalents of Li_2CO_3 yielded a brown solution. We assume that this solution contained Co^{II} complexes with benzene-*o*-dithiolato ligands. Upon aerial oxidation, the brown solution immediately turned deep blue, which indicates the formation of a Co^{III}–benzene-*o*-dithiolato complex. Addition of PNPCl [PNP^+ = bis(triphenylphosphoranylidene)ammonium] led to the precipitation of a blue solid, which was isolated and dried. The composition of the blue solid was established by ESI mass spectroscopy (Figure 1, negative ions). No peaks for a double-stranded complex of composition $[Co_2(\mathbf{1})_2]^{4-}$ are observed. Instead, three peaks are found at m/z = 351, 648, and 1241. These are assigned to the ions $[Co_4(\mathbf{1})_4]^{4-}$, $\{(PNP)[Co_4(\mathbf{1})_4]\}^{3-}$, and $\{(PNP)_2[Co_4(\mathbf{1})_4]\}^{2-}$. These assignments were corroborated by matching isotope patterns. Thus, the reaction of ligand H_4-**1** with $CoCl_2$ followed by aerial oxidation and precipitation with PNPCl does not yield a dinuclear complex, as was expected, but instead a tetranuclear complex of composition $(PNP)_4[Co_4(\mathbf{1})_4]$ (**7**).

To establish the molecular structure of the $[Co_4(\mathbf{1})_4]^{4-}$ anion, crystals suitable for an X-ray analysis were grown by slow vapour diffusion of pentane into a solution of **7** in dichloromethane. The molecular structure of tetraanion $[Co_4(\mathbf{1})_4]^{4-}$ is shown in Figure 2. The complex anion contains four $[Co(S_2C_6H_3R)_2]$ units arranged in a cyclic fashion. Each $\mathbf{1}^{4-}$ ligand bridges two cobalt atoms. Each of the cobalt atoms is coordinated by two benzene-*o*-dithiolato units from different ligands in a square-planar fashion. The Co–S and C–S distances in **7** are normal and match those reported for the mononuclear complex $(AsPh_3Me)[Co(S_2C_6H_3CH_3)_2]$.[20] Cobalt(III) complexes with electron-poor benzene-*o*-dithiolato ligands [$S_2C_6Cl_4$ or $S_2C_6H_2(CN)_2$] have been reported to dimerize.[21] In such dimers the $[Co(bdt)_2]^-$ (bdt = substituted benzene-*o*-dithiolate) units lie parallel to one another such that the cobalt atom of each $[Co(bdt)_2]^-$ unit is directly opposite a sulfur atom belonging to the second unit. This arrangement leads to the formation of two new Co–S bonds and a tetragonal-pyramidal coordination environment for each cobalt atom.

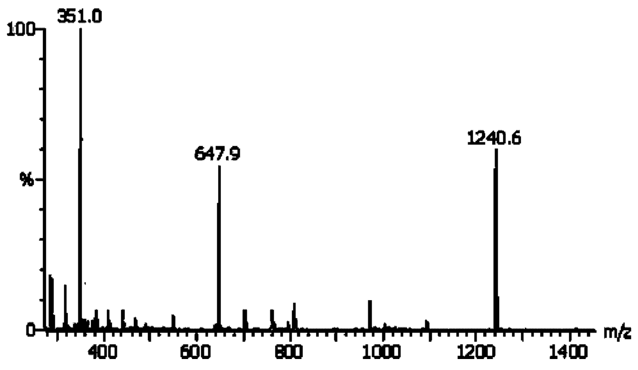


Figure 1. ESI mass spectrum (negative ions) of $(PNP)_4[Co_4(\mathbf{1})_4]$ (**7**).

No such extra Co–S interactions are observed in the anion $[Co_4(\mathbf{1})_4]^{4-}$. The $[Co_4(\mathbf{1})_4]^{4-}$ anions are well separated in the solid state, and no intramolecular Co–Co (shortest separation about 9 Å) and Co–S (shortest separation about 7 Å) or intermolecular Co–Co (shortest separation longer than 9 Å) and Co–S (shortest separation longer than 7 Å) contacts are found.

In contrast to the recently reported dinuclear nickel complex with an ethylene bridged bis(benzene-*o*-dithiolato) ligand (Scheme 1, **B**),[16] the tetranuclear complex $(PNP)_4$-

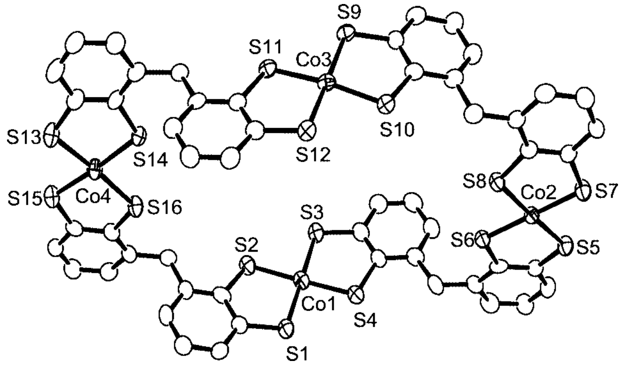


Figure 2. Molecular structure of the $[Co_4(\mathbf{1})_4]^{4-}$ anion of **7**. Hydrogen atoms and cations have been omitted for clarity. Selected ranges for bond lengths [Å] and bond angles [°]: Co–S 2.157(2)–2.176(2), C–S 1.746(6)–1.769(6), S–Co–S (intra ligand) 91.08(7)–91.84(7), Co–S–C 104.4(2)–105.9(2).

$[Co_4(\mathbf{1})_4]$ contains two metal centers with a slightly different coordination environment. Two cobalt atoms (Co1 and Co3) are coordinated by benzene-*o*-dithiolato units and the alkyl substituents are arranged in *anti* positions, while the other two cobalt atoms (Co2 and Co4) are coordinated by benzene-*o*-dithiolato units that have their alkyl substituents arranged in a *syn* fashion. This leads to two different C_2 axes along the two metal–metal connection lines Co1–Co3 and Co2–Co4 (Figure 3). The distances between the equivalent cobalt atoms are 9.661 Å (Co1–Co3) and 15.933 Å (Co2–Co4). A large internal cavity is formed by this arrangement. Two benzene rings of the PNP^+ cations partly fill this cavity without any interaction with the metallacycle. Complex **7** is, to the best of our knowledge, the first metallosupramolecular assembly that contains two differently coordinated metal centers even though a ligand with two identical donor sites has been used.

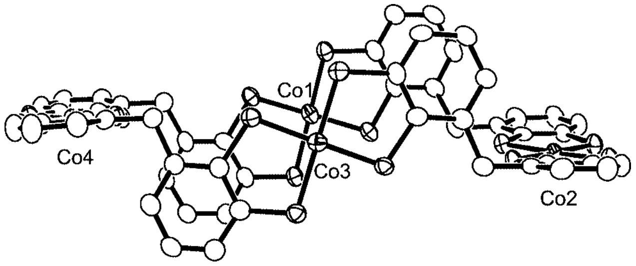
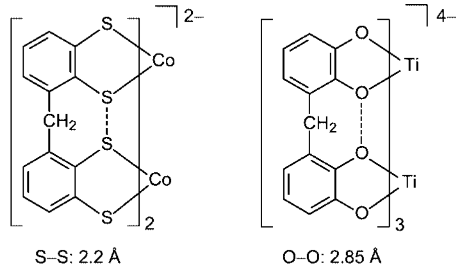


Figure 3. View along the Co1–Co3 axis showing the *syn* (Co2, Co4) and *anti* (Co1, Co3) arrangement of the substituted benzene-*o*-dithiolato ligands.

Although a tetranuclear complex $[Co_4(\mathbf{1})_4]^{4-}$ is entropically less favorable than two dinuclear complexes $[Co_2(\mathbf{1})_2]^{2-}$, the larger compound is exclusively formed. We believe that this occurs because of a strong steric interaction between the two sulfur atoms in the 2-positions of the aromatic rings that would occur in a hypothetical dinuclear complex $[Co_2(\mathbf{1})_2]^{2-}$ (Scheme 3, left). Albrecht et al. prepared a dicatechol ligand, with the same topology as H_4-**1**, that forms a dinuclear triple-stranded helicate with Ti^{IV} (Scheme 3, right).[18] In this complex, no repulsion between the oxygen atoms in the 2-positions is observed (intraligand O···O distance 2.85 Å). In addition, possible repulsion between these oxygen atoms is also compensated by coordination to hard lithium cations. This coordination is not possible and was not observed with the soft sulfur donor atoms. In a hypothetical dinuclear complex with benzene-*o*-dithiol ligands, steric interaction between the sulfur atoms in the 2-position would occur owing to the longer C–S bonds (1.76 Å versus 1.35 Å for the C–O bonds) and the larger intraring C–C–S angles (119° versus 114° for the C–C–O angles). On the basis of these parameters, the S···S distance in a dinuclear complex $[Co_2(\mathbf{1})_2]^{2-}$ would be around 2.2 Å, which is far too short for a nonbonding interaction (typically S–S bond lengths are 2.0 Å). Consequently, strong repulsion between the sulfur atoms must occur in the hypothetical $[Co_2(\mathbf{1})_2]^{2-}$ complex in which two cobalt atoms are coordinated in a square-planar fashion by two CH_2-bridged bdt ligands. In order to avoid this unfavourable repulsion, one benzene-*o*-dithiolato group of each $\mathbf{1}^{4-}$ ligand is rotated by about 90° around the Ar–CH_2 axis, which, in turn, leads to the formation of the tetranuclear metallacycle.



Scheme 3. Hypothetical complex $[Co_2(\mathbf{1})_2]^{2-}$ (left) and triple-stranded helicate (right).

Experimental Section

If not stated otherwise, all manipulations were carried out under dry argon by using standard Schlenk techniques. Hexane, tetrahydrofurane, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were freshly distilled from sodium/benzophenone prior to use. The starting material 1,2-bis(isopropylmercapto)benzene (**2**) was prepared as described before.[16]

2,3-Bis(isopropylmercapto)benzaldehyde (4): A sample of *n*-butyllithium (12.16 mL of a 2.5 M solution in hexane) was added dropwise to a solution of TMEDA (4.56 mL, 30.4 mmol) and 1,2-bis(isopropylmercapto)benzene (**2**, 6.9 g, 30.4 mmol) in hexane (100 mL) at 0 °C. After 30 min, the ice bath was removed, and the stirring was continued for 3 h at ambient temperature, which resulted in the formation of an off-white slurry. Dry *N*,*N*-dimethylformamide (3.53 mL, 45.6 mmol) was added, and the solution was stirred for 12 h. Water (100 mL) and hydrochloric acid (37%, 20 mL) were added, and the aqueous solution was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried with $MgSO_4$, and the solvent was removed in vacuo. Column chromatography (SiO_2, Et_2O/petroleum ether, 1:3) gave a yellow oil (7.33 g, 28.8 mmol, 95%). ^1H NMR ($CDCl_3$, 300.1 MHz): $\delta = 10.8$ (s, HC=O), 7.67 (dd, 1 H, Ar-H), 7.49–7.35 (m, 2 H, Ar-H), 3.54–3.32 (m, 2 H, SCH), 1.39 (d, $^3J = 7.0$ Hz, 6 H, CH_3), 1.23 (d, $^3J = 7.0$ Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta = 193.4$

(C=O), 146.5, 139.7, 136.4, 131.4, 129.2, 124.3 (Ar-C), 40.9 (SCH), 36.0 (SCH), 23.0 (CH_3), 22.6 (CH_3) ppm. GC/MS (EI, 70 eV): *m/z* (%) = 254 (66) $[M]^+$, 211 (10) $[M - C_3H_7]^+$, 179 (5) $[M - SC_3H_7]^+$, 41 (100) $[C_3H_5]$. $C_{13}H_{18}OS_2$ (254.40): calcd. C 61.38, H 7.13, S 25.20; found C 61.47, H 7.36, S 24.87.

Bis[2,3-bis(isopropylmercapto)phenyl]methanol (5): A sample of *n*-butyllithium (3.00 mL of a 2.5 M solution in hexane) was added dropwise to a solution of TMEDA (1.15 mL, 7.50 mmol) and 1,2-bis(isopropylmercapto)benzene **2** (1.7 g, 7.50 mmol) in hexane (30 mL) at 0 °C. After 30 min, the ice bath was removed, and the stirring was continued for 3 h at ambient temperature, which resulted in the formation of an off-white slurry. 2,3-Bis(isopropylmercapto)benzaldehyde (**4**, 1.91 g, 7.50 mmol) dissolved in hexane (10 mL) was added dropwise, and the solution was stirred for 12 h. Acidification with hydrochloric acid (37%) yielded a yellow precipitate, which was isolated by filtration, washed with hexane, and dried in vacuo to give **5** as a white powder (3.46 g, 7.20 mmol, 96%). ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 7.26–7.18 (m, 4 H, Ar-H), 7.01 (s, 1 H, C*H*–OH), 7.00 (dd, 2 H, Ar-H), 3.66 (sept, 2 H, SCH), 3.50 (sept, 2 H, SCH), 1.37 (d, 12 H, CH_3), 1.24 (d, 12 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 148.3, 144.9, 131.4, 128.7, 126.3, 124.5 (Ar-C), 72.0 (CH–OH), 39.1 (SCH), 36.1 (SCH), 25.5 (CH_3), 25.1 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3457 (br., O–H), 3050 (s, Ar-H), 2960, 2923, 2863 (s, $CHMe_2$), 1557 (m, Ar-C=C), 1443 (s, CH) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 480 (64) $[M]^+$, 437 (73) $[M - C_3H_7]^+$, 405 (100) $[M - SC_3H_7]^+$. $C_{25}H_{36}OS_4$ (480.16): calcd. C 62.45, H 7.55, S 26.68; found C 62.51, H 7.47, S 26.44.

Bis[2,3-bis(isopropylmercapto)phenyl]methane (6): Iodine (80 mg, 0.31 mmol) and bis[2,3-bis(isopropylmercapto)phenyl]methanol (**5**, 1.50 g, 3.10 mmol) were dissolved in concentrated acetic acid (60 mL). Hypophosphorous acid (1.60 mL, 50% solution by weight in water) was added, and the solution was stirred at 60 °C for 24 h. Water (100 mL) was added at ambient temperature, and the aqueous phase was extracted with hexane (3 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (2 × 20 mL) and dried with $MgSO_4$, and the solvent was removed in vacuo. Column chromatography (SiO_2, Et_2O/hexane, 1:5) gave **6** as a white powder (1.41 g, 3.04 mmol, 98%). ^{1}H NMR ($CDCl_3$, 300.1): δ = 7.20–7.15 (m, 4 H, Ar-H), 6.80–6.75 (dd, 2 H, Ar-H), 4.72 (s, 2 H, CH_2), 3.54 (m, 4 H, SCH), 1.45 (d, 12 H, CH_3), 1.30 (d, 12 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 149.1, 147.4, 134.3, 130.9, 128.6, 126.6 (Ar-C), 42.5 (CH_2), 41.3 (SCH), 38.1 (SCH), 25.5 (CH_3), 25.1 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3048 (Ar-H), 2960, 2923, 2863 (s, $CHMe_2$), 1443 (s, CH_2) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 464 (8) $[M]^+$, 421 (5) $[M - C_3H_7]^+$, 389 (100) $[M - SC_3H_7]^+$, 357 (53) $[M - S_2C_3H_7]^+$. $C_{25}H_{36}S_4$ (464.17): calcd. C 64.60, H 7.81, S 27.59; found C 64.47, H 7.87, S 27.72.

Bis(2,3-dimercaptophenyl)methane (H_4-1): Compound **6** (3.80 g, 8.19 mmol) and naphthalene (5.20 g, 41.0 mmol) were dissolved in tetrahydrofurane (80 mL), and pieces of sodium (1.90 g, 82 mmol) were added. The mixture was stirred for 12 h at ambient temperature, and degassed methanol (15 mL) was then added dropwise. After 10 min, the solvent was removed in vacuo, and the residue was dissolved in degassed water (30 mL). The aqueous phase was washed with degassed diethyl ether (3 × 20 mL), filtered, and acidified with hydrochloric acid (37%). The product was extracted with dichloromethane (3 × 20 mL), the combined organic layers were dried with $MgSO_4$, and the solvent was removed in vacuo to give H_4-**1** as an off-white powder (2.33 g, 7.78 mmol, 96%). ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 7.34 (dd, ^3J = 7.9, ^4J = 1.3 Hz, 2 H, Ar-H), 7.00 (t, ^3J = 7.9 Hz, 2 H, Ar-H), 6.78 (dd, ^3J = 7.9, ^4J = 1.3 Hz, 2 H, Ar-H), 4.18 (s, 2 H, CH_2), 3.84 (s, 2 H, SH), 3.81 (s, 2 H, SH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 141.5, 134.7, 133.2, 131.5, 129.7, 128.3 (Ar-C), 43.3 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3050 (s, Ar-H), 2894 (m, C–H), 2525 (m, S–H), 1443, 717 (C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 296 (76) $[M]^+$, 263 (85) $[M - SH]^+$, 230 (100) $[M - 2SH]^+$, 197 (47) $[M - 3SH]^+$. $C_{13}H_{12}S_4$ (295.98): calcd. C 52.67, H 4.08, S 43.25; found C 53.22, H 3.88, S 43.82.

$(PNP)_4[Co_4(1)_4]$ (7): A solution of H_4-**1** (50 mg, 0.169 mmol) and Li_2CO_3 (25 mg, 0.34 mmol) in methanol (10 mL) was added to a solution of $CoCl_2 \cdot 6H_2O$ (40 mg, 0.169 mmol) in methanol (10 mL). The mixture was stirred for 12 h, exposed to air for 10 min, and filtered. Addition of bis(triphenylphosphoranylidene)ammonium chloride (PNPCl) (97 mg, 0.169 mmol) to the filtrate gave a blue precipitate of **7**, which was isolated by filtration, washed with methanol, and dried in vacuo (110 mg, 0.031 mmol, 74%). MS (ESI, negative ions): *m/z* (%) = 351.0 $[Co_4(\mathbf{1})_4]^{4-}$, 648 $[(Co_4(\mathbf{1})_4)^{4-} + PNP^+]^{3-}$, 1241 $[(Co_4(\mathbf{1})_4)^{4-} + 2\,PNP^+]^{2-}$. $C_{196}H_{152}N_4P_8S_{16}Co_4$ (3559.7): calcd. C 66.13, H 4.30, N 1.57, S 14.41; found C 65.77, H 4.42, N 1.48, S 14.28.

X-ray Crystallographic Study of 7: A suitable crystal of **7** (0.15 × 0.10 × 0.08 mm) was mounted on a Bruker AXS APEX diffractometer equipped with a rotating molybdenum anode (λ = 0.71073 Å), cooling device, and graphite monochromator. $(PNP)_4[Co_4(\mathbf{1})_4]$, $C_{196}H_{152}N_4P_8S_{16}Co_4$, M = 3559.7, triclinic $P\bar{1}$, a = 18.473(7), b = 19.797(7), c = 24.497(9) Å, α = 80.724(7), β = 89.026(7), γ = 79.787(7)°, V = 8701(6) Å^3, Z = 2, $\rho_{calcd.}$ = 1.359 g cm^{-3}, μ = 0.696 mm^{-1}. 54025 Structure factors ($-19 \le h \le 19$, $-21 \le k \le 21$, $-26 \le l \le 26$, 2θ range 2.1–55.0°) were collected at 123(2) K. An empirical absorption correction was applied (T_{min} = 0.903, T_{max} = 0.947) before merging gave 22725 unique intensities (R_{int} = 0.069). Structure solution with SHELXS[22] and subsequent refinement of 2053 parameters against F^2 of 22725 unique intensities [13118 observed intensities $I > 2\sigma(I)$] using SHELXL[23] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model on calculated positions. Final residues R = 0.0591, wR = 0.1186. CCDC-284858 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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