

One-dimensional coordination polymers containing penta-supertetrahedral sulfide clusters linked by dipyriddy ligands

Jingli Xie,^a Xianhui Bu,^b Nanfeng Zheng^a and Pingyun Feng^{*a}

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Three new one-dimensional coordination polymers $[\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}\cdot\text{C}_{12}\text{H}_{10}\text{N}_2](1)$, $[\text{Zn}_7\text{CoS}(\text{SC}_6\text{H}_5)_{14}\cdot\text{C}_{13}\text{H}_{14}\text{N}_2](2)$ and $[\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}\cdot\text{C}_{13}\text{H}_{14}\text{N}_2](3)$ have been prepared containing penta-supertetrahedral clusters and linear crosslinking dipyriddy ligands; the two complexes show optical transitions with band gaps of ~ 3.44 eV (1) and ~ 3.54 eV (2).

The presence of transition-metal thiolate clusters at the metal-sequestering active sites of the metallothionein proteins highlighted interesting structural and biological implications.¹ The interest in these clusters has also led to a broader examination of other novel aspects including semiconductivity, photophysical and photochemical properties.² Dance *et al.* reported many metal thiolate anions including $[\text{Cd}_8\text{E}(\text{E}'\text{Ph})_{16}]^{2-}$ (E, E' = S, Se, Te), $[\text{M}_{10}\text{S}_4(\text{SPh})_{16}]^{4-}$ (M = Zn, Cd) that crystallized as quaternary ammonium or phosphonium salts.³ Neutral metal thiolates are also known that usually display either molecular or three-dimensional structures.^{4,5} In the case of polymeric structures, thiolate clusters are typically linked through sulfur sites at the corners of each cluster.^{4c-d}

There are few reports of transition-metal thiolate clusters linked by organic ligands. Such inorganic-organic hybrid materials may possess unique optical and photochemical properties due to the synergetic effect of both inorganic and organic components. For example, it was observed earlier that the photoluminescent properties of inorganic clusters could be enhanced by the presence of organic linkers that can absorb photon energies and transfer them to inorganic clusters.⁶ Such materials may also have applications as visible-light driven photocatalysts with enhanced efficiency.⁶ We now describe the synthesis and structural characterization of three neutral penta-supertetrahedral clusters linked by organic ligands to form different one-dimensional arrays.

All compounds were prepared by hydrothermal synthesis.⁷ Fig. 1 depicts the cluster structure found in all three phases. The central S^{2-} ion is coordinated to four inner Zn atoms that are each connected to three doubly bridging SC_6H_5 ligands. The central SZn_4 (denoted anti-supertetrahedral cluster or anti-T1) unit is capped on four faces by two ZnS_4 (regular supertetrahedral cluster or T1) units and two ZnS_3N units (Fig. 1), resulting in a cluster denoted as P1.⁶ Clusters consisting of an anti-supertetrahedral cluster at the core and four regular supertetrahedral

clusters coupled to each face of the anti-supertetrahedral cluster are called penta-supertetrahedral clusters, denoted P1.^{6b,6d}

All Zn atoms exhibit four-coordinate tetrahedral coordination. In 1, zinc-sulfur bond lengths range from 2.256(4) to 2.418(3) Å with relatively small variation, in contrast to the large variation found in the $[\text{Zn}_8\text{S}(\text{SCH}_2\text{C}_6\text{H}_5)_{16}]^{2-}$ complex.^{6c} The P1 cluster in 1 features two nitrogen ligand atoms from *trans* 1,2-bis(4-pyridyl)ethylene ligands that link the clusters to form a 1-dimensional zig-zag chain (Fig. 2). The zinc-nitrogen bond lengths are 2.007(11) and 2.020(8) Å, slightly less than that reported in $\text{Zn}_{10}\text{S}_4(\text{SC}_2\text{H}_5)_{12}\text{L}_4$ clusters.⁵

The use of the proper sulfide source is essential for the formation and assembly of the P1 nanocluster. Instead of the direct addition of Na_2S , sulfur or NaSH that may cause rapid precipitation of ZnS , thiourea is employed here to provide a gradual release of S^{2-} that may serve to promote crystal growth. In addition, the bridging dipyriddy ligand has two functions. It acts as a neutral ligand in place of two terminal SPh^- ligands to reduce the negative charge on the cluster to zero and in the meantime acts as the linker to assemble the P1 cluster into the 1-d chain structure.

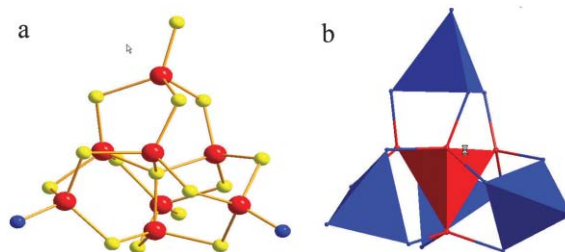


Fig. 1 (a) Ball and stick representation of the P1 cluster. Red: Zn, yellow: S; and blue: N. (b) Polyhedral representation of the P1 cluster. Red: SZn_4 anti-T1 cluster and blue: ZnS_4 and ZnS_3N T1 cluster. Phenyl groups are not shown for clarity.

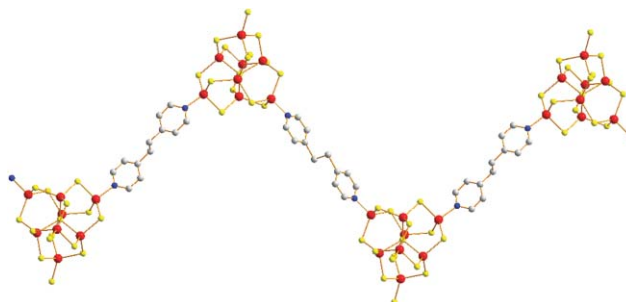


Fig. 2 1-D zig-zag chain structure in 1.

^aDepartment of Chemistry, University of California, Riverside, CA 92521, USA. E-mail: pingyun.feng@ucr.edu; Fax: 01 951 827 4713; Tel: 01 951 827 2043

^bDepartment of Chemistry and Biochemistry, California State University, 1250 Bellflower Blvd., Long Beach, CA 90840, USA

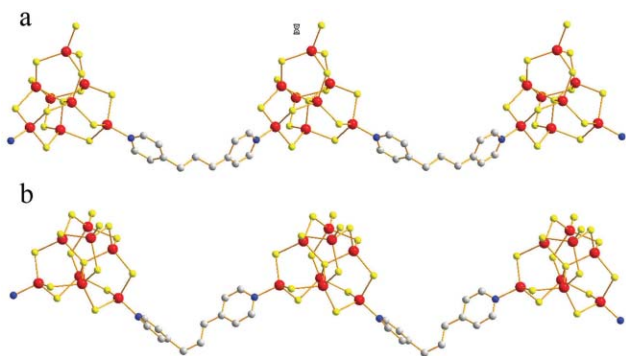


Fig. 3 One-dimensional straight chain structures of **2(a)** and **3(b)**. The same organic ligand occurs in **2** and **3**, but has a different conformation.

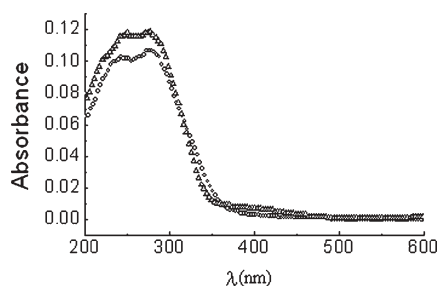


Fig. 4 UV absorption spectra of **1** (\circ) and **2** (Δ) as crystalline solid measured on a Shimadzu UV 3101 PC double-beam, double-monochromator spectrophotometer. The absorption data were calculated from reflectance data by using the Kubelka–Munk function. BaSO_4 powder was used as reference (100% reflectance).

Introduction of transition metal ions containing spin carriers into this system may induce interesting magnetic properties. Green cube-shaped single crystals of $[\text{Zn}_7\text{CoS}(\text{SC}_6\text{H}_5)_{14}\cdot\text{C}_{13}\text{H}_{14}\text{N}_2](\mathbf{2})$ containing a heterometallic cluster were prepared by a route similar to that used for **1**.⁷ The clusters in **1** and **2** are nearly identical with similar observed Zn–S and Zn–N bond lengths (2.260(3)–2.387(3) Å and 2.024(8)–2.039(10) Å, respectively). Due to the similar scattering factors between Zn and Co, the concentration of the Co ion could not be determined reliably through crystallographic refinement and the Zn to Co ratio of 7 was determined by inductively coupled plasma spectrometry (metal composition: Zn: 20.1%; Co: 2.6%). The length of 1,3-bis(4-pyridyl)propane (distance between the nitrogen atoms) in **2** is 9.676 Å, compared with 9.192 Å for 1,2-bis(4-pyridyl)ethylene in **1**. The substantial difference between two ligands leads to two distinctly different chain conformations (Fig. 2 and 3).

The linking mode similar to that found in **2** is also found in **3**. The Zn–S and Zn–N bond lengths in **3** range from 2.286(5) to 2.404(4) Å and from 2.043(8) to 2.048(10) Å, respectively. Also, compared with that in **2**, the length of the linker in **3** is shorter (8.638 Å) (Fig. 3), which demonstrates the conformational flexibility of 1,3-bis(4-pyridyl)propane.

The optical properties of these systems are of interest⁸ and Fig. 4 displays the UV absorption spectra of **1** and **2**. The optical transitions likely originate from charge transfer from the tetrahedral sulfur atom to nearby metal atoms.^{8a,9} The estimated band gaps are ~ 3.44 eV for **1** and ~ 3.54 eV for **2**.

In summary, **1**, **2** and **3** feature penta-supertetrahedral clusters (P1) linked by bipyrindyl ligands in one-dimensional polymeric chains. The present controlled assembly process holds considerable promise for the development of materials featuring larger clusters linked in one, two- or three-dimensional arrays.^{8a,10–12} Different organic linkers with various functionality are being actively pursued.† We would like to thank for the support of this work, the NSF (P. F.) and the donors of the Petroleum Research Fund (administered by the ACS) (X. B. and P. F.). P. Y. is an Alfred P. Sloan research fellow, Beckman Young Investigator, and Camille Dreyfus Teacher-Scholar. J. X. thanks Prof. Anthony G. Wedd, Dr Paul Donnelly for their evaluation of this work and Dr Brendan Abrahams for his help with structural refinement.

Notes and references

† Crystal data: $\text{C}_{96}\text{H}_{80}\text{N}_2\text{S}_{15}\text{Zn}_8$ (**1**), $M = 2265.48$, monoclinic, space group $P2_1/n$, $a = 14.606(3)$ Å, $b = 25.837(5)$ Å, $c = 26.907(5)$ Å, $\beta = 105.75(3)^\circ$, $V = 9773(3)$ Å³, $Z = 4$, $D_c = 1.540$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 2.294$ mm⁻¹, $\lambda = 0.71073$ Å. A crystal of dimensions $0.15 \times 0.10 \times 0.10$ mm³ was collected at 298 K. GOF = 1.072. ω -Scans covering reciprocal space up to $\theta_{\text{max}} 25.00^\circ$ with 99.9% completeness, total of 57 482 reflections (17 212 unique) with $R_{\text{int}} = 0.0887$. Final $R(F) = 0.0871$, $wR(F^2) = 0.2753$ with $I > 2\sigma(I)$. The carbon atoms on phenyl rings are disordered and constrained during refinement; $\text{C}_{97}\text{H}_{84}\text{CoN}_2\text{S}_{15}\text{Zn}_7$ (**2**), $M = 2275.08$, monoclinic, space group $P2_1/c$, $a = 19.0847(15)$ Å, $b = 18.4854(14)$ Å, $c = 27.494(2)$ Å, $\beta = 94.347(2)^\circ$, $V = 9671.8(13)$ Å³, $Z = 4$, $D_c = 1.562$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 2.242$ mm⁻¹, $\lambda = 0.71073$ Å. A crystal of dimensions $0.20 \times 0.15 \times 0.15$ mm³ was collected at 238 K. GOF = 1.017. ω -Scans covering reciprocal space up to $\theta_{\text{max}} 25.00^\circ$ with 99.8% completeness, total of 57 108 reflections (17 000 unique) with $R_{\text{int}} = 0.1201$. Final $R(F) = 0.0783$, $wR(F^2) = 0.1781$ with $I > 2\sigma(I)$; $\text{C}_{97}\text{H}_{84}\text{N}_2\text{S}_{15}\text{Zn}_8$ (**3**), $M = 2281.52$, monoclinic, space group $P2_1/c$, $a = 13.457(5)$ Å, $b = 17.681(5)$ Å, $c = 40.836(5)$ Å, $\beta = 92.864(5)^\circ$, $V = 9704(5)$ Å³, $Z = 4$, $D_c = 1.562$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 2.311$ mm⁻¹, $\lambda = 0.71073$ Å. A crystal of dimensions $0.15 \times 0.10 \times 0.10$ mm³ was collected at 293 K. GOF = 1.125. ω -Scans covering reciprocal space up to $\theta_{\text{max}} 25.00^\circ$ with 97.8% completeness, total of 64 136 reflections (16 694 unique) with $R_{\text{int}} = 0.0607$. Final $R(F) = 0.0939$, $wR(F^2) = 0.2463$ with $I > 2\sigma(I)$. Structure solution SHELXL-97, full matrix least-squares based on F^2 using SHELXL-97. CCDC 238689, 238690 and 247956 for **1**, **2** and **3**, respectively. See <http://dx.doi.org/10.1039/b508470a> for crystallographic data in CIF or other electronic format.

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- 7 To synthesize $[\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}\cdot\text{C}_{12}\text{H}_{10}\text{N}_2](1)$, $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (1.301 g, 5.93 mmol), *trans* 1,2-bis(4-pyridyl)ethylene (0.130 g, 0.71 mmol), thiourea (0.107 g, 1.41 mmol), thiophenol (1.01 g, 9.17 mmol), and distilled water (5.93 g) were combined in a 23 ml Teflon-lined stainless steel autoclave and stirred for 20 min. The sealed vessel was heated at 150 °C for 7 days. After cooling to room temperature, pale-yellow transparent block crystals were obtained with about 40% yield. To synthesize $[\text{Zn}_7\text{CoS}(\text{SC}_6\text{H}_5)_{14}\cdot\text{C}_{13}\text{H}_{14}\text{N}_2](2)$, $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (1.305 g, 5.94 mmol), 1,3-bis(4-pyridyl)propane (0.418 g, 2.11 mmol), thiourea (0.109 g, 1.43 mmol), $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.100 g, 0.34 mmol), thiophenol (0.997 g, 9.05 mmol), and H_2O (9.528 g) were mixed and then heated in autoclave ($T = 150$ °C). After 10 days, green cubic single crystals with about 45% yield were recovered. To synthesize $[\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}\cdot\text{C}_{13}\text{H}_{14}\text{N}_2](3)$, $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.660 g, 3.00 mmol), 1,3-bis(4-pyridyl)propane (0.198 g, 1.00 mmol), thiourea (0.038 g, 0.5 mmol), AgOAc (0.165 g, 1.00 mmol), thiophenol (0.665 g, 6.04 mmol), and H_2O (5.565 g) were mixed and then heated in an autoclave ($T = 165$ °C). After eight days, colorless cube-shaped crystals were recovered with about 40% yield.
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