

OPEN-FRAMEWORK SOLIDS WITH DIAMOND-LIKE STRUCTURES PREPARED FROM CLUSTERS AND METAL-ORGANIC BUILDING BLOCKS

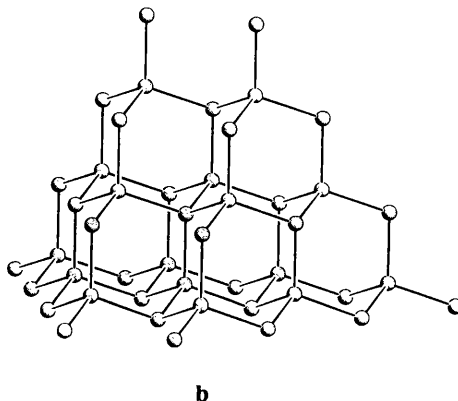
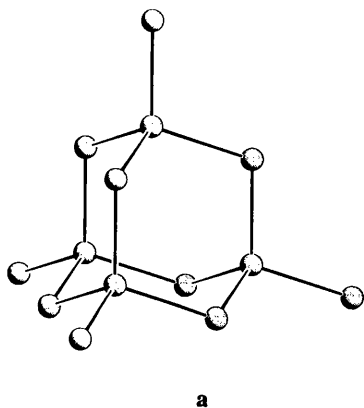
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ABSTRACT

The tetrahedral cluster $\text{Ge}_4\text{S}_{10}^{4-}$ and the rodlike ligand 4,4'-bipyridine are utilized in addition copolymerization reactions with the metal (II) ions of Mn, Fe, Co, Cu, and Zn in the preparation of 3-D open-framework solids, $\text{M}_x\text{Co}_{1-x}\text{Ge}_4\text{S}_{10}\cdot 2(\text{CH}_3)_4\text{N}$ ($x = 0.86$, $\text{M} = \text{Mn}$; $x = 1$, $\text{M} = \text{Mn}$, Fe, Co, and Zn), **1**, and $\text{Cu}(4,4'\text{-bpy})_2\cdot \text{PF}_6$, **2**, having diamond-like structures. These structures are viewed in terms of the cubic diamond structure, where the carbon atoms have been replaced by either a cluster or a metal ion and the C-C bond by a sulfide or the 4,4'-bpy. These compounds have been fully characterized by single crystal x-ray crystallography and their composition was confirmed by elemental analysis; they contain 3-D channel systems where cations or anions reside to balance the charge on the framework.

INTRODUCTION

The cubic diamond lattice can be viewed as composed of the adamantane unit, **a**, constructed from tetrahedral carbon atoms. These units are linked to form a 3-D network, **b**, which is not close-packed but is very dense (in terms of the number of atoms/unit area). Less dense lattices such as ZnS (zinc-blend), SiO_2 (cristobalite) and H_2O (ice- I_c) are related to the diamond structure by replacing the C atom with Zn, Si, or O and the C-C bond with S, O or H, respectively. Recently, we and others have used clusters and metal-organic complexes as building blocks in the preparation of open-framework structures that are also related to the diamond structure.^{1,2} In this study, we report the synthesis and structure of two classes of solids $\text{M}_x\text{Co}_{1-x}\text{Ge}_4\text{S}_{10}\cdot 2(\text{CH}_3)_4\text{N}$ ($x=0.86$, $\text{M} = \text{Mn}$; $x=1$, $\text{M} = \text{Mn}$, Fe, Co, and Zn), **1**, and $\text{Cu}(4,4'\text{-bpy})_2\cdot \text{PF}_6$, **2**,



both containing channels and having diamond-like open-framework structures. Here, it should be noted that an x-ray powder diffraction pattern for the class of compounds in **1** has been reported with no structural information,³ while compound **2** was reported by another group as this manuscript was being prepared.⁴ This report elaborates on their structures and their achievement as large crystals by using the building block approach in gel media, and by employing hydrothermal methods.

SYNTHESIS AND CHARACTERIZATION

M_xCo_{1-x}Ge₄S₁₀·2(CH₃)₄N ($x = 0.86$, $M = \text{Mn}$; $x = 1$, $M = \text{Mn, Fe, Co, and Zn}$), **1**: Two synthetic routes were utilized in the preparations of these compounds: (I) the compounds with $x = 0.86$ and **1**, having $M = \text{Mn}$ were synthesized hydrothermally; and (II) those with $x = 1$, $M = \text{Mn, Fe, Co, and Zn}$ were prepared in solution at room temperature.

Hydrothermal preparation giving crystals of up to 2.2 mm for $x = 1$ and $M = \text{Mn}$ was achieved as follows: GeS₂ (0.083 g, 0.61 mmol), aqueous 1.0 M (CH₃)₄NHCO₃ (0.3 ml, 0.33 mmol), aqueous 0.3 M (CH₃)₄NOH (0.3 ml, 0.090 mmol), manganese(II) acetate tetrahydrate (0.030 g, 0.12 mmol), 0.25 ml ethanol, and 1.9 ml of deionized water, were combined in a Pyrex lined stainless steel pressure vessel having an internal volume of 12 ml. This vessel incorporated a Nupro JB series valve to enable charging the mixture with 15 - 20 atm of dihydrogen sulfide gas. The sealed vessel was heated in a programmable furnace at 5°/min. to 150°C for 1 h, then cooled at 1°/min. to 110°C for 10 min. after which the mixture was further cooled at 0.1°/min. to 98°C for 4 h. The temperature was reduced at 1°/min. to 78°C for 2 h, then raised at 5°/min. to 150°C, and the entire process was repeated for a total of eight cycles after which the mixture was cooled to room temperature. The yellow crystals were washed with deionized water and methanol prior to drying in air to give 0.098 g. X-ray powder diffraction data were obtained for ground samples of this material and showed the following characteristic d-spacings (Å) and relative intensities: 7.824 (98), 7.064 (4), 6.652 (43), 4.855 (37), 4.721 (4), 4.055 (21), 3.938 (64), 3.344 (9), 3.163 (100), 3.081 (5), 3.031 (4), 2.843 (4), 2.761 (20), 2.629 (28), 2.585 (5), 2.439 (7), 2.364 (3), 2.296 (7), 2.271 (3), 2.235 (7). Elemental microanalysis was performed on such samples to give the formula MnGe₄S₁₀·2(CH₃)₄N: [Calcd. for C₈H₂₄NMnGe₄S₁₀: Ge, 35.66; Mn, 6.75; S, 39.38; C, 11.80; H, 2.97; N, 3.44. Found: Ge, 35.37 %; Mn, 6.52; S, 39.11; C, 11.54; H, 2.96; N, 3.31]. This compound was also prepared in solution as explained below.

Dark blue crystals of the compound with $x = 0.86$ were prepared using an identical procedure to that described above, where equimolar amounts (0.060 mmol) of the manganese (II) and cobalt (II) acetate tetrahydrates were used in the synthesis. X-ray powder diffraction data for these crystals was identical to that obtained for the $x = 1$ and $M = \text{Mn}$ compound. The composition of the dark blue was determined by elemental microanalysis to give the formula Mn_{0.86}Co_{0.14}Ge₄S₁₀·2(CH₃)₄N: [Calcd. for C₈H₂₄NMn_{0.86}Co_{0.14}Ge₄: Ge, 35.63 %; Mn, 5.80; Co, 1.01; S, 39.36; C, 11.79; H, 2.97; N, 3.44. Found: Ge, 35.29 %; Mn, 6.28; Co, 0.88; S, 39.07; C, 11.71; H, 3.02; N, 3.28]. A single crystal of this compound with 0.27 × 0.27 × 0.27 mm³ dimensions was analyzed at 25°C, tetragonal, space group *I*4 with $a = 9.532$ (1) Å, $c = 14.304$ (3) Å, $V = 1299.7$ (7) Å³, $Z = 2$, $\rho_{\text{calcd}} = 2.082$ g cm⁻³ and $\mu_{\text{a}}(\text{Mo K}\alpha) = 5.87$ mm⁻¹. Data were collected on a Siemens R3m/V autodiffractometer using graphite-monochromated Mo K α radiation and full 1.6° wide ω scans to a maximum of $2\theta = 50^\circ$, giving 726 unique reflections. The structure was solved by (SHELXTL PC) direct methods and the resulting structural parameters were refined by least-squares techniques to a standard discrepancy index $R = 0.0238$ and $R_w = 0.0249$ for 685 reflections with $F > 4 \sigma$ (F). Anisotropic thermal parameters were

refined for all non-hydrogen atoms and fixed thermal parameters were used for included hydrogens. Mn and Co were constrained to refine with equivalent anisotropic thermal parameters. Partial occupancy parameters for Mn and Co were constrained to sum to the full occupancy and allowed to refine. The resulting occupancy of 0.16 ± 0.07 for Co agrees well with the elemental analysis.

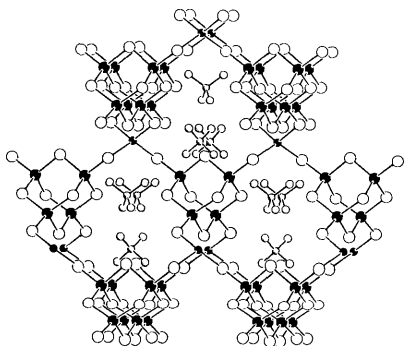
The preparation of the compounds with $x = 1$ and $M = \text{Fe, Co, and Zn}$ was accomplished in solution by following a published procedure for the manganese compound, which involves combination of aqueous mixtures of $M(\text{II})$ acetates and $[(\text{CH}_3)_4\text{N}]_4\text{Ge}_4\text{S}_{10}$ at room temperature.¹

Cu(4,4'-bpy)₂·PF₆, 2: Mixing two equivolume acetonitrile solutions of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (0.372 g, 1.00 mmol) and 4,4'-bpy (0.470 g, 3.00 mmol) at room temperature gave a yellow powder, which was washed with acetonitrile and ether to give 0.394 g (76% yield). This material was initially analyzed by elemental microanalysis to reveal the formula $\text{Cu}(4,4'\text{-bpy})_2\text{PF}_6$ [Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{PF}_6\text{Cu}$: C, 46.12; H, 3.10; N, 10.76; P, 5.95, Cu, 12.20. Found: C, 45.76; H, 3.03; N, 10.35; P, 5.68, Cu, 12.57], and it was found to be insoluble in aqueous and common nonaqueous solvent media. Repeated attempts to obtain crystals by varying the reaction conditions (such as solvent polarity, temperature or concentrations of reactants) were unsuccessful until we employed PEO gel as a diffusion and reaction medium. Orange crystals of this material were obtained by diffusion of an acetonitrile solution (3 mL, 0.2 M) of 4,4'-bpy into a gel that was formed by the addition of an acetonitrile solution (3 mL, 0.1 M) of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ to PEO powder ($M_w = 100,000$; 0.50 g). The homogeneity of the bulk product was confirmed by comparison of the observed x-ray powder diffraction (XRD) pattern with that calculated using single crystal diffraction pattern *vide infra*. In addition, the XRD pattern observed for the product obtained from the gel is in full agreement with that recorded for the powder material obtained from solution without PEO gel.

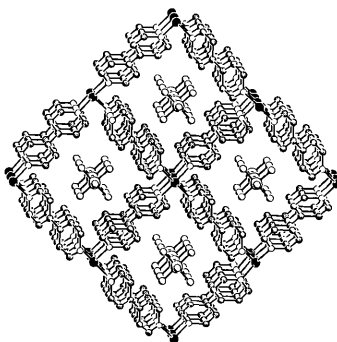
Single crystal x-ray analysis performed on $\text{Cu}(4,4'\text{-bpy})_2\text{PF}_6$: tetragonal, space group $P4/n$ with $a = 12.362$ (3) Å, $c = 6.986$ (2) Å, $V = 1067.6$ (5) Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.620$ g cm⁻³ and $\mu_a(\text{MoK}\alpha) = 1.165$ mm⁻¹. Data were collected on a Siemens R3m/V autodiffractometer using graphite-monochromated Mo K α radiation and full 1.6° wide ω scans to a maximum of $2\theta = 50^\circ$, giving 950 unique reflections. The structure was solved by (SHELXTL PC) direct methods and the resulting structural parameters were refined by least-squares techniques to a standard discrepancy index $R = 0.0691$ and $R_w = 0.0554$ for 510 reflections with $F > 3\sigma(F)$. Anisotropic thermal parameters were refined for all non-hydrogen atoms and fixed thermal parameters were used for included hydrogens.

RESULTS AND DISCUSSION

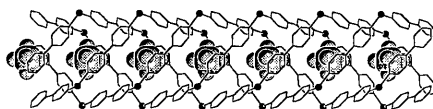
The structures of the compounds in **1** and that of **2** are best described in terms of the diamond structure shown in **b**. Each carbon atom in diamond is either substituted alternately by a tetrahedral $\text{Ge}_4\text{S}_{10}^{4-}$ cluster and a tetrahedral $M(\text{II})$ ion as in **1**, or by just tetrahedral $\text{Cu}(\text{I})$ centers as in **2**; each C-C bond is substituted by either an S^{2-} ion (**1**), or a rodlike 4,4' bpy as in (**2**). Such arrangements create 3-D open-frameworks with channels as shown in the crystal structure representations **c** and **d**, respectively. The channels are occupied by $(\text{CH}_3)_4\text{N}$ cations (**1**) or PF_6 anions (**2**) to balance the charge on the framework. An interesting aspect of the structure of **2** is that it is made up of four interlocked diamond-like networks. A closer look at the channels reveals that they are constructed from four independent copper bipyridine strands that are native to the four interlocked networks, as shown in **e**. This occurs presumably to fill the channel space



c



d



e

($20 \times 22 \text{ \AA}$ aperture) generated in a single diamond-like network.

Many examples of interlocking rings, knots and other interlacing of molecular threads are known in molecular organic chemistry; however, fewer are known as extended networks. The interlocking of four translationally equivalent networks, similar to that observed here, exists in one other compound, adamantane-1, 3, 5, 7-tetracarboxylic acid; however, in this case the very large empty space is completely filled by the interlocking networks leaving behind no voided space for inclusions.⁵ Its preparation as single crystals was facilitated by the use of PEO gel, which was utilized in slowing down the nucleation rate.

Compound **2** is stable up to 240°C under He atmosphere, and in boiling water for up to 1-2 hr in air. Preliminary investigations indicate that the PF_6^- anions may be decomposed at 140°C without major deformation to the metal-organic framework. The PF_6^- may be exchanged with SCN^- as indicated by the absence of P-F stretches in the infrared spectrum of the exchanged material, and as confirmed by solid state NMR. We have observed that this framework is reactive towards Lewis bases and can be converted to another open-framework material. Further experimentation aimed at evaluating its catalytic reactivity and ion-exchange capabilities, including its molecular sieving properties, are currently in progress.

This interlocking is not present in **1**, possibly due to the spherical shape of the GeS clusters compared to the rodlike shape of bpy. In the case of **1**, one of the cations makes van der Waals contacts to the framework ($\text{C-H}\cdots\text{S} = 4.202 \text{ \AA}$), and the other makes closer contacts to the framework and forms hydrogen bonds to the sulfide ($\text{C-H}\cdots\text{S} = 3.675 \text{ \AA}$). Thermal gravimetric

and residual gas analyses on **1** for $x = 1$ and $M = \text{Mn}$ reveal that the cations decompose to give a dark solid with N_2 , CH_4 , NH_3 , and amines evolved with no H_2S or any other sulfide-containing products were detected. The integrity of the framework is maintained at this temperature and begins to decompose at 500°C , as confirmed by x -ray powder diffraction. We have not yet established the nature of the species responsible for the electroneutrality of the resulting solid, and it is not clear whether the oxidation state (II) of the manganese is maintained. Presently, we are in the process of establishing its ion-exchange and its possible electronic properties.

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