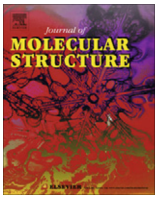
Journal of Molecular Structure 983 (2010) 104–111

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Five dimeric thiogermanates with transition metal complexes of multidentate chelating amines: Syntheses, structures, magnetism and photoluminescence

Guang-Ning Liu [a,b], Guo-Cong Guo [a,*], Ming-Sheng Wang [a], Li-Zhen Cai [a], Jin-Shun Huang [a]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China
[b] Graduate School, Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Article history:
Received 13 July 2010
Received in revised form 18 August 2010
Accepted 22 August 2010
Available online 26 August 2010

Keywords:
In situ metal/ligand reaction
Magnetism
Photoluminescence
Solvothermal synthesis
Thiogermanates
Transition metal complex

ABSTRACT

Five new thiogermanates, $[Ni^{II}(dien)_2]_2(Ge_2S_6)$ (dien = diethylenetriamine) (**1**), $[Ni^{II}(dien)_2](H_2pipe)(Ge_2S_6)$ (pipe = piperazine) (**2**), $\{[Mn^{II}(tren)]_2(\mu_2\text{-}Ge_2S_6)\}$ (tren = N,N,N-tris(2-aminoethyl)amine) (**3**) and $\{[M^{II}(tepa)]_2(\mu_2\text{-}Ge_2S_6)\}$ (M = Mn (**4a**), Ni (**4b**); tepa = tetraethylenepentamine), have been obtained solvothermally in the presence of tri-(L^3), tetra-(L^4) and penta-dentate (L^5) chelating amines and transition metal (TM) ions. Single-crystal X-ray diffraction analyses show that compounds **1**–**2** are comprised of discrete $(Ge_2S_6)^{4-}$ anions and TM complex (TMC) cations, while compounds **3**–**4b** are composed of each dimeric $(Ge_2S_6)^{4-}$ anion bridging two TMC cations via TM–S bonds to form a neutral molecule. Notably, two interesting *in situ* metal/ligand reactions were observed in the solvothermal syntheses of **2** and **3**. The present compounds exhibit wide optical gap ranging from 2.94 to 3.39 eV and photoluminescence with the emission maxima occurring around 440 (**1**, **2**, **3** and **4b**) and 489 nm (**4a**). Magnetic measurements show the presence of weak antiferromagnetic interactions between magnetic centers in the five compounds.

1. Introduction

The design and syntheses of new inorganic–organic hybrid chalcogenide materials have attracted considerable interest during the past decade, not only for their intriguing structural chemistry [1–7], but also for many potential applications as semiconductors, storage materials, and magnetic materials [8–15]. Under the relatively mild hydro(solvo)thermal conditions, the use of alkylammonium cations, organic amines as well as transition metal complexes (TMCs) as templates has been proved to be very effective in the syntheses of chalcogenides [4,16–20]. Recently, the incorporation of TMC into the inorganic main-group metal chalcogenide framework has received much attention, because it may generate unique topological structures and interesting properties [17,21,22]. The very important aspect is that the optical, electrical, and magnetic properties of the TMCs may integrate with the unique properties of inorganic main-group metal chalcogenide framework, which can be expected to give rise to complementary properties and synergistic effects [17,21,22].

A large number of main-group metal chalcogenides with TMCs as templates or structure-directing agents have been prepared in the presence of multidentate amine solvents such as bi-(L^2), tri-(L^3), tetra-(L^4) and penta-dentate (L^5) chelating amines. Up to now, in the known hybrid chalcogenogermanates, the TMCs are generally used as discrete counter-cations [23–25], while the examples of chalcogenogermannates integrated with TMCs via TM–S/Se bonds are limited, such as $\{[Cr(en)_2](GeS_4)\}^-$, $\{[Cr(en)]_2\ (GeSe_4)_2\}^{2-}$ [26], $\{[Mn(cyclam)]_2(\mu\text{-}Ge_2Se_7)\}\cdot CH_3OH\cdot 1.5H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) [27], $\{[Co(tepa)]_2(\mu\text{-}Ge_2S_6)\}$, $\{[M(tepa)]_2(\mu\text{-}Ge_2Se_6)\}$ (M = Mn, Fe) [28]. Although it is known that the size, shape and charge of the TMC cations play a very important role in the construction of the inorganic main-group metal chalcogenide anions, a clear relationship between them still not observed and more compounds need to be synthesized for further understanding.

We have been interested in studying the roles of TMCs as templates or structure-directing agents in the construction of inorganic main-group metal chalcogenide frameworks. By using the L^2 and L^3-dentate chelating amines solvents, we have successfully prepared several hybrid chalcogenoarsenates incorporated with TMCs [29]. By selecting three multidentate amines dien (diethylenetriamine), teta (triethylenetetramine), and tepa (tetraethylenepentamine), we obtained five thiogermanates, $[Ni^{II}(dien)_2]_2(Ge_2S_6)$ (**1**) and $[Ni^{II}(dien)_2](H_2pipe)(Ge_2S_6)$ (pipe = piperazine) (**2**) with TMCs as discrete counter-cations, and $\{[Mn^{II}(tren)]_2(\mu_2\text{-}Ge_2S_6)\}$ (tren = N,N,N-tris(2-aminoethyl)amine) (**3**) and $\{[M^{II}(tepa)]_2(\mu_2\text{-}Ge_2S_6)\}$ (M = Mn (**4a**), Ni (**4b**)) with the TMCs bonding to the dimeric thiogermanates anions. Of particular interest, recently solvo(hydro)thermal *in situ* metal/ligand reaction has provoked

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* Corresponding author. Tel.: +86 591 83705882; fax: +86 591 83714946.
E-mail address: gcguo@fjirsm.ac.cn (G.-C. Guo).

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doi:10.1016/j.molstruc.2010.08.039

significant interest in coordination chemistry and organic chemistry for discovering new organic reactions and making novel coordination complexes, especially those that are inaccessible in direct preparation from the ligand [30–39]. Notably, the reaction condition of **2** has resulted in the *in situ* cyclization of the dien, while the rearrangement reaction from teta to tren was observed in the synthesis of **3**. Herein, we report the syntheses, crystal structures, magnetism and photoluminescence of the five thiogermanates. Additionally, different roles of L^2, L^3, L^4, and L^5-dentate chelating amines on the construction of hybrid main-group metal chalcogenides are also illustrated.

2. Experimental section

2.1. Physical measurements

All reagents were purchased commercially and used without further purification. Elemental analyses of C, H, and N were performed on an Elementar Vario EL III microanalyzer. A NETZSCH STA 449C thermogravimetric analyzer was used to obtain TGA curve in N_2 with a ramp rate of 10 °C min^{-1} in the temperature range 30–1000 °C. An empty Al_2O_3 crucible was used as the reference. The FT-IR spectra were obtained on a Perkin–Elmer spectrophotometer using KBr disks in the range 4000–400 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were recorded on a PANalytical X'pert PRO diffractometer using Cu Kα radiation. The solid-state fluorescence excitation and emission spectra were performed on an Edinburgh EI920 fluorescence spectrophotometer at room temperature with a wavelength increment of 1.0 nm and integration time of 0.2 s. Optical diffuse reflectance spectra were measured at room temperature with a PE Lambda 900 UV–Vis spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. The samples were ground into fine powder and pressed onto a thin glass slide holder. The $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectra were calculated from reflectance spectra using the Kubelka–Munk function: $\alpha/S = (1\text{-}R)^2/2R$ [40], where α is the absorption coefficient, S is the scattering coefficient (which is practically wavelength independent when the particle size is larger than 5 μm), and R is the reflectance. Magnetic susceptibilities were measured using a MPMS XL Quantum Design SQUID magnetometer. All data were corrected for diamagnetism estimated from Pascal's constants.

2.2. Syntheses

2.2.1. Preparation of $[Ni^{II}(dien)_2]_2(Ge_2S_6)$ (**1**)

A mixture of GeO_2 (105 mg, 1 mmol), S (96 mg, 3 mmol), and $NiCl_2{\cdot}6H_2O$ (238 mg, 1 mmol) in 4 mL of a dien/H_2O solution (V/V = 4/1) was sealed in a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 140 °C for 6 days and finally cooled to room temperature. Pink crystals of **1** were filtered, washed with ethanol and diethyl ether, dried and stored under vacuum. Yield: 55% (based on Ni). Anal. Calc. for $C_{16}H_{40}Ge_2N_{12}Ni_2S_6$: C, 22.46; H, 4.71; N, 19.65. Found: C, 22.17; H, 5.88; N, 19.09. FT-IR (KBr, cm^{-1}): 3251(m), 3108(s), 2906(m), 1617(w), 1472(m), 1081(s), 956(s), 676(w), 597(w), 534(w) and 423(s).

2.2.2. Preparation of $[Ni^{II}(dien)_2](H_2pipe)(Ge_2S_6)$ (**2**)

Purple crystals of **2** can be obtained by two different methods:

(a) A mixture of GeO_2 (105 mg, 1 mmol), S (96 mg, 3 mmol), and $NiCl_2{\cdot}6H_2O$ (238 mg, 1 mmol) in 4 mL of a dien/H_2O solution (V/V = 4/1) was sealed in a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 180 °C for 6 days and finally cooled to room temperature. Purple crystals of **2** were filtered, washed with ethanol and diethyl ether, dried and stored under vacuum. Yield: 60% (based on Ni). Anal. Calc. for $C_{12}H_{32}Ge_2N_8NiS_6$: C, 21.05; H, 4.71; N, 16.37. Found: C, 20.91; H, 5.39; N, 16.23. FT-IR (KBr, cm^{-1}): 3262(s), 3166(s), 2878(w), 2512(w), 2364(m), 1583(w), 1560(w), 1449(s), 1070(s), 981(s), 864(w), 676(m), 588(s), 531(w) and 442(s).

(b) A mixture of GeO_2 (105 mg, 1 mmol), S (96 mg, 3 mmol), piperazine ($C_4H_{10}N_2{\cdot}6H_2O$, 97 mg, 0.5 mmol) and $NiCl_2{\cdot}6H_2O$ (119 mg, 0.5 mmol) in 4 mL of a dien/H_2O solution (V/V = 4/1) was sealed in a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 140 °C for 6 days and finally cooled to room temperature. Yield: 20% (based on Ni). Anal. Calc. for $C_{12}H_{32}Ge_2N_8NiS_6$: C, 21.05; H, 4.71; N, 16.37. Found: C, 21.08; H, 5.43; N, 16.53.

2.2.3. Preparation of $\{[Mn^{II}(tren)]_2(\mu_2\text{-}Ge_2S_6)\}$ (**3**)

A mixture of Ge (73 mg, 1 mmol), S (128 mg, 4 mmol), and Mn (55 mg, 1 mmol) in 3 mL of a teta/H_2O solution (V/V = 4/1, teta = triethylenetetramine) was sealed in a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 190 °C for 10 days and finally cooled to room temperature. Colorless crystals of **3** were filtered, washed with ethanol and diethyl ether, dried and stored under vacuum. Yield: 40% (based on Mn). Anal. Calc. for $C_{12}H_{30}Ge_2Mn_2N_8S_6$: C, 19.64; H, 4.12; N, 15.27. Found: C, 19.37; H, 4.64; N, 14.89. FT-IR (KBr, cm^{-1}): 3263(s), 3080(m), 2871(m), 1563(s), 1472(m), 1392(w), 1312(w), 1070(s), 1007(s), 881(m), 620(m), 520(s) and 440(s).

2.2.4. Preparation of $\{[Mn^{II}(tepa)]_2(\mu_2\text{-}Ge_2S_6)\}$ (**4a**)

A mixture of GeO_2 (105 mg, 1 mmol), S (128 mg, 4 mmol), and $MnCl_2{\cdot}4H_2O$ (198 mg, 1 mmol) in 4 mL of a tepa/H_2O solution (V/V = 4/1) was sealed in a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 180 °C for 7 days and finally cooled to room temperature. Colorless crystals of **4a** were filtered, washed with ethanol and diethyl ether, dried and stored under vacuum. Yield: 75% (based on Mn). Anal. Calc. for $C_{16}H_{36}Ge_2Mn_2N_{10}S_6$: C, 23.55; H, 4.45; N, 17.17. Found: C, 23.02; H, 5.28; N, 16.58. FT-IR (KBr, cm^{-1}): 3238(s), 3141(s), 3066(m), 2908(w), 2833(s), 1578(w), 1452(s), 1309(w), 1010(m), 824(s), 622(m), 531(w) and 440(s).

2.2.5. Preparation of $\{[Ni^{II}(tepa)]_2(\mu_2\text{-}Ge_2S_6)\}$ (**4b**)

Purple crystals of compound **4b** were prepared under conditions similar to those of **4a** instead of $MnCl_2{\cdot}4H_2O$ been replaced by $NiCl_2{\cdot}6H_2O$ (238 mg, 1 mmol). Yield: 68% (based on Ni). Anal. Cala. for $C_{16}H_{36}Ge_2N_{10}Ni_2S_6$: C, 23.34; H, 4.41; N, 17.01. Found: C, 23.17; H, 5.46; N, 16.83. FT-IR (KBr, cm^{-1}): 3328(m), 3188(s), 3071(m), 2857(m), 1572(m), 1437(m), 1338(m), 967(s), 982(w), 682(m), 608(m), 557(m) and 440(s).

2.3. Crystal structure determination

The intensity data sets of **1**, **3**, **4a** and **4b** were collected on a Rigaku SCXmini CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using an ω-scan technique at 293 K, while that of **2** was collected on a Rigaku AFC7R diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using $\omega - 2\theta$ scan technique at 293 K. The data sets were reduced by CrystalClear [41] and CrystalStructure [42] programs, respectively. Empirical absorption corrections, multi-scan for **1** and **3**–**4b** and psi-scan for **2**, were applied. The structures were solved by direct methods using the Siemens SHELXL package of crystallographic software [43]. The difference