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Solvothermal syntheses, crystal structures, and properties of lanthanide(III) thioarsenates $[Ln(\text{dien})_2(\mu\text{-}1\kappa,2\kappa^2\text{-AsS}_4)]_n$ (Ln==Sm, Eu, Gd) and $[Ln(\text{dien})_2(1\kappa^2\text{-AsS}_4)]$ (Ln==Tb, Dy, Ho)

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Solvothermal reactions of Ln_2O_3, As and S in diethylenetriamine (dien) at 170 °C for 6 days afforded two structural types of lanthanide thioarsenates with the general formulae $[Ln(\text{dien})_2(\mu\text{-}1\kappa,2\kappa^2\text{-AsS}_4)]_n$ [Ln=Sm(**1**), Eu(**2**), Gd(**3**)] and $[Ln(\text{dien})_2(1\kappa^2\text{-AsS}_4)]$ [Ln=Tb(**4**), Dy(**5**), Ho(**6**)]. The Ln_2O_3 oxides were converted to $[Ln(\text{dien})_2]^{3+}$ complex units in the solvothermal reactions. The As atom binds four S atoms, forming a tetrahedral AsS_4 unit. In **1**–**3**, the AsS_4 units interconnect the $[Ln(\text{dien})_2]^{3+}$ cations via Ln–S bonds as tridentate $\mu\text{-}1\kappa,2\kappa^2\text{-AsS}_4$ bridging ligands, resulting in the neutral coordination polymers $[Ln(\text{dien})_2(\mu\text{-}1\kappa,2\kappa^2\text{-AsS}_4)]_n$ (**Ln1**). In **4**–**6**, the AsS_4 units coordinate with the Ln^{3+} ion of $[Ln(\text{dien})_2]^{3+}$ as $1\kappa^2\text{-AsS}_4$ chelating ligands to form neutral coordination compounds $[Ln(\text{dien})_2(1\kappa^2\text{-AsS}_4)]$ (**Ln2**). The Ln^{3+} ions are in nine- and eight-coordinated environments in **Ln1** and **Ln2**, respectively. The formation of **Ln1** and **Ln2** is related with ionic size of the Ln^{3+} ions. Optical absorption spectra showed that **1**–**6** have potential use as semiconductors with the band gaps in the range 2.18–3.21 eV.

1. Introduction

Chalcogenidoarsenates have gained increasing interest because of their structural diversity and potential applications as optical, electrical and ion exchange materials [1–5]. A large number of chalcogenidoarsenates had been prepared using different methods [6–15]. Since the cobalt thioantimonate $[Co(\text{en})_3]CoSb_4S_8$ was prepared in ethylenediamine (en) under mild solvothermal conditions in 1996 [16], the solvothermal syntheses of transition-metal (*TM*) complex-contained chalcogenidometalates of the heavier Groups 15 and 16 elements in ethylene polyamines have attracted increasing attention for a few decades [17–20]. In the case of arsenic chalcogenides, a number of ternary *TM*-containing chalcogenidoarsenates have been prepared using coordinative polyamines, such as en and diethylenetriamine (dien), as the structure directing reagents [21–23]. The TM^{n+} ions are coordinated to the polyamines to form $[TM(\text{polyamine})_m]^{n+}$ complexes, which act as structural components in the chalcogenidoarsenates. *TM*s can be incorporated into the chalcogenidoarsenates networks when their coordinate sites are not saturated by the polyamines. A series of chalcogenidoarsenates incorporated with Mn complexes have been prepared using solvothermal methods [24–32].

Recently, we have demonstrated that the solvothermal technique is an effective route to syntheses lanthanide (*Ln*) chalcogenometalates in ethylene polyamine solvent. A series of *Ln*-selenidoarsenates and *Ln*-chalcogenidoantimonates have been prepared under solvothermal conditions, giving $[Ln(\text{en})(\text{trien})(1\kappa,2\kappa^2\text{-AsSe}_4)]$ (Ln=La, Nd) [33,34], $[Ln(\text{dien})_2(SbS_4)]$ (Ln=La, Ce, Pr, Nd) [35,36], $[Ln(\text{en})_4(SbSe_4)]$ (Ln=La, Ce, Pr, Nd), $[La(\text{dien})_2(1\kappa,2\kappa^2\text{-SbSe}_4)]$, $[Eu(\text{dien})_2(1\kappa^2\text{-SbSe}_4)]$, $[Ln(\text{en})_2(\text{dien})(1\kappa^2\text{-SbSe}_4)]$ (Ln=La, Ce, Nd), $[Ln(\text{en})_2(\text{dien})(SbSe_4)]$ (Ln=Sm, Gd, Dy), $[Ln(\text{en})(\text{trien})(1\kappa,2\kappa^2\text{-SbSe}_4)]_n$ (Ln=La, Ce, Nd; trien= triethylenetetramine) [37–40], $[Ln(\text{en})_3(H_2O)(1\kappa,2\kappa\text{-AsSe}_4)]$ (Ln= La, Ce, Nd), $[Ln(\text{dien})_2(1\kappa,2\kappa^2\text{-AsSe}_4)]$ (Ln=La, Ce, Pr, Nd, Sm), for example. In these ternary *Ln*-chalcogenometalates, the soft Lewis basic ligands $[SbS_4]^{3-}$, $[SbSe_4]^{3-}$ and $[AsSe_4]^{3-}$ can coordinate to the hard Lewis acidic Ln^{3+} ions with the coexistence of ethylene polyamine ligands. Furthermore, their coordination modes can be tuned by the ethylene polyamines. However, the solvothermal syntheses of thioarsenates containing lanthanide complexes are less explored with the only examples of $[Eu(\text{en})_3(AsS_4)]$ and $[Eu(\text{teta})(\text{en})(AsS_4)]$ [41], although lanthanide arsenic sulfides, such as $K_3Ln(AsS_4)_2$ (Ln=Nd, Sm, Gd) [42] and $Eu_3(AsS_4)_2$ [43], have been prepared via polythioarsenate flux methods at high temperature several years ago. Now, new *Ln*-thioarsenates $[Ln(\text{dien})_2(\mu\text{-}1\kappa,2\kappa^2\text{-AsS}_4)]_n$ [Ln=Sm(**1**), Eu(**2**), Gd(**3**)] and $[Ln(\text{dien})_2(1\kappa^2\text{-AsS}_4)]$ [Ln=Tb(**4**), Dy(**5**), Ho(**6**)] were synthesized by the reaction of Ln_2O_3, As and S under solvothermal conditions.

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2. Experimental section

2.1. Materials and physical measurements

All the solvents and reagents for synthesis were commercially available and used as purchased. Elemental analyses were performed on an EA1110-CHNS-O elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet Magna-IR 550 spectrometer on dry KBr discs over the $4000-400\ \mathrm{cm}^{-1}$ range. Room-temperature optical diffuse reflectance spectra of the powdered sample were obtained with a Shimadzu UV-3150 spectrometer. The absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function $\alpha/S=(1-R)^2/2R$ [44], where R is the reflectance at a given energy, α is the absorption, and S is the scattering coefficient. Powder X-ray diffraction (XRD) patterns were collected on a D/MAX-3C diffractometer using graphite monochromatized Cu$K\alpha$ radiation ($\lambda=1.5406$ Å). Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were performed on a SDT 2960 apparatus and all the samples were heated under a nitrogen stream of 100 ml/min with a heating rate of 5 °C/min.

2.2. Synthesis of [Sm(dien)$_2$(μ-1κ,2κ^2-AsS$_4$)]$_n$ (**1**)

Sm_2O_3 (174 mg, 0.5 mmol), As (74.9 mg, 1.0 mmol), and S (128 mg, 4 mmol) were dispersed in 1 mL of CH_3OH and 4 mL of diethylenetriamine (dien) by stirring, and the dispersion was loaded into a polytetrafluoroethylene (PTFE) lined stainless steel autoclave of volume 15 mL. The sealed autoclave was heated under autogenous pressure at 170 °C for 6 days. Upon cooling to room temperature, yellow block crystals of **1** were filtered off, washed with ethanol and stored under a vacuum (47% yield based on As). Anal. Found: C 16.98%, H 4.52%, N 14.86%. Calcd. for $C_8H_{26}N_6S_4SmAs$: C 17.16%, H 4.68%, N 15.01%. IR (KBr): 3452 (m), 3345 (m), 3241 (s), 2921 (s), 2873 (m), 1640 (s), 1564 (s), 1452 (m), 1435(s), 1327(m), 1280 (w), 1090 (s), 1012 (s), 973 (s), 783 (m), 640 (s), 519 (m), 450 (m) cm^{-1}.

2.3. Synthesis of [Eu(dien)$_2$(μ-1κ,2κ^2-AsS$_4$)]$_n$ (**2**)

Light yellow cubic crystals of compound **2** (57% yield based on As) were prepared with a procedure similar to that for the synthesis of **1**, except that Eu_2O_3 was used instead of Sm_2O_3. Anal. Found: C 16.94%, H 4.68%, N 14.82%. Calcd. for $C_8H_{26}N_6S_4EuAs$: C 17.11%, H 4.67%, N 14.97%. IR (KBr): 3252(m), 3118(m), 2926 (s), 2849 (m), 1641(s), 1585(s), 1459 (m), 1435 (s), 1328 (m), 1280 (w), 1090 (s), 1012 (s), 973 (s), 838 (w), 640 (s), 512 (w), 442 (m) cm^{-1}.

2.4. Synthesis of [Gd(dien)$_2$(μ-1κ,2κ^2-AsS$_4$)]$_n$ (**3**)

Light-yellow cubic crystals of compound **3** (53% yield based on As) were prepared with a procedure similar to that for the synthesis of **1**, except that Gd_2O_3 was used instead of Sm_2O_3. Anal. Found: C 16.85%, H 4.54%, N 14.69%. Calcd. for $C_8H_{26}N_6S_4GdAs$: C 16.95%, H 4.62%, N 14.83%. IR (KBr): 3296(m), 3258(s), 3095 (m), 2911 (w), 2865 (m), 1567(m), 1473 (m), 1314 (m), 1126 (m), 1075 (s), 1006 (s), 882 (w), 664 (m), 518 (m), 454 (m) cm^{-1}.

2.5. Synthesis of [Tb(dien)$_2$(1κ^2-AsS$_4$)] (**4**)

Colorless block crystals of compound **4** (45% yield based on As) were prepared with a procedure similar to that for the synthesis of **1**, except that Tb_2O_3 was used instead of Sm_2O_3. Anal. Found: C 16.78%, H 4.55%, N 14.65%. Calcd. for $C_8H_{26}N_6S_4TbAs$: C 16.90%, H 4.61%, N 14.78%. IR (KBr): 3457 (w), 3218((s)), 3106 (s), 2926 (s), 2864 (s), 1565 (s), 1468 (s), 1363 (m), 1332 (m), 1152(m), 1070 (s), 1005 (s), 975 (s), 825 (m), 756 (m), 595 (w), 582 (w), 455 (w) cm^{-1}.

2.6. Synthesis of [Dy(dien)$_2$(1κ^2-AsS$_4$)] (**5**)

Colorless block crystals of compound **5** (49% yield based on As) were prepared with a procedure similar to that for the synthesis of **1**, except that Dy_2O_3 was used instead of Sm_2O_3. Anal. Found: C 16.66%, H 4.41%, N 14.54%. Calcd. for $C_8H_{26}N_6S_4DyAs$: C 16.80%, H 4.58%, N 14.69%. IR (KBr): 3243 (m), 3209 (m), 2922 (m), 2885 (m), 1566 (vs), 1527 (m), 1466 (s), 1329 (s), 1150 (m), 1086 (s), 1001 (m), 971 (vs), 897 (m), 823 (w), 609 (m), 584 (m), 496 (m), 459 (s) cm^{-1}.

2.7. Synthesis of [Ho(dien)$_2$(1κ^2-AsS$_4$)] (**6**)

Colorless block crystals of compound **6** (51% yield based on As) were prepared with a procedure similar to that for the synthesis of **1**, except that Ho_2O_3 was used instead of Sm_2O_3. Anal. Found: C 16.65%, H 4.47%, N 14.55%. Calcd. for $C_8H_{26}N_6S_4HoAs$: C 16.73%, H 4.56%, N 14.63%. IR (KBr): 3348 (m), 3240 (m), 2928 (m), 2878 (m), 1582 (vs),, 1485 (s), 1385 (s), 1101 (m), 1006 (m), 988 (s), 856 (m), 822 (w), 656 (m), 588 (m), 496 (m), 461 (s) cm^{-1}.

2.8. X-ray crystallography

Data were collected on a Rigaku Mercury CCD diffractometer at 293(2) K (for **1**, **3**–**5**) or on a Rigaku Saturn CCD diffractometer at 223(2) K (for **2**), using graphite-monochromated Mo$K\alpha$ radiation with a ω-scanning mode to the maximum 2θ of 50.70° for **1**–**4**, **6** and 55.04° for **5**. An empirical absorption correction was applied to the data. The structures were solved with SHELXS-97 [45], and refinement was performed against F^2 using SHELXL-97 [46]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added geometrically and refined using the riding model. Atoms C(6) and C(7) in **2**, and C(4) in **5** are disordered with the occupancies being refined as 50% and 50%. The disordered atoms C(2) in **3**, and C(4) in **4** and **6** are refined as 60% and 40% occupancies. Technical details of data collections and refinement are summarized in Table 1. Crystallographic data have been deposited with the Ambridge Crystallographic DataCentre (CCDC ID: 942 452 (**1**), 812 760 (**2**), 942 453 (**3**), 942 454 (**4**), 812 761 (**5**), and 942 455 (**6**)). Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21E2, UK (fax: +44 1223/336033 or e-mail:deposit@chemcrys.cam.ac.uk).

3. Results and discussion

3.1. Syntheses

Title compounds were prepared via solvothermal methods. The reactions of Ln_2O_3 (Ln=Sm, Eu, Gd, Dy, Ho), As and S in 1: 1: 4 M ratio in mixed CH_3OH/dien [1:4 (v/v)] solvent at 170 °C for 6 days produced crystalline compounds **1**–**6** with yields in the range of 45–57%. The bulk phase purity of the products of **1** and **4** was confirmed by powder XRD study. The experimental PXRD patterns of **1** and **4** are similar to the simulated PXRD pattern based on the single-crystal X-ray diffraction data (Figs. 1 and 2), respectively. We found that the addition of CH_3OH was necessary in the syntheses of **1**–**6**. A small amount of unknown powders and clear yellow solutions were obtained when the reactions were carried out in pure dien solvent under the same conditions. However, in our previous investigation, we have successfully prepared lanthanide thioantimonates, selenidoantimonates and selenidoarsenates