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Clusters $[Co(As_3S_3)_2]^{2-}$, $[Ni(As_3S_3)_2]^{2-}$, and $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ with Co−As or Ni−As Bonds: Solvothermal Syntheses and Characterizations of Thioarsenates Containing Transition-Metal Complexes

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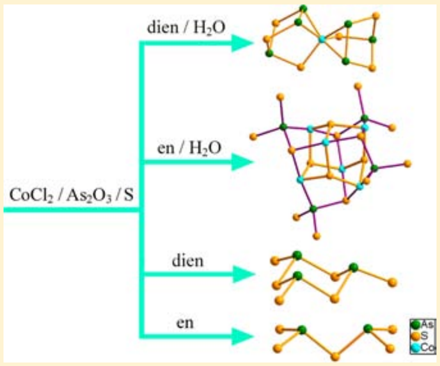
S Supporting Information

ABSTRACT: Solvothermal reactions of As_2O_3 and S with $CoCl_2·6H_2O$ or $NiCl_2·6H_2O$ in an aqueous solution of dien produced novel thioarsenates $[Co(dien)_2][Co(As_3S_3)_2]$ (**1**) and $[Ni(dien)_2][Ni(As_3S_3)_2]$ (**2**) (dien = diethylenetriamine), and the reaction with $CoCl_2·6H_2O$ in an aqueous solution of en afforded complex $[Hen]_2[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]$ (**3**) (en = ethylenediamine). In **1** and **2**, one transition-metal ion is coordinated by two dien ligands to form $[TM(dien)_2]^{2+}$ (TM = Co, Ni) complex cations. The As_3S_3 unit coordinates to the other TM(II) ion with both As- and S-donor atoms to form the $[TM(As_3S_3)_2]^{2-}$ anionic cluster, in which $TMAs_2$, $TMAs_2S_2$, and $TMAs_3S_2$ rings are formed. In **3**, each Co^{3+} ion is coordinated by an en ligand. Six Co(en) units are interlinked by four μ_3-S and four AsS_3 ligands to form a $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ cluster containing an adamantane-like Co_6S_4 core. The AsS_3 unit coordinates to Co atom in the η^1-As_1,η^2-S coordination mode with As binding Co(1) and S(1) binding Co(1) and Co(2). The As_3S_3 and AsS_3 ligands with both As- and S-donor atoms in **1**−**3** have never been obtained in amine solution before. The same reactions in pure dien and en solvents afforded compounds $[Co(dien)_2]_3[As_3S_6]_2$ (**4**) and $[Co(en)_3]_2As_2S_5$ (**5**) containing discrete anions $[As_3S_6]^{3-}$ and $[As_2S_5]^{4-}$, respectively. The band gaps of **1**−**3** are in the range of 1.37−1.55 eV, and the band gaps of **4** and **5** are 2.24 and 2.26 eV, which show the influence of the coordination mode of thioarsenate ligands on the electronic transitions in the TM-thioarsenates.



■ INTRODUCTION

Chalcogenidoarsenates have attracted increasing interest because of their structural diversity and potential applications as optical, electrical, and ion-exchange materials.[1−7] These arsenic chalcogenides are structurally based upon the condensation of $[AsQ_3]^{3-}$ and $[AsQ_4]^{3-}$ (Q = S, Se) units via As−Q, As−As, and/or Q−Q connections, which lead to a variety of chalcogenidoarsenate aggregates.[8] In the case of arsenic sulfides, a large number of thioarsenates with different compositions have been prepared and characterized.[9] However, the structural diversity of thioarsenates is reflected in the observations that the thioarsenate aggregates are versatile ligands for different types of metal centers via S-donor atoms. Thioarsenate anions $[AsS_2(S_2)]^{3-}$, $[AsS(S_2)_2]^{2-}$, $[AsS_3]^{3-}$, $[As_3S_7]^{5-}$, $[As_3S_6]^{3-}$, and $[AsS_3]^{3-}$ are observed to coordinate with main group metal centers with S atoms.[10−13] The $[AsS_3]^{3-}$, $[AsS_4]^{3-}$, and $[As_3S_7]^{5-}$ anions bind with lanthanide metal centers in Ln(III)-containing thioarsenates.[14−16] The binary thioarsenate aggregates are more often observed to coordinate to transition-metal (TM) centers under different conditions. Alkali metal polythioarsenate flux methods afforded Cu(I), Mn(II), and Cd(II) compounds KCu_2AsS_3,[17] $A_8[Mn_2(AsS_4)_4]$ (A = K, Rb, Cs), and $Rb_8[Mn_2(AsS_4)_2(AsS_5)_2]$[18] with $[AsS_3]^{3-}$, $[AsS_4]^{3-}$, and $[AsS_5]^{3-}$ ligands. The methanothermal synthesis gave silver thioarsenate $K[Ag_3As_2S_5]$ containing a $[As_2S_5]^{4-}$ unit.[19] The reaction of CH_2Cl_2 solution containing $PAs_3S_3·W(CO)_5$ and $As_4S_3·Cr(CO)_5$ with the CH_3CN solution of CuX produced complexes $(CuX)(As_4S_4)(PAs_3S_3)$ (X = Cl, Br), in which the As_4S_4 unit coordinates to Cu(I) as a monodentate ligand.[20] The hydrothermal reactions using organic cations as structure directors afforded a series of exciting TM complexes with $[As_3S_5]^{3-}$, $[AsS_4]^{3-}$, $[As_4S_9]^{6-}$, $[As_3S_6]^{3-}$, $[As_4S_8]^{4-}$, $[As_2S_5]^{4-}$, and $[As_3S_6]^{5-}$ ligands.[2,21−23] Interestingly, in $(Ph_4P)_4[Pd_7As_{10}S_{22}]$[21] and $(Ph_4P)_2[Pt(As_3S_5)_2]$,[22] the $[As_3S_6]^{5-}$ and $[As_3S_5]^{3-}$ units coordinate to Pd(II) and Pt(IV) centers not only via S atoms but also with As atoms forming a Pd−As or Pt−As bond, respectively. In recent years, a number of TM complexes with thioarsenates as S-donor ligands have been prepared by solvothermal methods with a chelating amine as the structure-directing molecule.[4,24]

It is well known that the solvent and structure-directing agent play important roles in the solvothermal syntheses. The dedicated use of suitable solvents and structure directors is thought to retain the chalcogenidometalate building units and

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Table 1. Crystal Data and Summary of X-ray Data Collection

	1	2	3	4	5
empirical formula	$C_8H_{26}N_6S_6Co_2As_6$	$C_8H_{26}N_6S_6Ni_2As_6$	$C_{16}H_{66}N_{16}S_{16}Co_6As_4$	$C_{24}H_{78}As_6N_{18}S_{12}Co_3$	$C_{12}H_{48}N_{12}S_5Co_2As_2$
fw	966.09	965.65	1649.07	1630.05	788.62
cryst syst	orthorhombic	orthorhombic	tetragonal	monoclinic	orthorhombic
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$I4_1/a$ (No. 88)	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)
a, Å	11.082(2)	11.0037(11)	13.065(2)	19.014(4)	15.4084(17)
b, Å	14.679(3)	14.7916(19)	13.065(2)	8.6662(17)	11.2176(13)
c, Å	16.523(3)	16.6696(17)	32.007(5)	18.243(4)	17.3415(18)
β/deg	90	90	90	94.92(3)	90
V, Å^3	2687.6(9)	2713.2(5)	5463.2(13)	2995.0(10)	2997.4(6)
Z	4	4	4	2	4
T, K	223(2)	223(2)	223(2)	223(2)	223(2)
calcd density, mg m^{-3}	2.388	2.364	2.005	1.807	1.748
F(000)	1856	1864	3296	1644	1616
2θ (max), deg	50.70	50.70	50.70	50.70	50.70
total reflns collected	10 734	9558	8544	28 025	9252
unique reflns	4857	4777	2500	5447	2721
flack value	0.039(14)	0.14(6)			
R_{int}	0.0483	0.0419	0.0380	0.0516	0.0390
no. of params	254	243	126	274	164
R1 [$I > 2\sigma(I)$]	0.0341	0.0417	0.0451	0.0664	0.0382
wR2 (all data)	0.0751	0.0893	0.1406	0.1097	0.0869
GOF on F^2	0.913	1.044	1.117	1.124	1.114

facilitate their controlled linkage in the solvothermal synthesis of chalcogenidometalates.[25] Now the As_2O_3/S/$CoCl_2$ (or $NiCl_2$) system is investigated in an aqueous solution of dien or en, and novel TM complexes with thioarsenate ligands $[Co(dien)_2][Co(As_3S_3)_2]$ (**1**), $[Ni(dien)_2][Ni(As_3S_3)_2]$ (**2**), and $[Hen]_2[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]$ (**3**) are prepared. Compounds **1**−**3** contain novel clusters $[Co(As_3S_3)_2]^{2-}$, $[Ni(As_3S_3)_2]^{2-}$, and $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ in which the As_3S_3 and AsS_3 units simultaneously coordinate to TM centers with both As and S atoms. Comparably, the reaction in pure dien and en solvent afforded compounds $[Co(dien)_2]_3[As_3S_6]_2$ (**4**) and $[Co(en)_3]_2As_2S_5$ (**5**) containing discrete $[As_3S_6]^{3-}$ and $[As_2S_5]^{4-}$ anions. Herein we report the solvothermal syntheses, crystal structures, and optical and thermal properties of compounds **1**−**5**.

■ EXPERIMENTAL SECTION

Materials and Methods. $[Co(en)_3]Cl_3$ was prepared by published methods.[26] Other starting chemicals were of analytical grade and were used as received. Elemental analyses were conducted using an EA1110-CHNS-O elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Magna-IR 550 spectrometer using dry KBr discs over the 4000−400 cm^{-1} range. Optical diffuse reflectance spectra of powder samples were obtained at room temperature using a Shimadzu UV-3150 spectrometer. Absorption (α/S) data were calculated from reflectance using the Kubelka−Munk function $\alpha/S = (1 - R)^2/2R$.[27] Powder X-ray diffraction (XRD) patterns were collected on a D/MAX-3C diffractometer using graphite-monochromatized Cu $\kappa\alpha$ radiation (λ = 1.5406 Å). Thermal TG and DSC analyses were conducted on a SDT 2960 microanalyzer, and the samples were heated at a rate of 5 °C min min^{-1} under a 100 mL min^{-1}nitrogen stream. XPS analysis was performed using a Kratos Axis-165 electron spectrometer with monochromatized Al $\kappa\alpha$ radiation (1486.6 eV).

Synthesis of $[Co(dien)_2][Co(As_3S_3)_2]$ (1). $CoCl_2\cdot 6H_2O$ (119 mg, 0.50 mmol), As_2O_3 (99 mg, 0.50 mmol), and S (96 mg, 3.00 mmol) were dispersed in 4 mL of a 40% aqueous solution of dien by stirring, and the dispersion was loaded into a polytetrafluoroethylene (PTFE)-lined stainless steel autoclave of 10 mL volume. The sealed autoclave was heated to 140 °C for 5 days and then cooled to ambient temperature. The resulting product contained black block crystals of **1** and some black powder. The crude product was transferred into a vial that was filled with a 40% aqueous solution of dien. Most of the black powder was suspended in the solution, which was then decanted, leaving behind crystals. This procedure was repeated until the water remained clear. The black powder was confirmed to be CoS by PXRD measurement. The black crystals were collected by filtration, washed with methanol, and stored under vacuum (64% yield based on As_2O_3). Anal. Calcd for $C_8H_{26}N_6Co_2As_6S_6$ (966.09): C 9.95, H 2.71, N 8.70. Found: C 9.80, H 2.62, N 8.53. IR (KBr): 3281(s), 3239 (s), 3018 (s), 2917 (m), 2871 (s), 1569 (s), 1449 (m), 1381 (w), 1327 (m), 1269 (w), 1145 (m), 1097 (m), 998 (s), 859 (m), 813 (w), 646 (s), 502 (s), 468 (m).

Synthesis of $[Ni(dien)_2][Ni(As_3S_3)_2]$ (2). Compound **2** was prepared with a procedure similar to that for the synthesis of **1**, except that $NiCl_2\cdot 6H_2O$ was used instead of $CoCl_2\cdot 6H_2O$. Black prism crystals of **2** (58% yield based on As_2O_3) were separated from a small amount of black NiS powder using the methods described in the synthesis of **1**. Anal. Calcd for $C_8H_{26}N_6Ni_2As_6S_6$ (965.65): C 9.96, H 2.72, N 8.72. Found: C 9.82, H 2.58, N 8.56. IR (KBr): 3261 (s), 3215 (s), 3122 (s), 2925 (m), 2870 (m), 1589 (s), 1570 (s), 1449 (s), 1386 (w), 1328 (s), 1269 (s), 1121 (w), 1099 (m), 990 (s), 859 (m), 626 (s), 495 (w), 456 (s).

Synthesis of $[Hen]_2[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]$ (3). $CoCl_2\cdot 6H_2O$ (119 mg, 0.50 mmol), As_2O_3 (99 mg, 0.50 mmol), and S (96 mg, 3.00 mmol) (1 mL) were dispersed in 4 mL of a 40% aqueous solution of en by stirring, and the dispersion was loaded into a PTFE-lined stainless steel autoclave of 10 mL volume. The sealed autoclave was heated to 140 °C for 5 days. After cooling to ambient temperature, the resulting black block crystals of **3** were filtered off, washed with ethanol, and stored in $CoCl_2\cdot 6H_2O$ under vacuum (68% yield based on As_2O_3). Compound **3** can also be prepared using $[Co(en)_3]Cl_3$ instead of $CoCl_2\cdot 6H_2O$ as a starting reagent. Anal. Calcd for $C_{16}H_{66}N_{16}Co_6As_4S_{16}$ (1649.07): C 11.65, H 4.03, N 13.59. Found: C 11.51, H 3.85, N 13.42. IR (KBr): 3299 (s), 3239 (s), 3119 (s), 2913 (s), 2869 (s), 1708 (w), 1680 (m), 1580 (s), 1547 (s), 1494 (s), 1419 (s), 1370 (m), 1267 (s), 1150 (w), 1100 (w), 1007 (s), 935 (w), 822 (w), 791 (w), 652 (m), 616 (m), 549 (w), 494 (w), 430 (s).

Synthesis of $[Co(dien)_2]_3[As_3S_6]_2$ (4). $CoCl_2\cdot 6H_2O$ (119 mg, 0.50 mmol), As_2O_3 (99 mg, 0.50 mmol), and S (96 mg, 3.00 mmol) were dispersed in 4 mL of dien by stirring, and the dispersion was loaded into a PTFE-lined stainless steel autoclave of 10 mL volume. The sealed autoclave was heated to 140 °C for 5 days. After cooling to ambient temperature, the resulting orange crystals of **4** were filtered off, washed with ethanol, and stored under vacuum (64% yield based on As_2O_3). Anal. Calcd for $C_{24}H_{78}As_6N_{18}Co_3S_{12}$ (1630.05): C 17.68, H 4.82, N 15.47. Found: C 17.51, H 4.70, N 15.32. IR (KBr): 3303 (s), 3248 (s), 3135 (s), 2941 (s), 2868 (s), 1624 (s), 1569 (s), 1460 (s), 1383 (w), 1321 (s), 1278 (w), 1105 (m), 1008 (s), 966 (s), 826 (w), 776 (w), 611 (s), 461 (s).

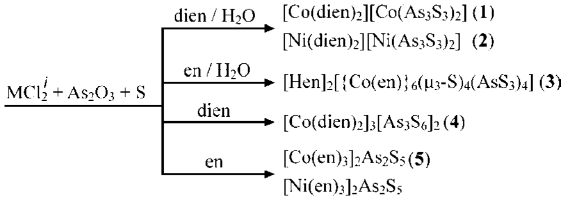
Synthesis of $[Co(en)_3]_2As_2S_5$ (5). Compound **5** (51% yield based on As_2O_3) was prepared with a procedure similar to that for the synthesis of **4** except that en was used instead of dien. Anal. Calcd for $C_{12}H_{48}N_{12}Co_2As_2S_5$ (788.62): C 18.28, H 6.14, N 21.31. Found: C 18.10, H 6.01, N 21.18. IR (KBr): 3285 (s), 3220 (s), 3120 (s), 2919 (s), 2878 (s), 1676 (s), 1584 (s), 1446 (s), 1380 (w), 1327 (s), 1267 (s), 1150 (w), 1098 (m), 1007 (s), 862 (w), 743 (w), 672 (s), 525 (s), 491 (w), 416 (s).

X-ray Crystal Structure Determination. Data were collected on a Rigaku Saturn CCD diffractometer at 223(2) K using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) with a ω-scan method to a maximum 2θ value of 50.70°. An absorption correction was applied for all compounds using the multiscan technique. The structures were solved with direct methods using the SHELXS-97 program[28] and refined by a full matrix least-squares technique based on F^2 using SHELXL-97.[28] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically and refined using the riding model. Atoms C(1) and C(2) in **3** are disordered with the occupancies being refined as 50% each. Disordered atoms As(1) and S(1) in **4** were refined as 50% occupancies each. Hydrogen atoms were added geometrically and refined using the riding model. The hydrogen atoms of two en molecules in **3** were not dealt with because of the disordered C and N atoms. Technical details of data acquisition and selected refinement results are summarized in Table 1.

■ RESULTS AND DISCUSSION

Synthesis and Infrared Spectra. The title compounds were prepared using dien and en as chelating ligands to transition-metal ions under solvothermal conditions (Scheme 1). Reactions of As_2O_3 and S with $CoCl_2·6H_2O$ or $NiCl_2·6H_2O$ in an aqueous solution of dien at 140 °C for 5 days produced black crystals of $[Co(dien)_2][Co(As_3S_3)_2]$ (**1**) and $[Ni(dien)_2][Ni(As_3S_3)_2]$ (**2**), respectively. A small amount of CoS and NiS powders were observed as byproducts in the solvothermal reaction. The same reaction in an aqueous solution of 40% en gave black crystals of $[Hen]_2[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]$ (**3**). The reaction with $[Co(en)_3]Cl_3$ instead of $CoCl_2·6H_2O$ also produced **3**. When the reaction was carried out in pure dien or in en solvent under the same conditions, orange crystals of $[Co(dien)_2]_3[As_3S_6]_2$ (**4**) and brown crystals of $[Co(en)_3]_2As_2S_5$ (**5**) were obtained, respectively. A homologue of **5**, $[Ni(en)_3]_2As_2S_5$, was prepared by the reaction of As_2O_3, S, and $NiCl_2·6H_2O$ in pure en.[29] Arsenic trioxide was converted to different thioarsenate units AsS_3, As_3S_3, As_3S_6, and As_2S_5 during the solvothermal reactions. The experimental PXRD patterns of bulk phases of **1**−**5** are similar to the simulated PXRD patterns based on the single-crystal X-ray diffraction data (Figure S1−S5 in the SI, respectively).

Scheme 1. Syntheses of Compounds 1−5 and a Homologue of 5, with ${}^iM$ = Co or Ni



In the IR spectra of compounds **1**−**5** (Figure S6−S10 in the SI, respectively), the absorptions located in the frequency range of 3108−3281 cm^{-1} could be assigned to the asymmetric and symmetric N−H stretching vibrations of the amino groups in dien and en. The C−H stretching vibrations occur between 2869 and 2925 cm^{-1}. The N−H and C−H deformation modes occur in the ranges of 1568−1584 and 1449−1488 cm^{-1}, respectively. The strong bands in 990−1007 cm^{-1} could be assigned to N−C stretching vibrations.

Crystal Structures of 1 and 2. Compounds **1** and **2** are isostructural. They crystallize with eight formula units in orthorhombic space group $P2_12_12_1$ (no. 19). They consist of TM complexes $[TM(As_3S_3)_2]^{2-}$ and $[TM(dien)_2]^{2+}$ (TM = Co, Ni). The crystal structure of **1** is depicted in Figure 1. There are two Co, six As, and six S crystallographically independent atoms in **1**. One Co^{2+} ion is coordinated by two inorganic As_3S_3 ligands, and the other Co^{2+} ion is coordinated by the dien ligand. The As(3) atom is coordinated by three S atoms, forming the typical trigonal pyramid AsS_3. The AsS_3 pyramid binds with an As_2 (containing As(1) and As(2)) unit with two S atoms, generating the As_3S_3 aggregate (Figure 1a). Another As_3S_3 aggregate is formed by As(4), As(5), As(6), S(4), S(5), and S(6) atoms with the same connections. The As−S bond lengths lie in the range of 2.183(2)−2.267(2) Å and are in agreement with those observed in thioarsenates.[20−23,30] Formal bond-valence sums suggest that the total charge of each As_3S_3 ligand is 2−, with each S atom in a 2− oxidation state. The oxidation state of the As atom that is not coordinated to the metal center is assigned as 3+, whereas the two Co-bound As atoms are assigned as 1+ for the As_2 subunit. The As−As bond lengths [2.3643(13) and 2.3700(14) Å for **1**; 2.3677(13) and 2.3725(13)Å for **2**] (Table 2) are comparable to those of the As_3Se_3 units in $[M(CO)_2(As_3Se_3)_2]^{2-}$ (M = Mo, W) (As−As = 2.348(6), 2.364(7) Å)[31] and $[Fe(CO)(As_3Se_3)_2]^{2-}$ (As−As = 2.381(4) Å)[32] but are distinctly shorter

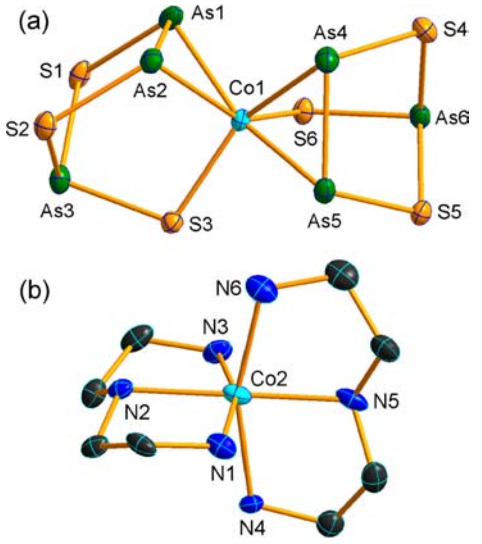


Figure 1. Crystal structures of (a) $[Co(As_3S_3)_2]^{2-}$ and (b) $[Co(dien)_2]^{2+}$ ions in **1** with labeling (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for 1 and 2

	1 (M = Co)	**2** (M = Ni)
As–S	2.183(2)–2.267(2)	2.184(3)–2.272(3)
As–As	2.3643(13), 2.3700(14)	2.3677(13), 2.3725(13)
As–M	2.3595(13)–2.4268(13)	2.3651(14)–2.4283(13)
M–S	2.269(2), 2.284(2)	2.272(2), 2.282(2)
M–N	2.063(9)–2.190(7)	2.064(10)–2.193(8)
S–As–S	95.51(9)–102.57(9)	95.47(9)–102.96(10)
S–As–As	100.97(7)–103.38(7)	100.97(7)–103.49(7)
S–As–M	100.97(7)–106.05(7)	101.32(7)–105.81(7)
As–As–M	58.99(4)–61.83(4)	59.08(4)–61.74(4)
As–M–As	59.16(4)–158.49(6)	59.19(4)–157.84(6)
As–M–S	86.30(7)–148.17(7)	87.36(7)–145.97(8)
S–M–S	98.73(9)	98.10(9)
As–S–As	101.92(9)–104.16(9)	101.79(9)–104.23(11)
As–S–M	104.37(9), 104.62(8)	104.10(9), 104.51(10)
trans-N–M–N	161.2(4)–179.0(3)	162.2(3)–178.1(4)
cis-N–M–N	79.4(3)–100.2(3)	80.3(3)–99.6(3)

than the As–As lengths of the As_4S_4 cage in complex $[CpCo(CO)(As_4S_4)]$ (Cp = C_5Me_5) (As–As = 2.519(6) Å).[33]

The As_3S_3 unit binds the $Co(1)^{2+}$ ion with two As atoms and one S atom as a $1\kappa^2As^1,As^2:1\kappa S^1$ chelating ligand (Figure 1a). The $Co(1)^{2+}$ ion is coordinated with two tridentate As_3S_3 ligands, forming a $[Co(As_3S_3)_2]^{2-}$ cluster. As a result, three-membered $CoAs_2$, five-membered $CoAs_2S_2$, and six-membered $CoAs_3S_2$ heterometallic rings are formed in the $[Co(As_3S_3)_2]^{2-}$ anion. The $Co(1)^{2+}$ ion is in a six-coordinate environment involved in four As and two S atoms from two As_3S_3 moieties, forming a severe distorted octahedron with the axial angles in the range of 144.95(7)–158.49(6)° and equatorial angles in the range of 59.16(4)–104.62(8)° (Table 2). The Co–S (2.269(2), 2.284(2) Å) and Ni–S (2.272(2), 2.282(2) Å) bond lengths are in the range of those reported in the literature.[2,35] The Co–As and Ni–As bond lengths vary over 2.3595(13)–2.4268(13) Å and 2.3651(14)–2.4283(13) Å (Table 2), respectively. The Co–As bond lengths are in the range of those observed in $[CpCo(CO)(As_4S_4)]$ (Co–As = 2.369(6), 2.383(6) Å),[33] and $[Cp_2Co_2(CO)(As_2S_2)]$ (Co–As = 2.275(4)–2.473(2) Å).[34] The $Co(2)^{2+}$ ion is coordinated by two tridentate dien ligands, forming a distorted octahedron with axial N–Co–N angles of 161.2(4)–179.0(3)° (Table 2). Both $[Co(dien)_2]^{2+}$ in **1** and $[Ni(dien)_2]^{2+}$ in **2** complexes are in the *mer* conformation (Figure 1b, Figure S11 in the SI). The TM–N bond lengths of 2.063(9)–2.190(7) Å for Co–N (average 2.110(7) Å) and 2.064(10)–2.193(8) Å for Ni–N (average 2.115(9) Å) (Table 2) are in agreement with those observed in $[Co(dien)_2]^{2+}$ and $[Ni(dien)_2]^{2+}$ complexes,[36] respectively.

Secondary weak S···S and As···As interactions are observed between the $[Co(As_3S_3)_2]^{2-}$ moieties. The $[Co(As_3S_3)_2]^{2-}$ moieties are connected in a chain running along the *a* axis via S(4)···S(5) weak interactions (Figure 2). The S···S distance is 3.562 Å, which is much shorter than the S···S distances reported in the literature (S···S = 3.85–4.29 Å).[37] Between the chains, secondary As···As interactions with an As···As distance of 3.766 Å is observed between As(1) and As(3) atoms. The As···As distance is comparable to those reported (As···As = 3.79 Å).[38] Taking into account these secondary S···S and As···As bonds, we find that the $[Co(As_3S_3)_2]^{2-}$ moieties are interconnected into a 2D layer perpendicular to the *c* axis (Figure 2). The $[Co(dien)_2]^{2+}$ cations are located between the anionic layers and interacts with the layers via N–H···S hydrogen bonds (N···S = 3.343(8)–3.787(8) Å, S···H–N = 130.8–164.8°) (Table S6 in the SI). Each $[Co(As_3S_3)_2]^{2-}$ anion has contacts to three $[Co(dien)_2]^{2+}$ cations via N–H···S bonds (Figure 3). The $[Co(As_3S_3)_2]^{2-}$ anions and $[Co(dien)_2]^{2+}$ cations are assembled into a 3D network via the S···S and As···As van der Waals' force, and N–H···S hydrogen bonds (Figure S12 in the SI).

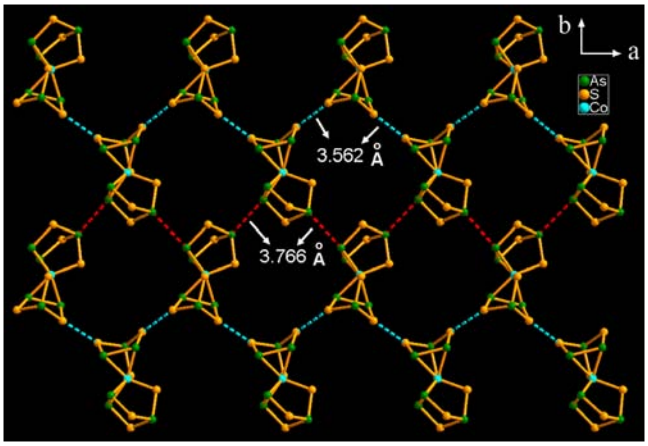


Figure 2. Crystal packing diagram of **1** viewed along the *c* axis, showing the layer assembled by $[Co(As_3S_3)_2]^{2-}$ moieties via secondary S···S and As···As interactions. The $[Co(dien)_2]^{2+}$ ions are omitted for clarity.

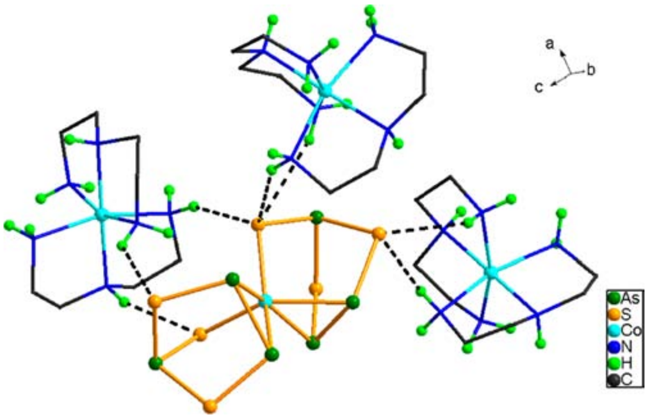


Figure 3. View of the environment of one $[Co(As_3S_3)_2]^{2-}$ anion in **1**, showing the N–H···S hydrogen bonds. The hydrogen atoms of CH_2 are omitted for clarity.

Crystal Structure of 3. Compound **3** crystallizes in the tetragonal crystal system in space group $I4_1/a$. It consists of a $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ anionic cluster and Hen^+ cations. The structural evolution of the $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ cluster is depicted in Figure 4 to elucidate its complex structure. There are two crystallographically independent Co, one As, and four S atoms in **3**. The $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ cluster contains an adamantane-like $Co_6(\mu_3\text{-}S)_4$ core that is built up from six Co (four Co(1) and two Co(2)) atoms joined by four μ_3-S (S4) ligands (Figure 4a,b). The As atom binds three S (S1, S2, and S3) atoms, forming a typical trigonal pyramid AsS_3 with As–S bond lengths in the range of 2.149(3)–2.264(2) Å (Table 3). The AsS_3 unit coordinates to the Co atoms of the $Co_6(\mu_3\text{-}S)_4$ core as a μ_3-$1,2\kappa S:3\kappa As$ bridging ligand, with As(1)

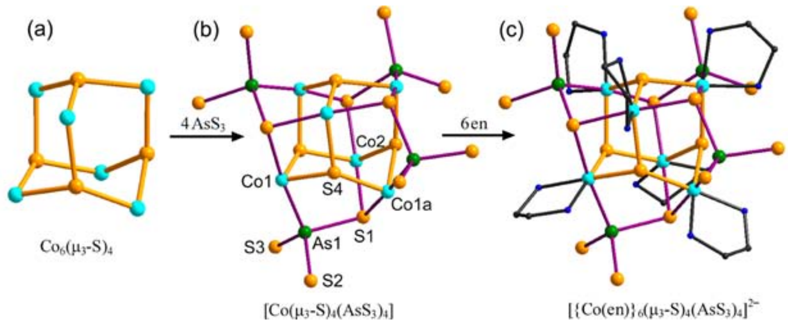


Figure 4. Structural evolution of the $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ cluster in **3** showing the crystal structure of the (a) $Co_6(\mu_3\text{-}S)_4$ core, (b) $[Co_6(\mu_3\text{-}S)_4(AsS_3)_4]$ unit, and (c) $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ cluster.

Table 3. Selected Bond Lengths (Angstroms) and Angles (Degrees) for 3

As−S	2.149(3)−2.264(2)	As−Co	2.3425(14)
Co−S	2.196(2)−2.326(2)	Co−N	2.025(8)−2.042(7)
S−As−S	104.78(11)−109.63(11)	S−As−Co	104.48(7)−114.75(9)
As−S−Co	103.14(8), 103.31(9)	Co−S−Co	94.24(8)−120.98(9)
As−Co(1)−S	84.10(6)−172.86(8)	As−Co(1)−N	89.8(2), 90.0(2)
S−Co(1)−S	80.81(8)−96.75(9)	S−Co(1)−N	89.9(2)−173.9(2)
N−Co(1)−N	83.4(3)	S−Co(2)−S	80.58(8)−171.50(12)
S−Co(2)−N	87.1(2)−168.3(2)	N−Co(2)−N	82.6(4)

coordinating to Co(1) and S(1) coordinating to Co(1A) and Co(2) (Figure 4b). The $Co_6(\mu_3\text{-}S)_4$ core is coordinated by four AsS_3 trigonal pyramids, and each Co atom is further bound with an en ligand, generating the novel $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ anionic cluster (Figure 4c). As a result, the Co(1) atom is coordinated by an As, two N, and three S atoms, and the Co(2) atom is coordinated by two N and four S atoms, forming octahedra $Co(1)AsN_2S_3$ and $Co(2)N_2S_4$, respectively. Because there are no polysulfide units in **3**, formal bond-valence sums[39] are consistent with an oxidation state of +3 for Co atoms in **3**. $CoCl_2{\cdot}6H_2O$ was oxidized to the Co(III) species during the solvothermal reaction. The XPS analysis indicates a Co(III) oxidation state in compound **3**. The XPS spectrum in the Co 2p region does not exhibit the satellite peak at 5 eV away from the main signal of Co $2p_{1/2}$ (Figure S14). These satellites were used as a fingerprint for the recognition of high-spin Co(II) species.[40] The Co−As (2.3425(14) Å), Co−S (average = 2.305(2) Å), and Co−N (average = 2.035(7) Å) (Table 3) bond lengths are, as expected, shorter than the corresponding bond lengths in **1**.

A layered structure self-assembled by the $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ clusters via the N−H···S H-bonds is formed in **3** (Figure 5). Each $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ cluster is in contacts with three neighbors via N−H···S intermolecular H-bonds with N···S distances of 3.355(7) Å and 3.737(8) Å and N−H···S angles of 166.6 and 167.7°. The layer contains circles constructed from six $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ clusters joined end to end (Figure S13 in the SI). The layers stack along the *b* axis to generate 1D channels in which the $[Hen]^+$ cations are located. The same layers and channels are formed along the *a* axis. The N−H···S H-bonds between the layers lead to a 3D network in **3**.

A number of TM complexes with thioarsenate ligands have been prepared in solution.[19−23] These thioarsenate ligands mostly bind TM ions with TM−S bonds via S-donor atoms. In particular, besides coordinating to metal centers with S atoms, the $[As_3S_6]^{5-}$ unit coordinates to Pd(II) also with the As atom forming a Pd−As bond in a methanol solution, and the $[As_3S_5]^{3-}$ unit coordinates to Pt(IV) with the As atom forming a Pt−As bond in an aqueous solution, resulting in $[Pd_7(As_{10}S_{22})]^{4-}$[21] and $[Pt(As_3S_5)_2]^{2-}$[22] clusters, respectively. Such a Pt−As bond is somewhat surprising considering that it involves a highly oxidized metal center and that it formed in aqueous solution.[22] Now we successfully prepared $[Co(As_3S_3)_2]^{2-}$, $[Ni(As_3S_3)_2]^{2-}$, and $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ clusters in the presence of chelating amines in aqueous solutions. In these clusters, the thioarsenate anions bind TM ions with both TM−As and TM−S (TM = Co, Ni) bonds, which represent the only examples of thioarsenate aggregates with both As- and S-donor ligands to TM centers in the aqueous solution of amines. The most closely related clusters of $[Co(As_3S_3)_2]^{2-}$ and $[Ni(As_3S_3)_2]^{2-}$ are observed in organo-

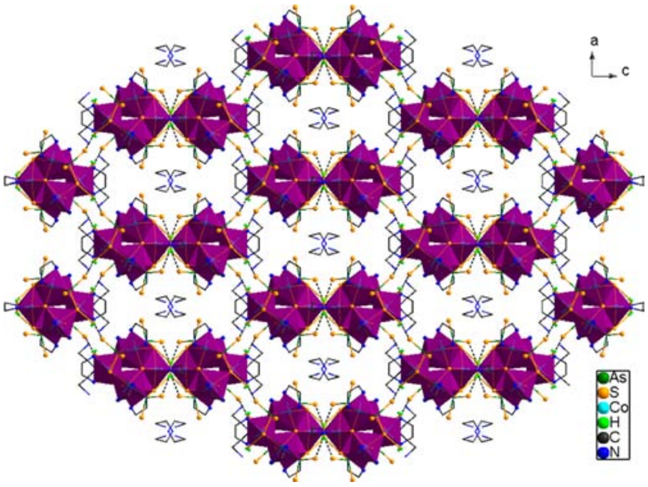


Figure 5. Crystal packing diagram of **3** viewed along the *b* axis, showing the layered structure self-assembled by the $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$ moieties via N−H···S H-bonds. The purple octahedra represent a $Co(1)AsN_2S_3$ and $Co(2)N_2S_4$ coordination sphere in $[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]^{2-}$. Hydrogen atoms of CH_2 and free en molecules are omitted for clarity.

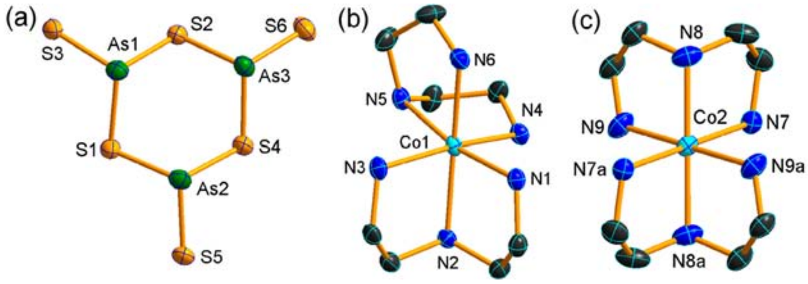


Figure 6. Crystal structures of (a) $[As_3S_6]^{3-}$, (b) $[Co(1)(dien)_2]^{2+}$, and (c) $[Co(2)(dien)_2]^{2+}$ ions in **4** with labeling (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Angstroms) and Angles (Degrees) for 4 and 5

	4	5
As−S	2.1269(18)−2.3134(18)	2.1350(13)−2.2460(11)
Co−N	2.094(6)−2.153(5)	2.105(3)−2.136(3)
S−As−S	95.71(6)−104.96(7)	98.04(7)−108.21(6)
As−S−As	93.18(6)−97. 75(7)	98.04(7)
cis-N−Co(1)−N	81.4(2)−97.18(19)	81.60(12)−94.08(12)
trans-N−Co(1)−N	167.67(19)−170.73(19)	171.42(12)−172.25(11)
cis-N−Co(2)−N	82.7(3)−98.6(2)	
trans-N−Co(2)−N	180.0(3)	

metallic complexes $[M(CO)_2(As_3Se_3)_2]^{2-}$ (M = Mo, W)[31] and $[Fe(CO)(As_3Se_3)_2]^{2-}$,[32] which were obtained in DMF solution under extremely anhydrous and anaerobic conditions.

Crystal Structures of 4 and 5. Compound **4** crystallizes in the monoclinic crystal system with space group $P2_1/c$ with two formula units in the unit cell. It consists of a discrete thioarsenate anion $[As_3S_6]^{3-}$ and $[Co(dien)_2]^{2+}$ cation. The heterocyclic $[As_3S_6]^{3-}$ anion is isostructural with the anion observed in $[enH_2]_3[As_3S_6]_2$.[9b] It is formed by three vertex-linked AsS_3 trigonal pyramids (Figure 6). A six-membered As_3S_3 heteroring is formed in the trimeric anion. The As−S bonds (As−S = 2.2844(17)−2.3134(18)Å) in the ring are longer than the As−S bonds (As−S = 2.1269(18)−2.1558(17) Å) outside the rings. There are two crystallographically independent Co^{2+} ions. Both ions are in an octahedral environment formed by six N atoms of two dien ligands. The $[Co(1)(dien)_2]^{2+}$ is in the *u-fac* conformation, containing a distorted octahedron CoN_6 with the *tran*-N−Co(1)−N angles in the range of 167.67(19)−170.73(19)° (Table 4). The $[Co(2)(dien)_2]^{2+}$ is much less distorted. It is in the *s-fac* conformation with a *tran*-N−Co(1)−N angle of 180.0(3)°. Co−N lengths range between 2.094(6) and 2.153(5) (Table 4) and are similar to the corresponding literature values for the $[Co(dien)_2]^{2+}$ complexes.[36] Compared to a few examples of thioarsenates with $[TM(dien)_2]^{2+}$ cations, a large number of binary thioantimonates have been prepared using $[TM(dien)_2]^{2+}$ as structure-directing cations.[41]

Compound **5** crystallizes in the orthorhombic crystal system with space group $P2_12_12_1$. It is isostructural with the compound $[Mn(en)_3]_2As_2S_5$.[29] It consists of an $[As_2S_5]^{4-}$ anion and octahedral $[Co(en)_3]^{2+}$ cations. Two AsS_3 trigonal pyramids are joined via corner sharing to form the bimeric $[As_2S_5]^{4-}$ anion in a cis conformation (Figure 7). The As(1) and S(1) atoms are disordered, and the occupancies of As/As′ and S/S′ are all refined as 50%. The Co^{2+} ion is 6-fold coordinated by three bidentate en ligands forming a distorted octahedral $[Co(en)_3]^{2+}$ complex cation. The $[Co(en)_3]^{2+}$ cation exhibits either a $\Lambda(\delta\delta\delta)$ or $\Delta(\lambda\lambda\lambda)$ (in inversion position) conformation. The Co−N lengths (2.105(3)−2.136(3) Å) and N−Co−N angles (171.42(12)−172.25(11)°) are typical of the octahedral $[Co(en)_3]^{2+}$ complexes.[42]

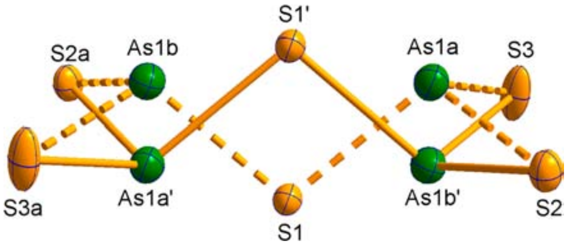


Figure 7. Crystal structure of the $[As_2S_5]^{4-}$ anion in **5** with labeling (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

The 3D arrangement of cations and anions is caused by N−H···S contacts in **4** and **5** (Figure S15 and S16 in the SI). In **4**, each $[As_3S_6]^{3-}$ anion contacts five $[Co(dien)_2]^{2+}$ cations (Figure 8) via N−H···S H-bonds with N···S distances of between 3.373(5) and 3.650(5) Å and N−H···S angles of between 144.7 and 173.6° (Table S6 in SI). In **5**, each $[As_2S_5]^{4-}$ anion interacts with eight $[Co(en)_3]^{2+}$ cations (Figure 9) via the N−H···S hydrogen bonds with N···S distances of 3.444(3)−3.749(3) Å and N−H···S angles of 150.2−172.7° (Table S6 in the SI). Only terminal S atoms of the $[As_2S_5]^{4-}$ unit are involved in H-bond formation.

Factors Influencing the Solvothermal Synthesis of the TM/As/S System. Several $[TM(en)_3]^{2+}$- or $[TM(dien)_2]^{2+}$-containing thioarsenates have been prepared from the TM/As/S system in en and dien solvents under solvothermal conditions. Solvothermal reaction of Mn, As, and S in en and dien respectively produced complexes $[Mn(en)_3]_2[Mn(en)_2AsS_4][As_3S_6]$ and $[Mn(dien)_2][Mn(dien)AsS_4]_2{\cdot}4H_2O$[4] in which the thioarsenate(V) anion $[AsS_4]^{3-}$ coordinated to the Mn^{2+} ion with the S-donor atom. The reactions of As_2O_3 and S with $TMCl_2$ gave compounds $[TM(en)_3]_2As_2S_5$ (TM = Mn, Ni,[29] Co(**5**)) in en and $[Co(dien)_2]_3[As_3S_6]_2$ (**4**) in dien, which contain the free thioarsenate(III) anions $[As_2S_5]^{4-}$ and

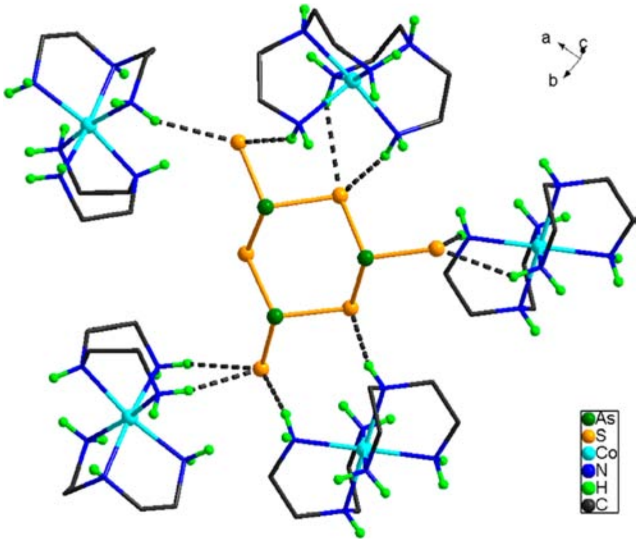


Figure 8. Sectional packing of compound **4**, showing the N−H···S hydrogen bonds between the anions and cations. The hydrogen atoms of CH_2 are omitted for clarity.

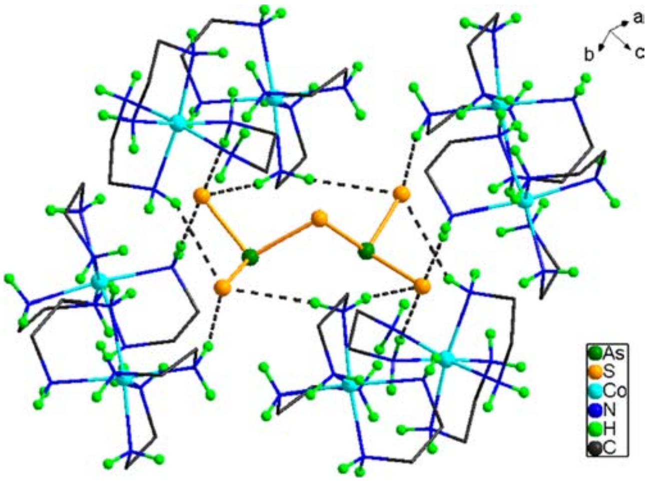


Figure 9. Sectional packing of compound **5**, showing the N−H···S hydrogen bonds between the anions and cations. The hydrogen atoms of CH_2 are omitted for clarity.

$[As_3S_6]^{3-}$. The reactions in aqueous solutions of dien and en afforded complexes $[Co(dien)_2][Co(As_3S_3)_2]$ (**1**), $[Ni(dien)_2][Ni(As_3S_3)_2]$ (**2**), and $[Hen]_2[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]$ (**3**) in which the thioarsenate anion coordinates to Co(II) and Ni(II) ions with both As- and S-donor atoms. This observation demonstrates that the pure amine and mixed amine/H_2O solution have different influences on the solvothermal synthesis of thioarsenates.

Optical Properties. The UV−vis reflectance spectroscopy of **1**−**5** was recorded on powder samples at room temperature. The absorption data from the reflectance spectroscopy by the Kubelka−Munk function[27] demonstrate that compounds **1**−**5** show well-defined abrupt absorption edges from which the band gaps can be estimated as 1.37 eV for **1**, 1.48 eV for **2**, 1.55 eV for **3** (Figure 10), 2.24 eV for **4**, and 2.26 eV for **5** (Figure S17 and S18 in SI). Compounds **1**−**3** are semiconductors with narrow bandgaps and exhibit a distinct red shift of the absorption edge compared to those for **4** and **5**. This might be caused by the binding between TM and As atoms in **1**−**3**. The bandgaps in **4** and **5** are comparable to those of TM−thioarsente complexes, such as band gaps of 2.2 eV for $(Ph_4P)_2[Ni_2As_4S_8]$,[2] 2.25 eV for $K_8[Mn_2(AsS_4)_4]$, and 2.26 eV for $Cs_8[Mn_2(AsS_4)_4]$.[18]

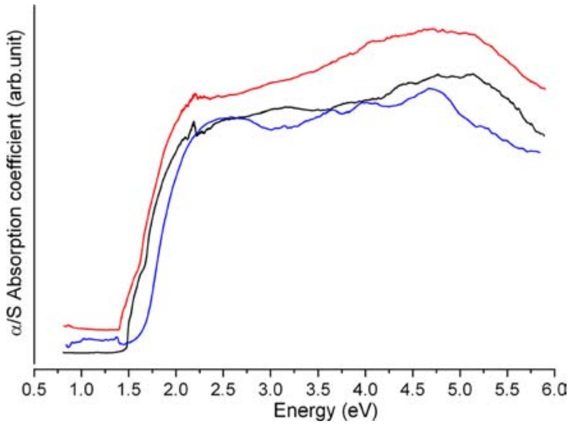


Figure 10. Solid-state optical absorption spectra of **1** (red), **2** (black), and **3** (blue).

Thermal Properties. Thermal stabilities of compounds **1**−**5** were investigated by a TG-DSC method under a nitrogen atmosphere in the temperature range of 50−500 °C. TG curves show that compounds **1** and **2** decompose in a single step with mass losses of 22.3 and 22.7%, respectively, which correspond to the loss of four dien ligands (theoretical value 21.4% for **1** and **2**) (Figures S19a and S19b in the SI). The decomposition processes are accompanied by an endothermic signal in the DSC curve with peak temperatures of 234.2 °C for **1** and 241.6 °C for **2**. Compound **3** starts to decompose at about 110 °C. It decomposes in two steps with weight losses of 8.8 and 21.4%, which are in good agreement with the removal of 1 mole of H_2S and 2 moles of free en molecules in the first step (theoretical value 9.3%) and 6 moles of en ligands in the second step (theoretical value 21.9%). The decomposition process is accompanied by two endothermic signals in the DSC curve with peak temperatures at 168.7 and 241.3 °C (Figure S19c). Both **4** and **5** decompose in a single step with mass losses of 37.1 and 44.4%, respectively, accompanied by an endothermic signal at 250.2 °C for **4** and 234.5 °C for **5** (Figure S19d,e). The mass losses match well with the removal of all dien ligands in **4** (theoretical value 38.0%) and all en ligands in **5** (theoretical value 45.7%).

■ CONCLUSIONS

Complexes with thioarsenate ligands $[Co(dien)_2][Co(As_3S_3)_2]$ (**1**), $[Ni(dien)_2][Ni(As_3S_3)_2]$ (**2**), and $[Hen]_2[\{Co(en)\}_6(\mu_3\text{-}S)_4(AsS_3)_4]$ (**3**) have been prepared in aqueous solutions. This result demonstrates that the coordination of thioarsenate anions to TM ions with both As and S atoms can be achieved in the presence of chelating ethylene polyamines, although the polyamines with N-donor atoms are stronger ligands than the thioarsenates with S- or(and) As-donor atoms. In aqueous solution, the Co(II) and Ni(II) ions can be coordinated not only by polyamines amines but also by As_3S_3 or AsS_3 units with both As and S atoms. The same synthesis in pure dien and en solvent afforded $[Co(dien)_2]_3[As_3S_6]_2$ (**4**) and $[Co(en)_3]_2As_2S_5$ (**5**) containing discrete thioarsenate anions. This result shows that pure amine and aqueous amine solutions exhibit much different effects on the solvothermal synthesis from the TM/As/S system.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data of compounds **1−5** in CIF format, selected bond lengths and angles for **1−5**, PXRD spectra, IR spectra, structural figures, XPS spectrum, optical absorption spectra, and TG-DSC curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Zank, G. A.; Rauchfuss, B.; Wilson, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 7621−7623.

(2) Chou, J.-H.; Hanko, J. A.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 4−9.

(3) Fu, M. L.; Guo, G. C.; Liu, X.; Liu, B.; Cai, L. Z.; Huang, J. S. *Inorg. Chem. Commun.* **2005**, *8*, 18−21.

(4) Fu, M. L.; Guo, G. C.; Cai, L. Z.; Zhang, Z. J.; Huang, J. S. *Inorg. Chem.* **2005**, *44*, 184−186.

(5) Wachhold, M.; Kanatzidis, M. G. *Inorg. Chem.* **1999**, *38*, 3863−3870.

(6) Wachhold, M.; Kanatzidis, M. G. *Inorg. Chem.* **2000**, *39*, 2337−2343.

(7) Bera, T. K.; Jang, J. I.; Song, J.-H.; Malliakas, C. D.; Freeman, A. J.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2010**, *132*, 3484−3495.

(8) (a) Sheldrick, W. S.; Wachhold, M. *Coord. Chem. Rev.* **1998**, *176*, 211−322. (b) Wachter, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 750−768. (c) Li, J.; Chen, Z.; Wang, R. J.; Proserpio, D. M. *Coord. Chem. Rev.* **1999**, *190−192*, 707−735. (d) Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **2000**, 3041−3052. (e) Kromm, A.; Almsick, T. V.; Sheldrick, W. S. *Z. Naturforsch.* **2010**, *65B*, 918−936. (f) Wachter, J. *Coord. Chem. Rev.* **2010**, *254*, 2078−2085. (g) Naumov, P.; Makreski, P.; Jovanovski, G. *Inorg. Chem.* **2007**, *46*, 10624−10631.

(9) (a) Sheldrick, W. S.; Kaub, J. *Z. Naturforsch.* **1985**, *40B*, 571−573. (b) Sheldrick, W. S.; Kaub, J. *Z. Naturforsch.* **1985**, *40B*, 19−21. (c) Sheldrick, W. S.; Kaub, J. *Z. Naturforsch.* **1985**, *40B*, 1130−1133. (d) Sheldrick, W. S.; Kaub, J. *Z. Naturforsch.* **1985**, *40B*, 1020−1022. (e) Smith, D. M.; Park, C.-W.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 6682−6687. (f) Vater, V.; Sheldrick, W. S. *Z. Naturforsch.* **1997**, *52B*, 1119−1124. (g) Vater, V.; Sheldrick, W. S. *Z. Naturforsch.* **1998**, *53B*, 1259−1264. (h) Du, K. Z.; Feng, M. L.; Li, J. R.; Huang, X. Y. *CrystEngComm* **2012**, *14*, 4959−4962.

(10) Iyer, R. G.; Kanatzidis, M. G. *Inorg. Chem.* **2002**, *41*, 3605−3607.

(11) R., G.; Lyer,Do, J.; Kanatzidis, M. G. *Inorg. Chem.* **2003**, *42*, 1475−1482.

(12) Chou, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1994**, *33*, 1001−1002.

(13) Wang, Z. Q.; Zhang, H. J.; Wang, C. *Inorg. Chem.* **2009**, *48*, 8180−8185.

(14) Kang, D.-H.; Schleid, T. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2170−2176.

(15) Wu, Y.; Näther, C.; Bensch, W. *Inorg. Chem.* **2006**, *45*, 8835−8837.

(16) Bera, T. K.; Iyer, R. G.; Malliakas, C. D.; Kanatzidis, M. G. *Inorg. Chem.* **2007**, *46*, 8466−8468.

(17) Jerome, J. E.; Wood, P. T.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1994**, *33*, 1733−1734.

(18) Iyer, R. G.; Kanatzidis, M. G. *Inorg. Chem.* **2004**, *43*, 3656−3662.

(19) Kanatzidis, M. G.; Chou, J.-H. *J. Solid State Chem.* **1996**, *127*, 186−201.

(20) Schwarz, P.; Wachter, J.; Zabel, M. *Inorg. Chem.* **2011**, *50*, 12692−12696.

(21) Hanko, J. A.; Chou, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1998**, *37*, 1670−1671.

(22) Chou, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1994**, *33*, 5372−5373.

(23) Chou, J.-H.; Kanatzidis, M. G. *Chem. Mater.* **1995**, *7*, 5−8.

(24) (a) Fu, M. L.; Guo, G. C.; Liu, X.; Chen, W. T.; Liu, B.; Huang, J. S. *Inorg. Chem.* **2006**, *45*, 5793−5798. (b) Pan, Y. L.; Jin, Q. Y.; Chen, J. F.; Zhang, Y.; Jia, D. X. *Inorg. Chem.* **2009**, *48*, 5412−5417. (c) Wang, X.; Sheng, T. L.; Hu, S. M.; Fu, R. B.; Chen, J. S.; Wu, X. T. *J. Solid State Chem.* **2009**, *182*, 913−919. (d) Liu, G. N.; Jiang, X. M.; Wu, M. F.; Wang, G. E.; Guo, G. C.; Huang, J. S. *Inorg. Chem.* **2011**, *50*, 5740−5746. (e) Liu, G. N.; Guo, G. C.; Chen, F.; Wang, S. H.; Sun, J.; Huang, J. S. *Inorg. Chem.* **2012**, *51*, 472−482.

(25) (a) Schur, M.; Bensch, W. *Z. Naturforsch.* **2002**, *57B*, 1−7. (b) Vaqueiro, P.; Chippindale, A. M.; Powell, A. V. *Inorg. Chem.* **2004**, *43*, 7963−7965. (c) Stähler, R.; Mosel, B.-D.; Eckert, H.; Bensch, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 4487−4489.

(26) Work, J. B.; McReynolds, J. P. Tris(Ethylenediamine)cobalt(III) Chloride. In *Inorganic Syntheses*; Fernelius, W. C., Eds.; John Wiley & Sons: Hoboken, NJ, 2007; Vol. 2, pp 221−222.

(27) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966.

(28) (a) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(29) Jia, D. X.; Zhao, Q. X.; Dai, J.; Zhang, Y.; Zhu, Q. Y. *Z. Anorg. Allg. Chem.* **2006**, *632*, 349−353.

(30) Brunner, H.; Leis, F.; Wachter, J.; Zabel, M. *J. Organomet. Chem.* **2001**, *628*, 39−45.

(31) O'Neal, S. C.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1992**, *31*, 888−894.

(32) Martin, T. M.; Wood, P. T.; Schimek, G. L.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1995**, *34*, 4385−4391.

(33) Brunner, H.; Kauermann, H.; Poll, L.; Nuber, B.; Wachter, J. *Chem. Ber.* **1996**, *129*, 657−659.

(34) Brunner, H.; Nuber, B.; Poll, L.; Wachter, J. *Angew. Chem., Int. Ed.* **1993**, *32*, 1627−1628.

(35) Pienack, N.; Lehmann, S.; Lühmann, H.; El-Madani, M.; Näther, C.; Bensch, W. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2323−2329.

(36) (a) Bensch, W.; Näther, C.; Stähler, R. *Chem. Commun.* **2001**, 477−478. (b) Stähler, R.; Mosel, B. D.; Eckert, H.; Bensch, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 4487−4489. (c) Stähler, R.; Näther, C.; Bensch, W. *J. Solid State Chem.* **2003**, *174*, 264−275. (d) Stähler, R.; Näther, C.; Bensch, W. *Eur. J. Inorg. Chem.* **2001**, 1835−1840. (e) Stähler, R.; Bensch, W. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1657−1662. (f) Jia, D. X.; Zhang, Y.; Zhao, Q. X.; Deng, J. *Inorg. Chem.* **2006**, *45*, 9812−9817.

(37) (a) Hudhomme, P.; Moustarder, S. L.; Durand, C.; Planas, N. G.; Mercier, N.; Blanchard, P.; Levillain, E.; Allain, M.; Gorgues, A.; Riou, A. *Chem.—Eur. J.* **2001**, *7*, 5070−5083. (b) Kobayashi, K.; Shimaoka, R.; Kawahata, M.; Yamanaka, M.; Yamaguchi, K. *Org. Lett.* **2006**, *8*, 2385−2388. (c) Arooj, M.; Kim, K. H.; Kim, D. H.; Kim, B. S.; Park, G. Y.; Jeong, S. H.; Shin, S. C.; Park, J. K. *Bull. Korean Chem. Soc.* **2009**, *30*, 3079−3081.

(38) Zukerman-Schpector, J.; Otero-de-la-Roza, A.; Luaña, V.; Tiekink, E. R. T. *Chem. Commun.* **2011**, 7608−7610.

(39) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192−197.

(40) (a) Briggs, D.; Gibson, V. A. *Chem. Phys. Lett.* **1974**, *25*, 493−496. (b) McIntyre, N. S.; Johnston, D. D.; Coatsworth, L. L.; Davidson, R. D.; Brown, J. R. *Surf. Interface Anal.* **1990**, *15*, 265−272. (c) Atzei, D.; Rossi, A.; Sadun, C. *Spectrochim. Acta* **2000**, *A56*, 1875−1886. (d) Barreca, D.; Massignan, C. *Chem. Mater.* **2001**, *13*, 588−593.

(41) (a) Bensch, W.; Näther, C.; Stähler, R. *Chem. Commun.* **2001**, 477−478. (b) Stähler, R.; Näther, C.; Bensch, W. *Eur. J. Inorg. Chem.* **2001**, 1835−1840. (c) Stähler, R.; Mosel, B.-D.; Eckert, H.; Bensch, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 4487−4489. (d) Stähler, R.; Bensch, W. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1657−1662. (e) Kiebach, R.; Studt, F.; Näther, C.; Bensch, W. *Eur. J. Inorg. Chem.* **2004**, 2553−2556. (f) Stähler, R.; Näther, C.; Bensch, W. *J. Solid State Chem.* **2003**, *174*, 264−275. (g) Lühmann, H.; Rejai, Z.; Möller, K.; Leisner, P.; Ordolff, M.-E.; Näther, C.; Bensch, W. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1687−1695.

(42) (a) Stephan, H. O.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1996**, *118*, 12226−12227. (b) Vaqueiro, P.; Chippindale, A. M.; Powell, A. V. *Inorg. Chem.* **2004**, *43*, 7963−7965. (c) Vaqueiro, P.; Darlow, D. P.; Powell, A. V.; Chippindale, A. M. *Solid State Ionics* **2004**, *172*, 601−605.