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Preparation and Characterization of the Skutterudite-Related Phases $CoGe_{1.5}S_{1.5}$ and $CoGe_{1.5}Se_{1.5}$

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Single crystals of new skutterudite-related compounds $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$ were grown by the chemical vapor transport method using iodine as the transport agent. The materials were characterized by x-ray analysis, density determinations, chemical analysis, and magnetic and thermogravimetric measurements. $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$ are diamagnetic and decompose in an oxygen atmosphere at temperatures of 800 and 1000 °C, respectively. They crystallize in a modification of the skutterudite ($CoAs_3$) structure with a short range order between the group 4A and group 6A atoms.

Introduction

The group of anion-rich pnictides with the formula MX_3, where M = Co, Rh, or Ir and X = P, As, or Sb, adopt the skutterudite structure. This structure (cubic space group *Im*3) can be viewed as a severe distortion of the ReO_3 structure in which the anions form four-membered σ-bonded rings (Figure 1). Whereas the metal atoms retain the sixfold coordination found in ReO_3, the anions are located on distorted tetrahedral sites with two anion and two metal neighbors. Recently, the crystal growth and characterization of the cobalt skutterudites CoP_3, $CoAs_3$, and $CoSb_3$ were reported.[1] Whereas $CoAs_3$ and $CoSb_3$ appear to show metallic behavior, CoP_3 is a semiconductor. In addition, CoP_3 was found to be stable in an oxygen atmosphere at temperatures exceeding 1000 °C.[2]

The substitution of an equiatomic combination of a group 4A and group 6A element for a pnicogen to give an isoelectronic, structurally related, ternary phase has been accomplished for several transition metal pnictides. The substitution of a germanium and a selenium atom for phosphorus in the pyrite PtP_2 results in the formation of the isoelectronic, structurally related ternary phase PtGeSe.[3,4] When a germanium and a sulfur atom are substituted for phosphorus in ZrP_2 (which adopts the $PbCl_2$ structure), the resulting isoelectronic ternary phase, ZrGeS, crystallizes with the closely related PbFCl structure.[5]

Consequently, the synthesis of ternary skutterudite-type phases by the simultaneous substitution of a group 4A and a group 6A atom for the pnicogen was attempted. The crystal growth and characterization of the new skutterudite-related phases $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$ are reported here.

Experimental Section

Crystal Growth. Several of the elements were purified prior to use. Cobalt (Leico 99.999%) was reduced by heating for 8 h at 500 °C in a 15% hydrogen/85% argon gas mixture. Sulfur (Atomergic 99.999%) was vacuum sublimed at 200 °C. Germanium (Atomergic 99.999%) and selenium (Leico 99.999%) were used as obtained from the manufacturers. Efforts to prepare single-phase polycrystalline samples were unsuccessful and therefore attempts to grow crystals of $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$ by the chemical vapor transport method[6] were made. Stoichiometric quantities of the purified elements are introduced into 11-mm i.d. silica tubes and the conditions for chemical vapor transport are given in Table I. The details for the use of iodine as a transport agent are discussed elsewhere.[7] Small crystals sufficient for chemical and structural analysis were grown; however, their small size precluded electrical and optical characterization.

The growth conditions for both compounds are listed in Table I. Prior to characterization, the crystals were washed in ethanol and 3 N H_2SO_4 to remove any soluble halides adhering to the crystal surfaces.

Materials Characterization. Density Measurements. The densities were determined on crystals of $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$ via a hydrostatic technique.[8] A Mettler H54 analytical balance was employed and the density fluid, perfluoro(1-methyldecalin), was calibrated with a high-purity silicon crystal (ρ = 2.328 g/cm^3 at T = 22 °C). Prior to any measurements the crystals were outgassed thoroughly to ensure accurate results.

Table I. Preparation and Properties of $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$

Compound	Transport agent	Charge zone	Growth zone	Duration
$CoGe_{1.5}Se_{1.5}$	I_2 (5 mg/cm^3)	740 °C	670 °C	3 weeks
$CoGe_{1.5}S_{1.5}$	I_2 (5 mg/cm^3)	790 °C	715 °C	4 weeks

	$CoGe_{1.5}Se_{1.5}$	$CoGe_{1.5}S_{1.5}$
Cell edge	a_0 = 8.299 (2) Å	a_0 = 8.017 (2) Å
Density	d_{exptl} = 6.62 (3) g/cm^3 d_{calcd} = 6.65 g/cm^3	d_{exptl} = 5.54 (3) g/cm^3 d_{calcd} = 5.58 g/cm^3
Wt % Co	% obsd = 20.4 (2) % calcd = 20.6	% obsd = 27.4 (2) % calcd = 27.3
Magnetic properties	Diamagnetic χ_M(300 K) = −38.4 emu/mol	Diamagnetic χ_M(300 K) = −50.6 emu/mol
Dec temp in oxygen	800 °C	1000 °C

Chemical Analysis. After crystals of $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$ were dissolved in aqua regia, the cobalt content was determined by the photometric cobalt–nitroso–R-salt method.[9]

Magnetic Measurements. The molar susceptibility of both compounds was measured in the temperature range from 77 to 300 K with a Faraday balance of the type described by Morris and Wold.[10] The absence of ferromagnetic impurities was verified by applying the Honda–Owens method.[11] No corrections were made for core diamagnetism.

Thermogravimetric Analysis. The thermal stability of the compounds was studied in an oxygen atmosphere. Several crystals of both compounds were ground, and only particles less than 74 μ in size were chosen. The thermogravimetric apparatus consisted of a Cahn RG electrobalance and a furnace through which oxygen gas could flow. The decomposition point was recorded at the temperature that a noticeable weight loss was first observed.

X-Ray Crystallography. The diffraction spectra of ground crystals of $CoGe_{1.5}S_{1.5}$ and $CoGe_{1.5}Se_{1.5}$ were recorded on a Norelco diffractometer equipped with a high-intensity copper source and a graphite monochromator. Scan rates of 0.25°/min were employed and ground silicon crystals served as internal standards. The spectra of each of the powders could be indexed on a primitive cubic cell as shown in Tables II and III (supplementary material). The intense reflections correspond to the condition *hkl*, $h + k + l = 2n$, and have an intensity pattern similar to that of skutterudite, $CoAs_3$. In addition, a few very weak superstructure reflections are present that eliminate the exact body-centered constraint. Photographs of a single crystal of $CoGe_{1.5}S_{1.5}$ were taken with a precession camera operating with Mo Kα radiation at ambient temperature. The diffraction pattern had cubic *m*3 Laue symmetry, and the superstructure reflections, although very weak, lay on strong streaks. Even on a photograph taken of the $l = {}^1/_2$ zone, the appearance of streaks was visible. This is evidently an indication of the lack of complete long-range order.

Intensity data were collected on a single crystal of $CoGe_{1.5}S_{1.5}$ on a Picker FACS-I diffractometer over one hemisphere of reciprocal space between the angular limits of $5 \leq 2\theta \leq 50°$ in the Mo radiation sphere. The data (1993 reflections) were reduced in the normal manner and corrections for absorption (μ = 259 cm^{-1}, t_{min} = 0.027,

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Table IV. Results of Least-Squares Refinements

Crystal system	Space group	Reflec included	Atom	Atomic positions x	y	z	Temp factor B	No. of param	No. of reflec	R, %	R_w, %
Cubic	*Im*3	$h + k + l = 2n$	Co	1/4	1/4	1/4	0.37 (7)	6	99	4.3	4.7
			Av anion	0	0.1480 (2)	0.3398 (2)	0.38 (6)				
Rhombohedral	*R*3	All	Co(1)	1/4	1/4	1/4		35	535	11.5	15.3
			Co(2)	0.759 (1)	0.759 (1)	0.759 (1)					
			Co(3)	0.752 (2)	0.256 (4)	0.262 (3)	0.1 (1)				
			Co(4)	0.748 (3)	0.748 (3)	0.238 (2)					
			S(1)	−0.004 (3)	−0.146 (3)	0.668 (3)					
			S(2)	−0.002 (3)	0.140 (3)	0.352 (3)					
			S(3)	0.489 (3)	0.638 (3)	0.166 (3)	−0.3 (2)				
			S(4)	0.493 (3)	0.353 (3)	0.853 (3)					
			Ge(1)	0.006 (1)	−0.154 (2)	0.331 (2)					
			Ge(2)	0.008 (2)	0.144 (2)	0.658 (2)	0.2 (1)				
			Ge(3)	0.498 (2)	0.647 (2)	0.825 (2)					
			Ge(4)	0.501 (2)	0.348 (2)	0.155 (2)					

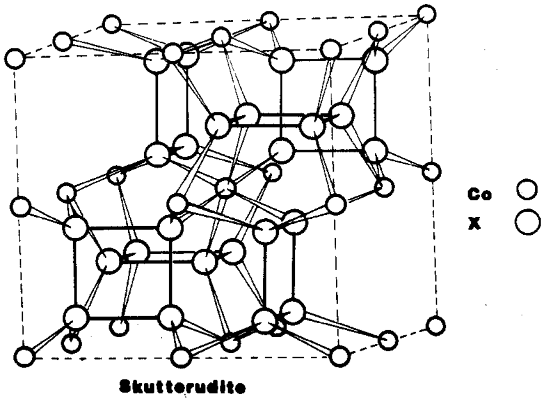

Figure 1. Skutterudite structure. The unit cell origin is displaced by $^1/_4$, $^1/_4$, $^1/_4$, from the origin of the dotted axes.

t_{max} = 0.071) were applied.[12] In all the least-squares calculations the program ORXFLS 3 was used and isotropic secondary extinction corrections were applied. Scattering factors for the neutral atoms were taken from Cromer's compilation[13] and the anomalous dispersion corrections of Cromer and Liberman were applied.[14] The diffraction data were treated in two steps. First, an attempt to corroborate the skutterudite-type substructure was made, and, second, an effort to best approximate the superstructure was tried.

In attempting to solve the substructure, only those reflections with $h + k + l = 2n$ were treated. These reflections were averaged consistent with the Laue symmetry (*m*3) of the *Im*3 space group to yield a total of 97 independent reflections with $I_{av} \geq 2\sigma(I_{av})$. In the *Im*3 space group the skutterudite structure is described completely by one cation and one anion site. Consequently, scattering factors for the anion were computed by averaging the values of germanium and sulfur atoms at each $(\sin^2 \theta)/\lambda$ value. The excellent agreement between the observed and calculated structure factors (R = 4.3%, R_w = 4.7%) proves that the structure of the new ternary compound $CoGe_{1.5}S_{1.5}$ is related closely to the parent $CoAs_3$ skutterudite structure.

Because of the lack of long-range order, the solution of the superstructure could only be approximated. The ordering of the anions can occur either between anions in rings related by the approximate body-centering translation, within the four-membered ring themselves, or by both means.

The best results were obtained from a model that contained four-membered rings with germanium and sulfur pairs in trans positions. This model can be described in the trigonal crystal system on rhombohedral axes (α = 90.0°) in space group *R*3. The anion rings are related to one another by a threefold axis along one body diagonal of the cell, but they no longer lie at the intersection of the mirror planes. Because the approximate body-centering translation relates an anion of one type to an anion of the other type, superstructure lines appear in the basic skutterudite pattern. This model was refined to R = 11.5%, R_w = 15.3%, but several problems remained (relatively high R factors, slightly negative temperature factor parameters on the sulfur atoms) as a result of treating a structure with some disorder with a completely ordered model.

Table IV summarizes the results of the least-squares refinements of the substructure and the best approximation of the superstructure.

Results and Discussion

Well-formed small crystals of $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$ were grown by the chemical vapor transport method using iodine as the transporting agent.

The x-ray data obtained from ground crystals could be indexed on the basis of a primitive cubic cell. The refinement of the intensity data collected on a crystal of $CoGe_{1.5}S_{1.5}$ indicates that the compounds crystallize in an ordered variant of the skutterudite structure. However, the problems associated with the lack of long-range order in this system prevented a complete solution of the superstructure.

Lattice constants and measured densities are listed in Table I. The experimental densities compare well with the calculated densities derived from the measured cell edges and the assumed $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$ stoichiometries. The results of the cobalt analysis (Table I) and the observed density values establish the stoichiometry of these new ternary phases as $Co_{1.00(3)}Ge_{1.50(3)}Se_{1.50(3)}$ and $Co_{1.00(3)}Ge_{1.50(3)}S_{1.50(3)}$.

The magnetic susceptibility of these compounds was found to be independent of temperature with χ_M (300 K) equal to −33.4 and −50.6 emu/mol for the selenide and sulfide, respectively. This is indicative of diamagnetic behavior and is consistent with a low-spin d^6 electronic configuration for the cobalt atom.

$CoGe_{1.5}Se_{1.5}$ decomposed at 800 °C under a flowing stream of oxygen gas, whereas $CoGe_{1.5}S_{1.5}$ decomposed at 1000 °C. On the other hand, the skutterudite CoP_3 was found to be more stable and did not decompose in an oxygen atmosphere at temperatures exceeding 1000 °C.[2]

In conclusion, new ternary phases with the $CoGe_{1.5}Se_{1.5}$ and $CoGe_{1.5}S_{1.5}$ stoichiometry have been synthesized by the simultaneous substitution of a group 4A and group 6A atom for a group 5A pnicogen. The resulting compounds are isoelectronic with and structurally related to the parent skutterudite compounds.

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Registry No. $CoGe_{1.5}Se_{1.5}$, 63039-68-9; $CoGe_{1.5}S_{1.5}$, 63039-67-8.

Supplementary Material Available: X-ray spectrum for $CoGe_{1.5}Se_{1.5}$ (Table II), x-ray spectrum for $CoGe_{1.5}S_{1.5}$ (Table III), and structure factor amplitudes for $CoGe_{1.5}S_{1.5}$ (4 pages). Ordering information is given on any current masthead page.

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Studies on Main-Group Metal–Transition Metal Bonded Compounds. 5. Structure of $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnBr_2\cdot DMF$

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The crystal and molecular structure of $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnBr_2\cdot DMF$ has been determined from single-crystal x-ray data collected by counter methods. The adduct crystallizes in the space group $P2_1/c$ with four molecules per unit cell of dimensions $a = 13.189$ (4) Å, $b = 7.825$ (2) Å, $c = 16.531$ (4) Å, and $\beta = 99.55$ (2)°. Full-matrix least-squares refinement gave discrepancy factors $R_1 = 0.054$ and $R_2 = 0.097$ for 1568 independent diffractometer data for which $I > 2.5\sigma(I)$. The structure contains a tetrahedral zinc atom coordinated to two bromine atoms, one oxygen atom, and one molybdenum atom. The molybdenum atom is sandwiched between two cyclopentadienyl groups which are tilted up from the zinc (dihedral angle = 36.6°). The hydrogen atoms, as located in the final difference map, form an asymmetric bridge between the Mo and Zn atoms, and it is proposed that this interaction leads to the stabilization of the complex. The complex is prepared from the reaction of $(\eta^5\text{-}C_5H_5)_2MoH_2$ and EtZnBr in which $ZnBr_2$, formed from the self-proportionation equilibrium $2EtZnBr \rightleftharpoons Et_2Zn + ZnBr_2$, coordinates preferentially with the transition metal moiety or alternatively is prepared from the direct reaction of the hydride with $ZnBr_2$. Similar complexes are prepared using other group 2B metal halides.

Introduction

The structure[1] of Cp_2MoH_2 (Cp = $\eta^5\text{-}C_5H_5$) consists of a molybdenum atom sandwiched between two cyclopentadienyl rings; the normals from the centers of each ring pass through the molybdenum atom, although the rings are tilted to form a dihedral angle of 34.1°. This description is qualitatively consistent with a theoretical model proposed by Ballhausen and Dahl,[2] in which three localized orbitals are sandwiched between the rings (Figure 1). The hydrogen atoms are expected to reside at the two outer orbitals leaving a lone pair of electrons between these ligands which may serve as a basic site.

Alternatively Alcock[3] has suggested that the lone pair of electrons resides principally in a d orbital orthogonal to this axis and possesses no directional character (Figure 1). This model is consistent qualitatively with the structure and better accounts for the relatively small L–M–L bond angles observed in a wide number of related molecules and with the decrease in angle on proceeding from d^0 to d^1 to d^2 electronic configurations as indicated by Prout et al.[4] Dahl and co-workers in several papers[4–6] have proposed a bonding model similar in many respects to that of Alcock[3]—with most of the electron density in d^1 and d^2 systems located in an orbital orthogonal to the axis suggested by Ballhausen and Dahl.[2] The stereochemical effect results in the reduction of the L–M–L bond angle for the $(\eta^5\text{-}C_5H_5)_2ML_2$ systems as the number of electrons increases from 0 to 1 to 2. Finally Lauher and Hoffmann[7] have provided an extensive treatment of the bonding in these and other bis(cyclopentadienyl) complexes and have concluded that the various models proposed result from different linear combinations of the atomic orbitals, with each model emphasizing a particular facit of the possible modes of bonding.

The preponderance of evidence now indicates that the unshared pair of electrons resides in an orbital orthogonal to that proposed by Ballhausen and Dahl;[2] however, this electron pair does serve as a base as amply demonstrated by protonation,[8] by the formation of BF_3 adducts,[9,10] and by characterization of the aluminum adducts $Cp_2MH_2\cdot AlR_3$ (M = Mo, W; R = CH_3, C_2C_5, C_6H_5)[11,12] and $Cp_2ReH\cdot Al(CH_3)_3$.[11] Unfortunately no structures of these adducts have been determined. Rather the structures of the polymeric crystalline materials resulting from the elimination reactions of Al_2Me_6,[13,14] cyclohexylmagnesium bromide,[15] butyllithium,[16] or diethylzinc[17] with Cp_2MoH_2 have appeared. The structures of these materials, with the exception of the product resulting from the reaction with diethylzinc, have been determined by x-ray methods and reveal the presence of metal–metal bonding but do not show the formation of the simple adduct or its structure.

Formation of addition compounds which contain metal–metal bonds has been reported in a number of cases and, in the instance of $(CO)_4CoHgX_2$ species, the structure clearly shows metal–metal bonding.[18] There has, however, been only a very limited amount of work on systems other than those involving mercury species and to the best of our knowledge no structural studies involving main group adducts of Cp_2MoH_2, Cp_2WH_2, or CpReH have appeared.

Experimental Section

Solvents were dried over $LiAlH_4$ and were used immediately or stored in evacuated vessels. The WCl_6, $ZnBr_2$, and $MoCl_6$ were obtained from RIC/ROC, opened and stored in an argon filled drybox, and used without further purification. Et_2Zn was obtained from Ethyl Corp. and distilled under vacuum as it was used.

Preparation of EtZnBr. An excess of Et_2Zn was distilled onto $ZnBr_2$ and mixed for 2 or 3 h. The excess Et_2Zn was distilled from the solid which was subsequently dissolved in diethyl ether. The concentration of EtZnBr was determined by measuring the partial pressure of ethane evolved from hydrolysis of the solution. The solution was stored under argon in a septum bottle at −20 °C.

Reaction of EtZnBr with Cp_2MoH_2. On addition of 2.0 mL of 1.4 × 10^{-1} M EtZnBr to 0.064 g of Cp_2MoH_2 (0.014 mol) a yellow solid precipitated immediately with no apparent evolution of gases. The