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Synthesis and Structure of the New Layered Ternary Selenide $Na_4Cd_3Se_5$

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The new ternary compound $Na_4Cd_3Se_5$ has been prepared by the reaction of CdSe with Na_2Se_4 at 300/350°C. $Na_4Cd_3Se_5$ crystallizes in space group D_{2h}^{16}-*Pnma* of the orthorhombic system with four formula units in a cell of dimension $a = 14.026(1)$ Å, $b = 4.234(2)$ Å, $c = 20.105(1)$ Å at 110 K. The structure consists of zigzag layers of $^2_\infty[Cd_3Se_5^{4-}]$ separated by Na^+ cations. Alternatively, these layers can be considered as trimers of corner-sharing $CdSe_4$ tetrahedra. The Cd atoms are each tetrahedrally coordinated to four Se atoms at distances ranging from 2.604(1) Å to 2.718(1) Å. Each Na atom is surrounded in a square pyramidal manner by five Se atoms at distances of 2.82 to 3.11 Å.

Introduction

Use of a chalcogenide flux in the growth of crystals of binary metal chalcogenides is well known (*1–3*). However, its use as a reactant as well as a flux (the reactive flux method) in the synthesis of ternary and quaternary chalcogenides is recent (*4*). Many of the compounds synthesized in this way contain Q_n fragments, $n = 2–5$, Q = S, Se, or Te (*4–7*), that were inaccessible through conventional synthetic routes. In fact, the reactive flux method has been successfully applied to the synthesis of a number of unusual new materials, mainly chalcogenides. These materials exhibit a wide range of structures, ranging from three-dimensional to one-dimensional (*4, 8–16*). Although most of the work from this laboratory has focused on ternary compounds in the *A/M/Q* system, where *A* is a Group I metal, *M* is a Group IV or Group V metal, and *Q* is a chalcogenide (*Q* = S, Se, or Te), it is clear from other work (*5–8, 13, 17*) that new, interesting compounds remain to be discovered and characterized where *M* is a late transition or main-group metal (*9*). While a number of Hg compounds have been prepared by the reactive flux method (*15*), no Cd compounds have. Here we report the synthesis of the new ternary compound $Na_4Cd_3Se_5$ and its structural characterization.

Experimental

Synthesis. The compound $Na_4Cd_3Se_5$ was prepared by the reaction of CdSe and Na_2Se_4. Na_2Se_4 was prepared by the stoichiometric reaction of Na and Se in liquid ammonia. CdSe was purchased from Merck & Co., Inc., Rahway, NJ. A dry quartz tube

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was loaded with CdSe (191 mg, 1 mmol) and Na_2Se_4 (362 mg, 1 mmol), evacuated to 5×10^{-4} Torr, and then sealed. The tube was placed in a furnace, heated to 350°C, kept there for 48 h, and then cooled to room temperature over a period of 48 h. The black melt so obtained, after being washed with H_2O and Me_2CO to remove excess polyselenide, afforded a red microcrystalline powder and a few red needle-shaped crystals of what proved to be $Na_4Cd_3Se_5$. Yield was 20%. Alternatively, the compound can be synthesized at 300°C with the addition to the above reactants of a small amount of H_2O (0.01 ml). This modification produces better quality crystals and increases the yield to 38% (based on Cd). Quantitative elemental analyses performed on several crystals with the use of an EDAX (energy dispersive analysis by X-rays) equipped Hitachi S570 scanning electron microscope gave slightly varying atomic compositions in the range $Na_{1.23}CdSe_{1.61}$ to $Na_{1.11}CdSe_{1.73}$. The infrared spectrum of $Na_4Cd_3Se_5$ is featureless in the O–H stretching region. The exact composition of $Na_4Cd_3Se_5$ for the chosen crystal was established by a single crystal X-ray diffraction study. Under similar conditions reaction of stoichiometric quantities of the elements produced only mixtures of binary phases. Use of excess polyselenide seems to be essential for the formation of the $Na_4Cd_3Se_5$ phase.

Crystallography. X-ray unit cell and intensity data were collected from a needle-shaped crystal at 110 K on an Enraf-Nonius CAD4 automatic four circle diffractometer. As the systematic absences and Laue symmetry led to the orthorhombic space groups *Pnma* and $Pn2_1a$, data were collected for the $h, \pm k, -l$ reflections from 2° to 20° and for the $h, -k, -l$ reflections from 20° to 48°. Additional data collection parameters are tabulated in Table I. Six standard reflections were measured after every 100 reflections. There were no significant variations in the intensities of these standard reflections.

TABLE I

CRYSTAL DATA FOR $Na_4Cd_3Se_5$

Formula	$Na_4Cd_3Se_5$
Formula mass (amu)	823.96
Space group	D_{2h}^{16}-*Pnma*
a, Å	14.026(1)
b, Å	4.234(2)
c, Å	20.105(1)
V	1194.0(4)
T, K	110
Z	4
D_{calc} (g cm^{-3})	4.582
Radiation	monochromated Mo($\lambda(K\alpha_1)$ = 0.7093 Å)
Crystal shape and size	needle 0.262 × 0.070 × 0.070 mm bound by $(1\bar{1}2)$, $(10\bar{1})$, (102), $(\bar{1}1\bar{2})$, $(\bar{1}0\bar{2})$, $(\bar{1}01)$
Linear abs. coefficient (cm^{-1})	204.6
Transmission factors	0.192–0.338
Scan type	θ–2θ
Scan speed	8°/min (θ = 2°–20°) 4°/min (θ = 20°–48°)
Range of θ measurement	2.0°–48.0°
Data collected	2°–20°, $h, \pm k, -l$; 20°–48°, $h, -k, -l$
Total no. of data collected	7613
No. of unique data	6169
No. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2890
No. of variables	73
$R(R_w)$ on F^2	0.121 (0.133)
$R(R_w)$ on F ($F_o^2 > 3\sigma(F_o^2)$)	0.055 (0.055)
Error in observation of unit weight (e^2)	1.06

All calculations were carried out on a Stardent ST2500 computer with methods and programs standard in this laboratory (*18*). The direct methods approach (*19*) revealed the positions of the Cd and Se atoms in space group *Pnma*. The positions of the Na atoms were found in subsequent difference electron density maps. The program STRUCTURE TIDY was used to standardize the crystal structure (*20*). With the com-

TABLE II

POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS (Å^2) FOR $Na_4Cd_3Se_5$

Atom	x	y	z	B_{eq}
Cd(1)	0.206422(40)	1/4	0.464443(28)	0.57(1)
Cd(2)	0.317100(40)	1/4	0.783092(28)	0.57(1)
Cd(3)	0.575899(42)	1/4	0.629725(28)	0.58(1)
Se(1)	0.116203(57)	1/4	0.348263(39)	0.51(1)
Se(2)	0.138601(57)	1/4	0.747395(40)	0.55(1)
Se(3)	0.353071(60)	1/4	0.031188(40)	0.57(1)
Se(4)	0.386146(56)	1/4	0.656755(38)	0.48(1)
Se(5)	0.392812(57)	1/4	0.445339(39)	0.53(1)
Na(1)	0.00098(27)	1/4	0.23326(17)	0.84(7)
Na(2)	0.00809(31)	1/4	0.58250(21)	1.32(9)
Na(3)	0.11215(27)	1/4	0.05172(18)	0.95(7)
Na(4)	0.27593(29)	1/4	0.16594(18)	0.93(7)

position $Na_4Cd_3Se_5$ established, the data were corrected for absorption with the use of the analytical method as employed in the local program AGNOST (*21*). Averaging of symmetry equivalent reflections in Laue symmetry *mmm* afforded an R index for averaging of 3.1% and additional evidence for the centrosymmetric space group Pnma. In the final refinement cycle on F^2 all atoms were refined anisotropically. The final positional and equivalent isotropic thermal parameters are given in Table II. The equivalent thermal parameters are reasonable; there is no indication of nonstoichiometry. The most prominent peak in a final difference electron density map has a height 10% that of an Na atom in this structure. Anisotropic thermal parameters and structure amplitudes are given as supplementary material in Table IV.[1]

[1] See NAPS document No. 04973 for 23 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $10.15. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $5.50 for postage and handling, $1.75 for postage of any microfiche order.

Results and Discussion

In an attempt to synthesize $Na_2Cd(Se_n)_2$, a hypothetical molecular species, we reacted CdSe with an Na_2Se_4 flux at 350°C without addition of water and at 300°C in the presence of a small amount of water. We added water, since the hydrothermal approach used so successfully by Sheldrick and co-workers (*22–27*) has been applied by Kanatzidis and co-workers to the synthesis of some polyselenide clusters, including $[K_2Mo_3Se_{18}]_n$, $K_8Mo_9Se_{40}$ (*28*), and $K_4[Pd_2(Se_4)_2(Se_6)_2]$ (*29*). But we have not synthesized any compound containing an Se–Se bond; rather we have synthesized $Na_4Cd_3Se_5$, apparently a new structural type. However, we used far less water than is typical in the hydrothermal reactions, and the fact that we can make the compound without using H_2O suggests that the added water is a carrier, rather than a solvent. $Na_4Cd_3Se_5$ appears to be a stoichiometric compound of Na(+I), Cd(+II), and Se(−II).

In the Na/Cd/S system the three ternary phases Na_2CdS_2, Na_4CdS_3, and Na_6CdS_4 are known (*30*). None of these have been structurally characterized. Recently $A_2Hg_3Q_4$ and $A_2Hg_6Q_7$ (*15*), A = K, Cs; Q = S, Se have also been reported. But $Na_4Cd_3Se_5$ has

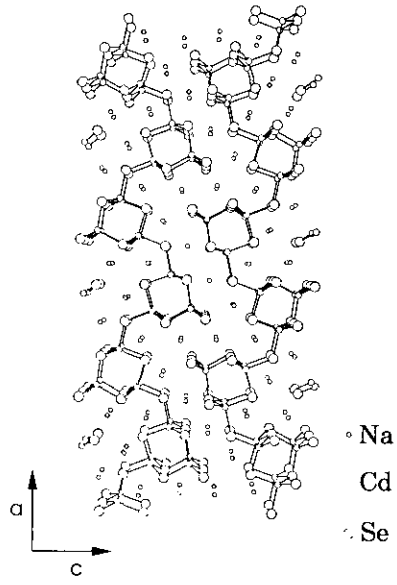

FIG. 1. A view of the $Na_4Cd_3Se_5$ structure down the *b* axis.

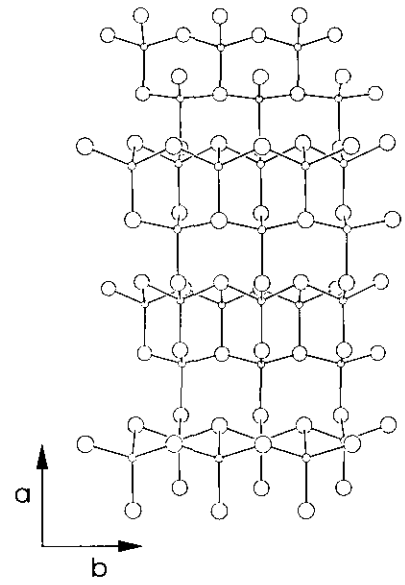

FIG. 2. A sketch of a $^2_\infty[Cd_3Se_5^{4-}]$ layer.

no similarity with these phases. It consists of zigzag layers of $^2_\infty[Cd_3Se_5^{4-}]$ repeating units.The Na cations reside in between the layers. Each Na atom is surrounded in a square pyramidal manner by five Se atoms at distances of 2.82 to 3.11 Å. The $^2_\infty[Cd_3Se_5^{4-}]$ repeating unit comprises three Cd atoms bridged by three Se atoms. This arrangement gives rise to a cyclohexane-like ring; Se atoms form bridges between such rings. The Cd_3Se_3 rings are in the chair configuration. A view down the *b* axis showing the layer stacking is given in Fig. 1. Figure 2, which emphasizes an individual layer, is a view down the *c* axis. Alternatively the layer can be described as trimers of corner-sharing $CdSe_4$ tetrahedra and this is emphasized in the polyhedral representation of Fig. 3. Each of the three crystallographically independent Cd atoms is in a distorted tetrahedron of Se atoms. Among the five independent Se atoms there are two structural types: (i) intraring Se atoms that bridge two Cd atoms and (ii) interring Se atoms that bridge two Cd_3Se_3 rings. The Cd–Se(intraring) distances range between 2.604(1) Å and 2.718(1) Å while the Cd–Se(interring) distances range from 2.637(1) Å to 2.660(1) Å (Table III). For comparison the average Cd–Se distance in $Cd(Se_4)_2^{2-}$ is 2.642(2) Å (*31*).

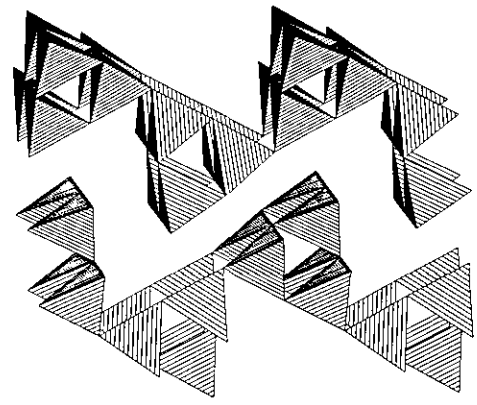

FIG. 3. Polyhedral representation of part of the $Na_4Cd_3Se_5$ structure.

TABLE III

SELECTED DISTANCES (Å) AND ANGLES (°) FOR $Na_4Cd_3Se_5$

Cd(1)–Se(1)	2.657(1)
Cd(1)–Se(3)	2.642(1)
Cd(1)–Se(5)	2.642(1)
Cd(2)–Se(1)	2.660(1)
Cd(2)–Se(2)	2.604(1)
Cd(2)–Se(4)	2.718(1)
Cd(3)–Se(2)	2.622(1)
Cd(3)–Se(4)	2.716(1)
Cd(3)–Se(5)	2.637(1)
Se(1)–Cd(1)–Se(5)	110.09(3)
Se(1)–Cd(1)–Se(3)	107.23(2)
Se(3)–Cd(1)–Se(3)	106.53(3)
Se(3)–Cd(1)–Se(5)	112.73(2)
Se(1)–Cd(2)–Se(2)	118.28(2)
Se(1)–Cd(2)–Se(1)	105.50(3)
Se(1)–Cd(2)–Se(4)	109.57(2)
Se(2)–Cd(2)–Se(4)	94.87(3)
Se(2)–Cd(3)–Se(5)	118.91(2)
Se(2)–Cd(3)–Se(4)	98.05(3)
Se(4)–Cd(3)–Se(5)	106.11(2)
Se(5)–Cd(3)–Se(5)	106.82(3)

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