

Synthesis, Structure, and Characterization of a Cubic Thallium Cluster Phase of the Bergman Type, $\text{Na}_{13}(\text{Cd}_{\sim 0.70}\text{Tl}_{\sim 0.30})_{27}$

Bin Li and John D. Corbett*

Ames Laboratory—DOE¹ and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received January 12, 2004

Samples of $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$ crystallize with a cubic Bergman-type $Im\bar{3}$ structure (formerly called the R-phase) ($Z = 4$, $a \approx 15.92 \text{ \AA}$) and exhibit a small phase width, $0.24 < x < 0.33$. The crystal structure exhibits a Cd/Tl (=M) network of concentric empty M_{12} and Cd_{12} icosahedra and M_{60} buckyball clusters, with the sodium cations in the annuli between clusters. The compound is unusually electron deficient with respect to electron counting rules applied to most Bergman phases with less electropositive cations, and because of the sodium component it is probably better described as an electron-poor Zintl phase. The new compound is metallic according to both EHTB band calculations for the anion and the measured resistivities and magnetic susceptibilities. Site preferences observed for Na, Cd, and Tl among the seven crystallographic sites are consistent with their relative Mulliken electron populations.

Introduction

Exploratory synthesis efforts within the alkali-metal–triell systems, particularly for Ga, In, and Tl, have disclosed a unique field of chemistry that is very rich in its novelty. Gallium forms many anionic network structures but only a couple of phases that contain isolated cluster units.^{2,3} Indium provides a mix of both network and discrete cluster examples,^{4,5} and thallium exhibits predominantly isolated clusters, Tl_4^{8-} ,⁶ Tl_5^{7-} ,⁷ Tl_6^{6-} ,⁸ Tl_9^{9-} ,⁷ Tl_{11}^{7-} ,^{9,10} and Tl_{13}^{10-} ,¹¹ plus a few novel networks.^{5,12} Introduction of late transition or earlier post-transition elements into these binary triell systems has led to many novel and unanticipated chemistries

and structures, principally as discrete heteroatomic clusters that often contain only modest amounts of the third element. Examples include alkali metal salts of centered clusters $\text{Tl}_{10}\text{Zn}^{8-}$,¹³ $\text{In}_{10}\text{M}^{10-}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$),¹⁴ $\text{Tl}_{12}\text{M}^{12-}$ ($\text{M} = \text{Mg}, \text{Zn}, \text{Cd}, \text{Hg}$),¹⁵ and $\text{Tl}_9\text{Au}_2^{9-}$ ¹⁶ and $\text{Tl}_8\text{Cd}_3^{10-}$,¹⁷ the substituted versions of the pentacapped trigonal prismatic Tl_{11}^{7-} . The heteroelement of interest here, Cd, is also known to bond in condensed cluster versions, the novel $[\text{Cd}_2\text{Tl}_{11}^{5-}]$ chains in $\text{Cs}_5\text{Cd}_2\text{Tl}_{11}$,¹² the tubular $\text{Cd}_{12}\text{In}_6$ in $\text{Na}_8\text{K}_{23}\text{Cd}_{12}\text{In}_{48}$,¹⁸ $\text{Cd}_9\text{Tl}_{10}^{7-}$ in the layered $\text{K}_{14}\text{Cd}_9\text{Tl}_{21}$,¹⁹ and the related Bergman phase $\text{Na}_{13}\text{Cd}_{20}\text{Pb}_7$.²⁰

Ongoing research on derivatization of triell clusters by late transition and early post-transition elements has now led to the discovery of the first ternary Na–Cd–Tl compound that turns out to be a Bergman-type phase and the first thallium example, $\text{Na}_{13}\text{Cd}_{\sim 19.2}\text{Tl}_{7.8}$ or $\text{Na}_{13}\text{M}_{27}$ ($\text{M} = \text{Cd}/\text{Tl}$). The structure type derives from the long-known Mg–Zn–Al structure first reported by Bergman, Waugh, and Pauling^{21,22}

* Author to whom correspondence should be addressed. E-mail: jcorbett@iastate.edu.

- (1) This research was supported by the Office of the Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy (DOE). The Ames Laboratory is operated for DOE by Iowa State University under Contract No. W-7405-Eng-82.
- (2) Belin, C. H. E.; Tillard-Charbonnel, M. *Prog. Solid State Chem.* **1993**, *22*, 59.
- (3) Henning, R. W.; Corbett, J. D. *Inorg. Chem.* **1997**, *36*, 6045.
- (4) Corbett, J. D. In *Chemistry, Structure and Bonding of Zintl Phases and Ions*; Kauzlarich, S., Ed.; VCH Publishers: New York, 1996; Chapter 3.
- (5) Corbett, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 670.
- (6) Smith, J. F.; Hansen, D. A. *Acta Crystallogr.* **1967**, *22*, 836.
- (7) Dong, Z.-C.; Corbett, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 3429.
- (8) Dong, Z.-C.; Corbett, J. D. *Inorg. Chem.* **1996**, *35*, 2301.
- (9) Dong, Z.-C.; Corbett, J. D. *J. Cluster Sci.* **1995**, *6*, 187.
- (10) Dong, Z.-C.; Corbett, J. D. *Inorg. Chem.* **1996**, *35*, 1444.
- (11) Dong, Z.-C.; Corbett, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6447.
- (12) Kaskel, S.; Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 3086.

- (13) Dong, Z.-C.; Henning, R. W.; Corbett, J. D. *Inorg. Chem.* **1997**, *36*, 3559.
- (14) Sevov, S. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 9089.
- (15) Dong, Z.-C.; Corbett, J. D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1006.
- (16) Dong, Z.-C.; Corbett, J. D. *Inorg. Chem.* **1996**, *35*, 2162.
- (17) Huang, D. P.; Corbett, J. D. *Inorg. Chem.* **1999**, *38*, 316.
- (18) Flot, D. M.; Tillard-Charbonnel, M. M.; Belin, C. H. E. *J. Am. Chem. Soc.* **1996**, *118*, 5229.
- (19) Tillard-Charbonnel, M.; Chahine, A.; Belin, C.; Rousseau, R.; Canadell, E. *Chem.—Eur. J.* **1997**, *3*, 799.
- (20) Todorov, E.; Sevov, S. C. *Inorg. Chem.* **1997**, *36*, 4298.
- (21) Bergman, G.; Waugh, J. L. T.; Pauling, L. *Nature* **1952**, *169*, 1057.

A Cubic Thallium Cluster Phase of the Bergman Type

and recently studied in detail by Lee and Miller^{23,24} and by Miller et al.²⁵ (We suggest that the R-phase designation often applied to this series be dropped as it carries no information, coming from an alphabetical assignment in a series of unknowns.²⁶) All structures containing gallium or indium icosahedra are uncentered and exo-bonded^{2,5,27,28} whereas thallium icosahedra have to date always been isolated and centered, as by Na,²⁹ Tl,¹¹ or M (M = Mg, Zn, Cd, Hg) atoms.^{15,30} However, in this structure the innermost icosahedron with 12 exo-bonds is empty and geometrically nearly perfect (point group T_h). As with earlier members of the Bergman family, the present compound is useful for detailed investigations of the interrelationships among composition, structure (elemental site preferences), bonding, and properties. Moreover, the electropositive sodium cations in a more polar compound raise questions about its electronic classification with more traditional Bergman phases.²⁵

Experimental Section

Syntheses. All materials were handled in N₂- or He-filled gloveboxes that had moisture levels below 0.1 ppm (volume). The surfaces of the sodium chunks (99.9%, Alfa-Aesar) and cadmium tear drops (99.9%, Ames Lab) were first scraped to remove oxide films and then combined in different ratios with Tl powder (99.999%, Alfa-Aesar). These were enclosed in welded niobium tubes that were in turn sealed in evacuated fused silica jackets by methods and techniques described previously,^{7,14,28} heated at 500 °C for 12 h, and then cooled at 3 °C/h to room temperature. (An additional annealing at 300 °C gave visually identical powder patterns.) All products were silvery and brittle and very sensitive to moisture and air. Reaction products were characterized by Guinier X-ray powder patterns with the aid of an Enraf-Nonius Guinier camera, Cu K α radiation ($\lambda = 1.540562 \text{ \AA}$), and NIST silicon as an internal standard. A single crystal of the title compound was first obtained from a mixture with Na: Cd: Tl = 13:13:14. Most examples of this structure type show mixed occupancies of lattice sites, such as for Mg₃₂(Zn,Al)₄₉,^{23,24} Li₅₂Cu₅₇Si₅₁,³¹ and Na₁₃Cd₂₀-Pb₇.²⁰ As expected, a phase width was also found for the Na₁₃(Cd,Tl)₂₇ compound, as first shown by shifts in the positions of the powder pattern lines and in the cubic cell parameters refined for samples loaded with different proportions. These data are summarized in Table 1. The same structure does not form following individual substitutions of K or Zn or In for Na or Cd or Tl, respectively.

Single-Crystal Structure Determinations. Crystal qualities were first checked by Laue photographs for their singularity. Diffraction data for detailed structural analyses were collected at 293 K with the aid of a Bruker SMART APEX CCD instrument and mono-

Table 1. Summary of Reaction Compositions and Phases Identified by Guinier X-ray Powder Diffraction for Na₁₃(Cd_{1-x}Tl_x)₂₇ Samples Equilibrated at 500 °C

no.	reaction composition	x	phases	a^a
1	Na ₁₃ Cd ₂₇	0	NaCd ₂ ~95%	
2	Na ₁₃ Cd _{23.5} Tl _{3.5}	0.130	Na ₁₃ M ₂₇ ~10% + Na(Cd/Tl) ₂ ~90%	
3	Na ₁₃ Cd ₂₂ Tl ₅	0.185	Na ₁₃ M ₂₇ ~85% + Cd	15.876(4)
4	Na ₁₃ Cd _{20.4} Tl _{6.6}	0.244	Na ₁₃ M ₂₇ >95%	15.875(4)
5	Na ₁₃ Cd _{19.2} Tl _{7.8}	0.288	Na ₁₃ M ₂₇ >95%	15.912(3)
6	Na ₁₃ Cd _{18.1} Tl _{8.9}	0.330	Na ₁₃ M ₂₇ >95%	15.984(5)
7	Na ₁₃ Cd ₁₃ Tl ₁₄	0.519	Na ₁₃ M ₂₇ ~80% + Tl	15.985(4)
8	Na ₁₃ Cd _{10.6} Tl _{16.4}	0.607	Na ₁₃ M ₂₇ ~80% + unknown	15.983(5)
9	Na ₁₃ Cd ₈ Tl ₁₉	0.704	Na ₁₃ M ₂₇ ~80% + Tl	15.989(3)
10	Na ₁₃ Tl ₂₇	1	NaTl + Tl	

^a For Na₁₃M₂₇ phase; refined from Guinier powder data with Si as internal standard, $\lambda = 1.540562 \text{ \AA}$, 23 °C.

Table 2. Some Crystallographic Data for the Three Na₁₃(Cd_{1-x}Tl_x)₂₇ Samples

	1	2	3
composition			
reacted	Na ₁₃ Cd ₂₂ Tl ₅	Na ₁₃ Cd _{19.4} Tl _{7.6}	Na ₁₃ Cd ₁₃ Tl ₁₄
refined	Na ₁₃ Cd _{20.4(1)} Tl _{6.6(1)} $x = 0.244(4)$	Na ₁₃ Cd _{19.2(1)} Tl _{7.8(1)} $x = 0.289(4)$	Na ₁₃ Cd _{18.1(1)} Tl _{8.9(1)} $x = 0.330(4)$
fw	3939.98	4046.67	4155.42
space group, Z		$Im\bar{3}$ (No. 204), 4	
a (Å) ^a	15.874(2)	15.9121(5)	15.987(2)
V (Å ³)	4000.0(8)	4028.9(2)	4086.2(10)
d_{calc} (g/cm ³)	6.543	6.672	6.755
abs coeff μ (mm ⁻¹)	37.158	40.913	44.382
$R1/wR2$	0.0298/0.0625	0.0285/0.0663	0.0328/0.0592
$[I > 2\sigma(I)]$			
largest peak and hole (e/Å ³)	1.45, -4.32	2.01, -1.21	1.60, -2.31

^a Diffractometer refinement.

chromatic Mo K α radiation. Data sets from at least two separate crystals were collected from each of three samples refined to check for variations of the refined composition. Data were collected over one hemisphere via four sets of frames with an exposure time of 10 s per frame. The unit cell parameters were determined from data for 999 indexed reflections. The reflection intensities were integrated with the SAINT subprogram in the SMART software package.³² The data were corrected for Lorentz and polarization effects, and for absorption empirically with the aid of the program SADABS.³³

The XPREP subprogram in the SHELXTL 6.1 software package³⁴ was used for the space group determination. Systematic absences and the intensity statistics clearly indicated a centrosymmetric, body-centered cubic crystal system in Laue group $m\bar{3}$, and the space group $Im\bar{3}$ was chosen for subsequent structural analysis. Table 2 summarizes the crystallographic data from three samples, crystals from the two extremes in Cd:Tl ratios (from samples 3 and 7 in Table 1) plus one from an intermediate composition (no. 5). The solution process for sample 3 is used as example. Direct methods provided four positions at distance suitable for Cd/Tl, and three of them were assigned to Tl and the other to Cd. A few least-squares cycles followed by a difference Fourier map revealed three less strongly diffracting atoms with distances appropriate for three sodium atoms, and they were so assigned.

(32) SMART; Bruker AXS, Inc.; Madison, WI, 1996.

(33) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(34) SHELXTL; Bruker AXS, Inc.; Madison, WI, 2000.

(22) Bergman, G.; Waugh, J. L. T.; Pauling, L. *Acta Crystallogr.* **1957**, *10*, 254.

(23) Lee, C.-S.; Miller, G. J. *J. Am. Chem. Soc.* **2000**, *122*, 4937.

(24) Lee, C.-S.; Miller, G. *Inorg. Chem.* **2001**, *40*, 338.

(25) Miller, G. J.; Lee, C.-S.; Choe, W. In *Inorganic Chemistry Highlights*; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley-VCH: New York, 2002; Chapter 2.

(26) Handy, H. K.; Silcock, J. M. *J. Inst. Met.* **1956**, *84*, 423.

(27) Li, B.; Corbett, J. D. *Inorg. Chem.* **2002**, *41*, 3944.

(28) Li, B.; Corbett, J. D. *Inorg. Chem.* **2003**, *42*, 8768.

(29) Dong, Z.-C.; Corbett, J. D. *Inorg. Chem.* **1995**, *34*, 5709.

(30) Tillard-Charbonnel, M.; Belin, C.; Chouaibi, N.; Manteghetti, A.; Flot, D. *Inorg. Chem.* **1996**, *35*, 2583.

(31) Doering, W.; Seelentag, W.; Buchholz, W.; Schuster, H. U. *Z. Naturforsch.* **1979**, *34B*, 1715.

Table 3. Atomic Positional Coordinates, Isotropic Displacement Parameters, and Site Occupancies for $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$ Samples

atom	site	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	site occ ^a
$\text{Na}_{13}\text{Cd}_{20.4(1)}\text{Tl}_{6.6(1)}$						
Cd1	24g	0	0.3142(1)	0.1770(1)	20(1)	1.00
M2	24g	0	0.1554(1)	0.0958(1)	15(1)	0.626/0.374(8)
M3	48g	0.0951(1)	0.3109(1)	0.3412(1)	18(1)	0.781/0.219(7)
M4	12e	0.0921(1)	0	0.5	25(1)	0.43/0.57(1)
Na1	12e	0.3000(4)	0	0.5	20(1)	1.00
Na2	16f	0.1873(2)	0.1873(2)	0.1873(2)	26(1)	1.00
Na3	24g	0	0.1166(3)	0.3043(3)	19(1)	1.00
$\text{Na}_{13}\text{Cd}_{19.2(1)}\text{Tl}_{7.8(1)}$						
Cd1	24g	0	0.3141(1)	0.1764(1)	19(1)	1.00
M2	24g	0	0.1555(1)	0.0960(1)	13(1)	0.578/0.422(9)
M3	48h	0.0951(1)	0.3106(1)	0.3411(1)	16(1)	0.723/0.277(7)
M4	12e	0.0925(1)	0	0.5	22(1)	0.37/0.63(1)
Na1	12e	0.2997(4)	0	0.5	17(1)	1.00
Na2	16f	0.1877(2)	0.1877(2)	0.1877(2)	24(1)	1.00
Na3	24g	0	0.1165(3)	0.3045(3)	18(1)	1.00
$\text{Na}_{13}\text{Cd}_{18.1(1)}\text{Tl}_{8.9(1)}$						
Cd1	24g	0	0.3136(1)	0.1754(1)	24(1)	1.00
M2	24g	0	0.1555(1)	0.0960(1)	17(1)	0.537/0.463(8)
M3	48g	0.0949(1)	0.3098(1)	0.3411(1)	24(1)	0.664/0.336(7)
M4	12e	0.0932(1)	0	0.5	25(1)	0.29/0.71(1)
Na1	12e	0.3004(4)	0	0.5	9(2)	1.00
Na2	16f	0.1870(3)	0.1870(3)	0.1870(3)	30(2)	1.00
Na3	24g	0	0.1164(3)	0.3046(3)	18(1)	1.00

^a The Cd/Tl proportions.

There are seven distinct crystallographic sites in this structure type, three of which are typically occupied by electropositive metals like Na and four others, by more electronegative metals such as Cd/Tl. But it became clear after a few more cycles that thallium alone was too heavy for the three positions M2–M4. At this point R1 and the highest difference peak were 8.24% and 12.22 $e/\text{\AA}^3$, respectively. Allowing cadmium to admix at three of the original thallium positions while varying the isotropic displacement parameters gave significant improvements in R1 (5.52%) and in the highest difference peak (4.79 $e/\text{\AA}^3$, close to M3) before the final refinements of positional and anisotropic displacement parameters for all atoms with fixed occupancies (R1 = 0.0328, wR2 = 0.0592). As is customary, the M1 position was found to be occupied only by cadmium within 1σ (0.98(2)). These site assignments are consistent with the earlier theoretical studies on this structure type^{23,24} and our calculational results (below). Single phase products according to the Guinier patterns were subsequently obtained from reactions loaded with the compositions refined from X-ray data (no. 4 and 6 in Table 1), indicating that the terminal compositions were close to the refined limits within the detection limit of impurity phases ($\leq 5\%$). Additional data collections and refinements for two crystals from these last reactions both gave the same fractional compositions for Tl and Cd within 0.1%.

Table 3 gives the atomic positional, occupancy, and isotropic-equivalent displacement parameters for crystals from samples 3, 5, and 7, and Table 4 contains the important interatom distances for the three compositions. More detailed crystallographic and refinement data and the anisotropic displacement parameters are available in the Supporting Information.

Electrical Resistivity and Magnetic Susceptibility Measurements. Electrical resistivities were measured by the electrodeless “Q” method with the aid of a Hewlett-Packard 4342A Q meter.³⁵ The method is particularly suitable for measurements on highly air sensitive samples. For this purpose, 92.4 mg of a powdered sample of $\text{Na}_{13}\text{Cd}_{18.1(1)}\text{Tl}_{8.9(1)}$ with grain diameters between 150 and

Table 4. Selected In Interatom Distances (\AA) for (1) $\text{Na}_{13}\text{Cd}_{20.4(1)}\text{Tl}_{6.6(1)}$, (2) $\text{Na}_{13}\text{Cd}_{19.2(1)}\text{Tl}_{7.8(1)}$, and (3) $\text{Na}_{13}\text{Cd}_{18.1(1)}\text{Tl}_{8.9(1)}$

	1	2	3
Cd1–M2	2.831(1)	2.8292(9)	2.828(1)
Cd1–M3	2.9098(7)	2.9187(6)	2.9402(9)
Cd1–M3	3.0118(8)	3.0274(8)	3.054(1)
Cd1–M4	3.244(1)	3.2461(9)	3.256(1)
Cd1–Na3	3.368(2)	3.367(2)	3.368(3)
M2–M2	3.043(1)	3.055(1)	3.070(2)
M2–M2	3.0485(7)	3.0582(6)	3.0729(9)
M2–Na2	3.347(5)	3.364(5)	3.362(6)
M2–Na3	3.365(3)	3.374(3)	3.390(5)
M3–M3	3.0125(6)	3.0181(4)	3.0312(7)
M3–M3	3.0205(9)	3.0274(8)	3.035(1)
M3–M4	3.3180(7)	3.3256(5)	3.3403(9)
M3–Na1	3.423(1)	3.429(3)	3.443(3)
M3–Na1	3.426(3)	3.437(1)	3.460(1)
M3–Na2	3.458(3)	3.457(3)	3.478(4)
M3–Na3	3.465(2)	3.477(2)	3.494(5)
M4–M4	2.923(2)	2.943(1)	2.981(2)
M4–Na1	3.300(6)	3.297(6)	3.312(7)
Na1–Na3	3.377(5)	3.386(5)	3.396(6)
Na2–Na2	3.45(1)	3.43(1)	3.48(4)

250 μm was dispersed with chromatographic alumina and sealed under He in a Pyrex tube. Measurements were made at 34 MHz over the range 93–268 K. The measured resistivities increase linearly from 26.6 to 36.8 $\mu\Omega\cdot\text{cm}$ over the range (0.2% K^{-1}), which change is taken as the defining characteristic of a metal. The extrapolated ρ_{298} value is about 37.5 $\mu\Omega\cdot\text{cm}$. Magnetic susceptibility data were obtained from a 72.1 mg ground sample of the same sample sealed under He. The magnetization data measured over the range 6–360 K on a Quantum Design MPMS SQUID magnetometer gave almost temperature independent paramagnetic susceptibilities, $(2.7\text{--}2.8) \times 10^{-4}$ emu/mol over the range after container and ion core corrections. These are typical for a Pauli-like behavior, in agreement with the expected metallic behavior (below) and the measured resistivities. Graphical data from both measurements are available in the Supporting Information.

Electronic Structure Calculations. Calculations according to the well-established extended Hückel tight-binding band methods were performed with the aid of the CAESAR program package developed by Whangbo and co-workers.³⁶ Calculations were performed on the anionic framework by treating the sodium atoms only as electron donors. Cd atomic orbital parameters were used for the Cd-only site, and Tl atomic orbital parameters were used for the three mixed M sites (M2–M4). Calculations performed with Cd-only or different combinations of Cd and Tl parameters for the latter gave qualitatively the same results. Atomic orbital parameters used were as follows (H_{ii} = orbital energy (eV), ζ = Slater exponent): Tl 6s, –11.6, 2.52; 6p, –5.8, 1.77;³⁷ Cd 5s, –12.50, 2.30; 5p, –6.60, 2.1.³⁸ To elucidate the site potentials for the different crystallographic positions, extended Hückel calculations were also performed on the whole structure in which all atom sites were necessarily given the same Cd parameters. Since this calculation was carried out with the same atomic orbital parameters at each site in the structure, the resulting Mulliken populations reflect the atomic coordination environment and the relative strengths of the various interatomic orbital interactions. This method has proven to be very useful in the characterization of site preferences between different elements in such intermetallic systems.^{23,24}

(36) Ren, J.; Liang, W.; Whangbo, M.-H. *CAESAR for Windows*; Prime-Color Software, Inc.: North Carolina State University: Raleigh, NC, 1998.

(37) Janiak, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 5924.

(38) Mercier, H.; Mathey, Y.; Canadell, E. *Inorg. Chem.* **1987**, *26*, 963.

(35) Zhao, J. T.; Corbett, J. D. *Inorg. Chem.* **1995**, *34*, 378.

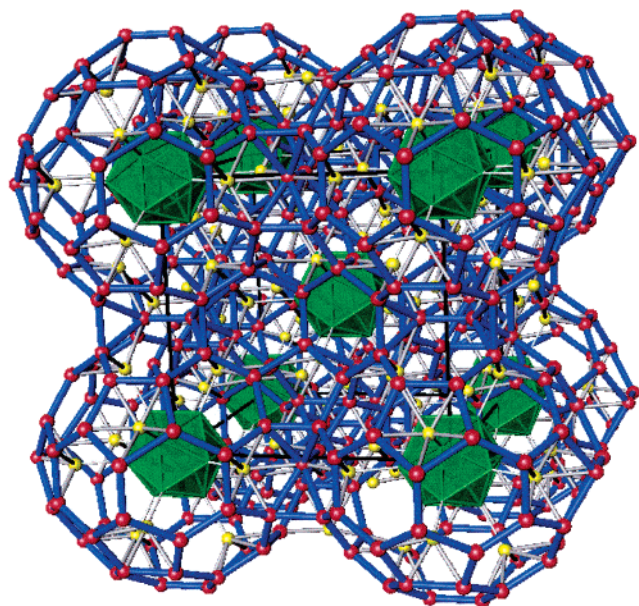


Figure 1. $\sim[100]$ view of the bcc crystal structure of $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$. The icosahedra formed by M2 (mixed Cd/Tl) are shaded green. M3, M4, and Cd1 are red, red, and yellow, respectively. Na atoms are omitted for clarity.

Results and Discussion

Structure Description. A general view of a little more than the bcc unit cell in Figure 1 outlines the 3D network formed, in which all M–M separations ($M = \text{Cd/Tl}$) less than 3.5 Å are outlined. The most tractable and useful description of the structure is in terms of multiply endohedral (concentric) shells of atoms around each lattice point (0, 0, 0; $1/2, 1/2, 1/2$), Figure 2. The innermost shell (green) is the empty icosahedron of M2 from Figure 1 with 12 exo bonds. The point group of this icosahedron is T_h , the highest symmetry possible for an icosahedron in a normal crystalline structure. Twenty sodium atoms (Na2, Na3) surmount the triangular faces of the central icosahedron to form shell two, the dual pentagonal dodecahedron. In the third shell (sometimes considered part of the second shell), twelve Cd1 atoms in a larger icosahedral arrangement cap the pentagonal faces of the sodium dodecahedron and are also radially bonded to M2 atoms in shell 1 with the shortest M–M distances observed, 2.831 Å. The latter is consistent with the general observation that intercluster bonds tend to be nearer conventional 2-center–2-electron types in character, in contrast to the longer delocalized and electron-deficient bonding within clusters. The Cd1 atoms within shell 3, which are not interbonded, also cap pentagons in the fourth shell. The last consist of 48 M3 atoms and 12 M4 atoms in the form of a buckminsterfullerene or “buckyball” cluster (a truncated icosahedron). Every atom in this shell is also shared with those in a like shell of an adjacent unit centered on the lattice points; the M3 hexagons are shared along the cell body diagonals, and pairs of M4 atoms lie in the cell faces. The remaining Na1 atoms in shell 5 cap the pentagonal faces of the truncated icosahedron, shell 4, and thereby occur in squares on the faces of the unit cell. All the anion sites can also be described in terms of large interpenetrating M_{84}

clusters called Samson polyhedra although not in the sense of building blocks. The general formula starting at the origin can be written as $[(\text{M}2)_{12}(\text{Na}2)_8(\text{Na}3)_{12}(\text{Cd}1)_{12}] - [(\text{M}3)_{48/2}(\text{M}4)_{12/2}](\text{Na}1)_{24/4} \equiv \text{Na}_{26}\text{M}_{54} = 2\text{Na}_{13}\text{M}_{27}$ or, better, $\text{Na}_{13}\text{M}_{21}\text{Cd}_6$.

Variable Stoichiometry and the Phase Width. The present compound evidently has all lattice sites fully occupied; instead the proportions of Cd and Tl on three sites vary somewhat. The overall composition is $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$, which we describe as of variable stoichiometry, not non-stoichiometric, which implies vacant sites or interstitial additions. Even mixing of cadmium and thallium on the same positions may seem unreasonable a priori, although the two elements are in neighboring groups and the binary CdTl_{27} also has mixed a Cd–Tl site over a narrow range on the Cd-rich side (0–3.6 atom % Cd).³⁹ The mixing of cadmium and thallium occurs in other intermetallic systems as well, such as $\text{CaCd}_{1-x}\text{Tl}_x$ ($0 \leq x \leq 1$)⁴⁰ and $\text{LiCd}_{1-x}\text{Tl}_x$ ($0 \leq x \leq 1$),⁴¹ the latter of which also shows a phase change that is dependent on x . The variable stoichiometry of the present phase is in fact common with most Bergman phases especially among three or four of the four negatively polarized sites, such as in $\text{Mg}_{1.63}(\text{Zn},\text{Al})_{3.37}$,²³ $\text{Li}_{1.63}(\text{Zn},\text{Al})_{3.37}$,²⁴ $\text{Li}_{52}\text{Cu}_{57}\text{Si}_{51}$,³¹ Li_3CuAl_5 ,⁴² $\text{Mg}_{36}\text{Na}_{16}\text{Zn}_{68}\text{Al}_{40}$,⁴³ and $\text{Na}_{13}\text{Cd}_{20}\text{Pb}_7$.²⁰

Generally nonparallel variabilities in the three distributions should accompany a variable stoichiometry, and so a series of reactions, $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$ ($0 \leq x \leq 1$), were run as listed in Table 1. According to X-ray powder patterns, some $\text{Na}_{13}\text{M}_{27}$ phase was observed over $0.704 \geq x \geq 0.185$, and substantially single-phase products were identified for the refined compositions at the endpoints of $0.330 \geq x \geq 0.244$. Not surprisingly, the end composition $\text{Na}_{13}\text{Cd}_{27}$ results instead in almost pure NaCd_2 , a much more complicated structure with ca. 1192 atoms in the unit cell.^{44,45} Addition of a little thallium as $\text{Na}_{13}\text{Cd}_{23.5}\text{Tl}_{3.5}$ gave mainly the solid solution $\text{Na}(\text{Cd/Tl})_2$ isostructural with NaCd_2 with a small shift of the cell size, and the appropriate although rough single-crystal structural solution was so refined. At the other extreme, only NaTl and elemental Tl are observed if no Cd is loaded. In fact, this Bergman structure type has to date been found only in ternary or higher systems. The Cd occupancies on the three sites (M2–M4) vary directly with the value of $(1-x)$ in $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$, but not in exact parallel as shown in Figure 3, and the a dimension and the cell volume V show the opposite trend, increasing with an increase in x (Tl). The variation in cell volume over the range is $\sim 2.15\%$, comparable with $\sim 2.03\%$ variation in $\text{Li}_{1.63}(\text{Zn}_x\text{Al}_{1-x})_{3.37}$ ($0.24 \leq x \leq \sim 0.53$).²⁴ Variations in atom

(39) Suganuma, R. *J. Phys. Soc. Jpn.* **1960**, *15*, 1395.

(40) Marcoll, D. D.; Schmidt, P. C.; Weiss, A. *Z. Naturforsch., A* **1974**, *29*, 473.

(41) Baden, W.; Schmidt, P. C.; Weiss, A. *Phys. Status Solidi A* **1979**, *51*, 183.

(42) Cherkashin, E. E.; Kripyakevich, P. I.; Oleksiv, G. I. *Sov. Phys.—Crystallogr.* **1963**, *8*, 681.

(43) Elding-Ponten, M.; Lidin, S. *J. Solid State Chem.* **1995**, *115*, 270.

(44) Yang, Q. B.; Andersson, S.; Stenberg, L. *Acta Crystallogr.* **1987**, *B43*, 14.

(45) Bergman, G. *Acta Crystallogr.* **1996**, *B52*, 54.

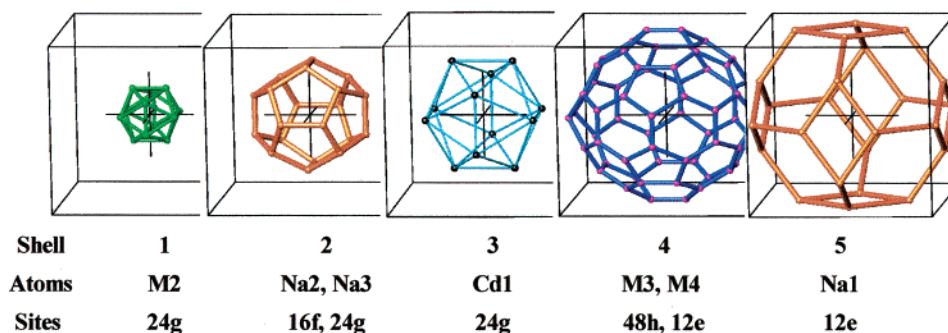


Figure 2. Illustration of the $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$ structure in terms of concentric shells of atoms around each lattice point. Lines in shells 2, 3, 5 outline polyhedra, not bonds.

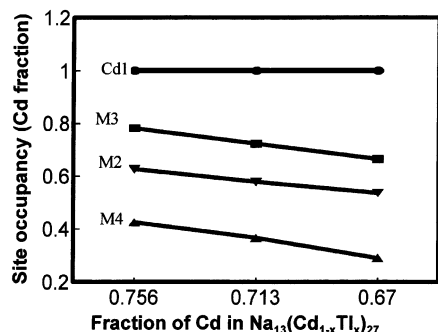


Figure 3. Relationship between Cd site occupancies for Cd1 and M2–M4 and the fraction of Cd (1–x) in $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$ according to the X-ray diffraction results.

distributions on each site have been shown to be directly related to the bonding characteristics of each.^{24,25}

Electronic Classifications and Band Calculations. Simply counting the electrons needed for bonding in the different segments of many structures of valence (Zintl) phases has often proven to afford a very useful, even elegant, method for rationalizing the bonding. But in the present and related cases, it is difficult to do so because some polyhedra are heavily fused to others. However, two similar electron counting schemes have been proposed according to the sharing of hexagonal faces and edges between the Samson 84-atom polyhedra ($\text{M}_{12}@\text{M}_{72}$, Figure 1). These give vec values (valence electron concentrations/atom, including cations) of 2.125 (170/80) or 2.20 (176/80) according to the models by King⁴⁶ or Miller et al.,²⁵ respectively, or 340 or 352 electrons per cell. The isotypic Li–Mg–Zn–Al phases occur over a vec range of 2.00 to 2.28 with only $\text{Li}_{1.00}\text{Mg}_{0.60}\text{Zn}_{3.09}\text{Al}_{0.31}$ and $\text{Li}_{1.0}\text{Mg}_{0.63}\text{Zn}_{2.4}\text{Al}_{0.98}$ giving lower vec values, 1.86²⁴ and 1.87. Although many more Hume–Rothery type intermetallic “electron” compounds occur in the neighborhood of vec = 2.20, attempts to synthesize phases of last two with higher values led to vacancies on some lattice sites.²⁵

The present $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$ compositions, though isostructural, fall well short of the ideal range, the vec values of 1.84–1.90 meaning they are short nearly 50 electrons per cell, nominally too Cd rich. We note that several similar isotypic Na–Au–Tl phases (Tl = Si–Sn), e.g., $\text{Na}_{13}\text{Au}_{20}\text{Ge}_{7+}$, have been reported that have even lower vec

values, 1.54–1.65, although these also have some extra gold centering the inner icosahedron.³¹ These differences probably arise from the presence of sodium in the cation site rather than the less electropositive Li, Mg, etc. The latter are thought to participate in delocalized bonding within the networks in such intermetallics just as they seem to do in quasicrystals and their approximants.⁴⁷ This feature and the absence of a near local minimum in the DOS probably preclude quasicrystal formation in this system. It would require about 46 more electrons per cell to reach the first DOS minimum at –6.4 eV (below).

The other bonding extreme for the present phase would be as a Zintl phase⁴ in which the electropositive elements are considered to donate their electrons to the anion lattice, which then follows its own valence rules, more or less. The traditional area here lies with compounds in which the atoms follow (achieve) octet rules, with vec values of ≥ 4.0 .²⁵ But there are many intermediate phases, with triels especially, that achieve local closed shell configurations with normal electron-deficient clusters (as expressed by Wade’s rules etc.) or condensed versions of the same in nets. Numerous examples are found with lower vec values, ranging down to ~ 3.2 in nets.⁵ The present Bergman phase $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$ has vec values for the anion structure that are even lower, only 2.72–2.81, which leave it in an intermediate and far less interpretable region. A few phases containing transition metals *Tn* such as AeTnTl_2 for Ae = Sr, Ba, Tn = Pd, Pt, with a vec (anion) value of 2.67⁴⁸ and the perhaps analogous $\text{Na}_{13}\text{Au}_{\sim 20}\text{Tl}_{\sim 7}$ ³¹ Bergman structures, for which vec (anion) is 2.26–2.43, also appear in this low region.

The character of EHTB results sometimes affords some clear distinctions between intermetallic types. Figure 4 illustrates the DOS and COOP curves for the anion portion of the present $\text{Na}_{13}\text{M}_{27}$ structure utilizing Tl parameters for the mixed sites, the latter covering all M–M bonds with $d < 3.5$ Å. Two Fermi energies marked by dashed lines represent the observed range for $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$. As expected, there is no band gap in the Fermi level range, but there is a DOS minimum at high energies that corresponds to a vec = 2.16. The M2 (red) and M3 (green) sites make particular contributions to DOS around E_F . The PDOS curves for interactions of the central Cd1 with M2–M4 show that

(47) Tsai, A. P. In *Physical Properties of Quasicrystals*; Stadnik, Z. M., Ed.; Springer: New York, 1999; p 5.

(48) Liu, S.; Corbett, J. D. *Inorg. Chem.* **2003**, *42*, 4898.

(46) King, R. B. *Inorg. Chim. Acta* **1991**, *181*, 217.

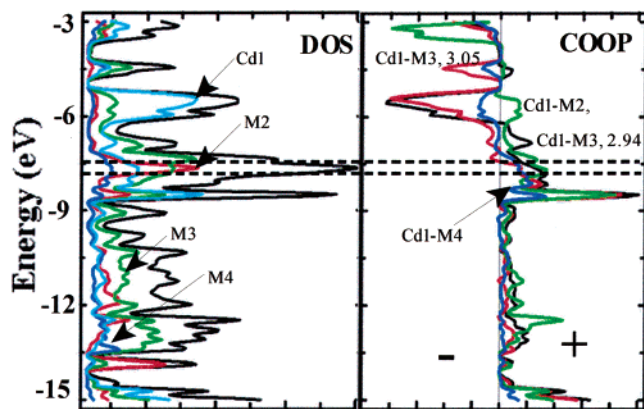


Figure 4. (a, left) Densities of states for $[(\text{Cd}_{1-x}\text{Tl}_x)_{27}]^{13-}$. Cd1, M2, M3, and M4 are light blue, red, green, and dark blue, respectively, and the total DOS is black. (b, right) COOP curves for the four different bonds around Cd1. Cd1–M2 is green, Cd1–M3, 2.94 Å, is black, Cd1–M3, 3.05 Å, is red, and Cd1–M4 is blue. The two dotted lines denote the Fermi energies corresponding to the observed stoichiometry range in $\text{Na}_{13}(\text{Cd}_{1-x}\text{Tl}_x)_{27}$.

the contributions of these are all positive and vary somewhat differently across the range. The chemical proportions at the three M sites would be expected to also vary as E_F varies, as they do, Figure 3. This differs a little from the behavior of the Li–Mg–Zn–Al system, in which only two sites vary much in their contribution across the vec range even though all four have mixed atom constitutions.²⁴ Only Cd1–M3 is optimized at the upper stoichiometry limit, indicating that bond energies must be only part of the stability factors. In contrast, in the quaternary Li–Mg–Zn–Al Bergman phase, the model $[\text{Al}_{26}][\text{Al}_{54}]$ calculations showed that the relative contributions of orbitals from the four anion sites and the three cation sites are in each group very similar over the vec range in the DOS without much discrimination and that the vec range actually is defined more by the A–A and A–M interactions.²⁶ Further analysis of interatomic potentials for the title compound may be useful to elucidate the driving forces in forming the present structure.

As before,²⁵ the site preferences for different elements among the crystallographic sites are readily compared according to their relative site Mulliken electron populations when Cd is placed at all Na and M sites as a probe. The relative site populations equal the difference between the average value for all sites and that for a given position. As seen in Figure 5, these show that all Na sites are reasonably

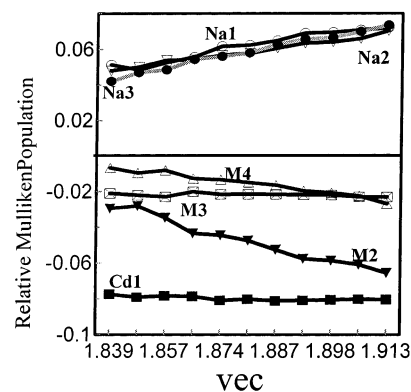


Figure 5. Relative Mulliken atomic populations of Na1–Na3, Cd1, and M2–M4 sites as a function of the vec range according to the calculational model $[\text{Cd}_{13}][\text{Cd}_{27}]$. Na1: open circles. Na2: open triangles. Na3: solid circles.

positively polarized and all M and Cd sites are negatively polarized over the vec range. In parallel with the relative Mulliken electronegativities of those atoms (Cd, 4.33; Tl, 3.2⁴⁹), the most negatively polarized M1 site is clearly favorable for cadmium, and the least amount of Cd goes in the least negative M4 site. The distributions over lattice sites in the isotopic $(\text{Li},\text{Mg})_{1.63}(\text{Zn},\text{Al})_{3.37}$ and $\text{Li}_{1.63}(\text{Zn},\text{Al})_{3.37}$ systems are fairly parallel (Figure 4²⁴) except for a reversal of the M2 and M1 (Cd) sites, but at a notably larger e/a value: ~ 2.3 . The least electronegative Al (3.23) goes into the least negative M4 site, and the most electronegative Zn (4.45), into M2 by a small margin. In $\text{Na}_{13}\text{Cd}_{20}\text{Pb}_7$ ²⁰ 100% Cd orders in what is here called the M1 site, with $\text{M3} > \text{M2} > \text{M4}$ therebeyond. However, the lead phase has a much smaller difference in the same electronegatives for Cd and Pb, only 0.43. It is interesting that this Na–Cd–Pb phase has very similar atom proportions, but the extra valence electrons from lead raise the vec range for the anion to 3.00.

Acknowledgment. We are indebted to S. Budko for the magnetic susceptibility data.

Supporting Information Available: Tables of additional crystallographic and refinement parameters for all three samples, and figures of magnetic susceptibility and resistivity data for $\text{Na}_{13}\text{Cd}_{18.1(1)}\text{Tl}_{8.9(1)}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0400033

(49) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734.