

# Heteroatomic Centering of Icosahedral Clusters. Crystal and Electronic Structure of the $K_6(NaCd)_2Tl_{12}Cd$ Compound Containing the Not-So-Naked $Tl_{12}Cd^{12-}$ Polyanion

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The title compound was synthesized in a niobium container by fusion of the elements followed by slow cooling. In the first stage, the stoichiometric proportion  $KNaCd_3Tl_7$  yielded a heterogeneous product containing a few single crystals of the compound  $K_6(Na_{2.36(9)}Cd_{1.64(9)})Tl_{12}Cd$ , the structure of which was established by a single crystal X-ray diffraction technique (cubic,  $Im\bar{3}$ ,  $a = 11.352(2)$  Å,  $Z = 2$ ,  $R(F) = 3.24\%$ ,  $R_w(F) = 4.60\%$ ). Occurrence of a stoichiometry range for the compound was indicated after a new reaction starting from the composition  $K_6Na_2Cd_3Tl_{12}$  gave a quite homogeneous and well-crystallized product (refined composition  $K_6(Na_{1.93(7)}Cd_{2.07(7)})Tl_{12}Cd$ ,  $Im\bar{3}$ ,  $a = 11.321(2)$  Å,  $Z = 2$ ,  $R(F) = 3.98\%$ ,  $R_w(F) = 4.99\%$ ). The structure of  $K_6(NaCd)_2Tl_{12}Cd$  is distinguishable from that reported for  $Na_4K_6Tl_{13}$  by replacement of the icosahedron centering thallium and of half the sodium cations by cadmium. Statistical occupation disorder occurs on the  $\delta(c)$  position of the outer Cd/Na atom. The structure contains the 50-electron closed shell centered  $Tl_{12}Cd^{12-}$  icosahedral cluster with  $\bar{3}m$  symmetry ( $T_h$ ). Extended Hückel molecular orbital and band calculations were carried out to analyze the centering effect on the anion stability and look at the electron transfer, especially from cadmium lying within the first coordination shell of the icosahedral cluster. Electron localization within the Cd-centered icosahedron is not as evident as in the Tl-centered thallium icosahedral clusters described elsewhere; actually, cadmium is found to bridge icosahedra within a more three-dimensional network than sodium by forming bonds that are mainly covalent. The compound is a semiconducting Zintl phase with closed shell bonding.

## Introduction

During the last decade, exploration of systems between group 13 elements and alkali metals has uncovered a field of chemistry very rich in its novelty and originality. In these systems, the electronegative elements are surprisingly able to adapt their bonding and their coordination to fit a wide range of electron counts. It is the remarkable variety of cluster frameworks in alkali metal–gallium intermetallic phases that has sparked further research with the group 13 heavier elements indium and thallium.

Intermetallic compounds of gallium are at the border of metallic phases and valence compounds where the octet and the  $(8 - N)$  rules hold (Zintl phases). Like boron, gallium behaves in these compounds as a hypoelectronic element that needs to be reduced by the electropositive elements to form clusters and fused clusters as well as various fragments.<sup>1</sup> So far, a unique naked cluster has been reported for gallium,<sup>2</sup> but numerous cluster frameworks are known, which can be simple in  $K_3Ga_{13}$ <sup>3</sup> or very complicated in some ternary or quaternary phases (for example,  $Li_{38}(Zn_{0.337}Ga_{0.663})_{101}$ <sup>4</sup>) and where atom defects, substitutions, disorder, or nonstoichiometry obscure the understanding of electronic and bonding requirements. Gallium intermetallic phases exhibit globally delocalized electrons since coordination numbers within clusters are larger than available bonding electron pairs. Nevertheless, these clusters have structures which are adapted to well-defined electron counts that more often conform to classical Wade's rules.

Anionic charges higher than would be required for naked clusters are generally palliated by intercluster  $2c-2e$  classical bonding. Some gallium intermetallic phases, as for example  $Na_7Ga_{13}$  and  $Na_{22}Ga_{39}$ ,<sup>5-7</sup> contain clusters that have one or more non-exo-bonded atoms bearing lone electron pairs. These clusters may be regarded as intermediate steps toward the formation of naked anions.

In great contrast with gallium, heavier group 13 elements indium and thallium have recently been reported to form alkali metal compounds that may contain naked clusters reminiscent of the well-known  $B_nH_n^{2-}$  borane family. Naked homoatomic clusters of indium remain rare:  $In_4^{8-}$ <sup>8</sup> and  $In_5^{9-}$  if we neglect weak intercluster bonding in the crystal.<sup>9</sup> These clusters have classical electron counts, but  $In_{11}^{7-}$  is hypoelectronic.<sup>10,11</sup> Interestingly, centering of clusters by heteroatoms provides electron counts that are still hypoelectronic with respect to Wade's electronic requirements but yields geometries that look more conventional ( $In_{10}Ni^{10-12}$  and  $In_{10}Zn^{8-13}$ ). On the other hand, indium also behaves like gallium in forming extended frameworks with  $2c-2e$  intercluster bonding ( $A_3Na_{26}In_{48}$ ,<sup>14</sup> for example).

Even though the intermetallic chemistry of thallium has proven to be very rich in discrete clusters,  $Tl_4^{8-}$ ,<sup>15</sup>  $Tl_5^{7-}$ ,<sup>16</sup>  $Tl_6^{6-}$ ,<sup>17</sup>  $Tl_9^{9-}$ ,<sup>16</sup>  $Tl_{11}^{7-}$ ,<sup>18,19</sup>  $Tl_{13}^{10-}$ ,<sup>20,21</sup> and  $Tl_{13}^{11-}$ ,<sup>21</sup> gallium-

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or indium-like frameworks are very rare.  $K_{14}Cd_9Tl_{21}$  represents a beautiful example of a layered structure containing both the naked  $Tl_{11}^{7-}$  anion and a two-dimensional metallic framework [ $Cd_9Tl_{10}^{7-}$ ].<sup>22</sup> Recently a similar network has been found in  $A_{15}Tl_{27}$  ( $A = Rb$  or  $Cs$ ).<sup>2</sup>

An isolated  $Tl_{12}$  icosahedron centered by a thallium atom has been reported in the compounds  $NaK_9Tl_{13}$ ,<sup>20</sup>  $Na_3K_8Tl_{13}$ , and  $Na_4A_6Tl_{13}$  where  $A = K$ ,  $Rb$ , or  $Cs$ .<sup>21</sup> The structures of the cubic ( $Im\bar{3}$ )  $NaK_9Tl_{13}$  and  $Na_4K_6Tl_{13}$  compounds are virtually identical and contain  $Tl$ -centered thallium icosahedra. These icosahedra are surrounded immediately by eight alkali atoms sitting at the apices of a cube. This first shell contains 6 potassium and 2 sodium atoms in  $NaK_9Tl_{13}$  and 8 sodium atoms in  $Na_4K_6Tl_{13}$  while a well-separated second shell of 24 potassium atoms forms a truncated octahedron. It is worth noting that occupation of the small sodium cation site in  $Na_4K_6Tl_{13}$  by 75% potassium produces impossibly short  $K-Tl$  distances of 3.14 Å (instead of 3.6–3.8 Å generally observed), which makes the  $NaK_9Tl_{13}$  composition very dubious. In the rhombohedral ( $R\bar{3}m$ )  $Na_3K_8Tl_{13}$  compound, the first shell is somewhat distorted and contains 6 sodium and 2 potassium atoms, while the second shell contains 24 potassium atoms. Packings in cubic and rhombohedral structures differ in the way in which potassium atoms in the second shell are shared between neighboring icosahedra, which is responsible for the distinct stoichiometry of the two compounds and for different electron counts for the centered icosahedron.

In  $Na_4K_6Tl_{13}$ , in the assumption where alkali metals transfer their electrons to thallium atoms in the scheme conceptually formulated by Zintl and Klemm, the  $Tl$ -centered icosahedron has a valence electron count (VEC) of 49, which is one electron shorter than the number required for an isolated anion, i.e., 26 skeletal bonding electrons (Wade's rules) and 24 nonbonding electrons (one pair per atom) as in  $Na_3K_8Tl_{13}$ .<sup>21</sup> Although hypoelectronic counts have been recently found in naked clusters of thallium, this surprising electron deficiency within the  $Tl_{13}$  cluster seems to result mainly from cation packing limitations.<sup>21</sup> These  $Tl_{13}^{n-}$  ( $n = 10$  or  $11$ ) anions are interesting for three reasons: (i) noncentered  $Tl_{12}$  icosahedra have not yet been found in thallium intermetallic phases, (ii) these centered icosahedra are apparently isolated (or naked), i.e., without strong interactions with the alkali cations, and (iii) in opposition to Wade's closed shell requirements, they can exhibit electron deficiencies.

With the aim of modeling the structure of our previous lamellar compound  $K_{14}Cd_9Tl_{21}$ , we have prepared a quaternary alloy  $KNaCdTl$ . In this work, we describe the preparation and crystal structure of the new compound  $K_6(NaCd)_2Tl_{12}Cd$ . To understand the chemical bonding, we have analyzed the electronic structure using extended Hückel molecular orbital and band methods.<sup>23,24</sup> The former has widely shown its ability to rationalize electron counting rules in deltahedral clusters.

## Experimental Section

Cadmium (Prolabo 99.999% pure) and thallium (Fluka 99.99% pure) were used after surfaces were scraped to remove oxide films. Sodium and potassium from Merck Laboratories were purified using the procedure described elsewhere.<sup>25,26</sup> In the first stage, an alloy of

nominal composition  $KNaCd_3Tl_7$  was prepared by melting together the elements in a niobium reactor which had been weld-sealed in an argon atmosphere.

The mixture was heated up to 500 °C for 24 h, homogenized and then allowed to cool slowly to room temperature at a rate of 4 deg/h for crystal growth. The product of the reaction, being very sensitive to air, was examined under a microscope inside a glovebox filled with purified argon. It was not homogeneous but contained a few shiny black chunks which were broken and checked for singularity by preliminary oscillation and Weissenberg diffraction techniques after crystals were inserted into Lindemann glass capillaries to avoid any contact with air and moisture.

Conventional atomic absorption analyses of single crystals, previously checked by X-ray diffraction, revealed the presence of the elements K, Na, Cd, and Tl in the ratio 1/0.385(5)/0.45(1)/2.01(6). Oscillation and Weissenberg investigations indicated the crystals to be rhombohedral. Accurate rhombohedral lattice parameters were determined by least-squares refinement of angular positions of 25 reflections collected and automatically centered on an Enraf-Nonius CAD-4 four-circle diffractometer using graphite-monochromated  $Mo\ K\alpha$  radiation:  $a = b = c = 9.837(2)$  Å,  $\alpha = 109.52(2)^\circ$ , hexagonal axes  $a = b = 16.069(3)$ ,  $c = 9.811(2)$  Å. Although these parameters indicated the possible transformation into a body-centered cubic cell, integrated diffraction intensities of 1355 reflections were collected at room temperature within the octants  $hkl$  and  $h\bar{k}l$  of the hexagonal cell. Profile analysis of a few angle reflections indicated that an  $\omega-\theta$  scan method was the most appropriate for data collection. Scan ranges were calculated from the formula  $Sr = A + B \tan \theta$  where  $A$  depends upon the mosaic spread of the crystal and  $B$  allows for increasing peak width due to  $K\alpha_1$  and  $K\alpha_2$  splitting;  $A$  and  $B$  were taken as 1.2 and 0.35, respectively. Maximum scan times of 60 s were programmed. During data collection, the intensities of three standard reflections were checked after every 100 reflections and no significant loss was observed. Data were corrected for background and Lorentz polarization effects. After the accurate composition of the crystal was known, data were also corrected for the absorption effect using the numerical procedure provided by SHELX 76<sup>27</sup> and then transformed into data for a body-centered cubic cell ( $a = 11.352(2)$  Å). Intensities of equivalent reflections average well ( $R_{int} = 4.7\%$ ) in the corresponding  $m\bar{3}$  Laue class.

**Structure Solution and Refinement.** The structure was solved in the rhombohedral space group  $R\bar{3}$  by the direct methods of SHELXS-86.<sup>28</sup> After thallium and cadmium atom positions were refined, a subsequent Fourier synthesis revealed the remaining peaks of sodium and potassium.

In the first step, least-squares refinement by full matrix (program SHELX 76) in the centrosymmetric space group  $Im\bar{3}$  has been carried out using isotropic temperature factors for all atoms.

A thallium atom in the special position  $24(g)$  forms an icosahedron with symmetry  $m\bar{3}$  which is centered by a cadmium atom  $Cd(1)$  (0,0,0) at the  $2(a)$  position. The potassium atom was found at the special position  $12(e)$  (0,x,1/2). The thermal parameter of the atom in special position  $8(c)$  (1/4,1/4,1/4), formerly considered as cadmium, was found to be abnormally large; therefore the atomic site was filled complementarily by sodium and cadmium. In a first stage, refinement with fixed 50% occupations gave satisfactory temperature factors. Atomic positions were refined with anisotropic thermal parameters for all atoms, and convergence was obtained by minimizing the function  $w(|F_o| - |F_c|)^2$ .

Agreement factors  $R(F) = 3.24\%$  and  $R_w(F) = 4.60\%$  obtained with refined occupations of the  $8(c)$  position by cadmium and sodium (41(2)% and 59(2)%, respectively) are slightly better than those obtained with fixed 50% occupations ( $R(F) = 3.32\%$  and  $R_w(F) = 4.77\%$ ).

The problem of the occupational disorder of site  $8(c)$  in the  $Im\bar{3}$  unit cell could not be overcome by choosing primitive space groups

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**Table 1.** Selected Data Collection and Refinement Parameters for  $K_6(\text{NaCd})_2\text{Ti}_{12}\text{Cd}$ 

	$K_6(\text{Na}_{2.4}\text{Cd}_{1.6})\text{Ti}_{12}\text{Cd}$ composition I	$K_6(\text{NaCd})_2\text{Ti}_{12}\text{Cd}$ composition II
formula weight	3034.4	3070.2
space group, $Z$	$Im\bar{3}$ (No. 204), 2	$Im\bar{3}$ , 2
lattice parameter (Å)	11.352(2)	11.321(2)
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	6.891	7.030
$\lambda$ (Å), $2\theta$ limit (deg)	0.71073, 50	0.71073, 60
abs coeff Mo $K\alpha$ (cm <sup>-1</sup> )	689.58	696.28
range of transmission coeff	0.255–0.030	0.098–0.042
no. of unique rflns, criterion	165, $I > 3\sigma(I)$	247, $I > 4\sigma(I)$
no. of variables <sup>a</sup>	15	15
$R^b$ , $RW^c$ (%)	3.24, 4.60	3.98, 4.99
max shift/ $\sigma$	0.00	0.00
residual electron density (e/Å <sup>3</sup> )	2.4	1.9

<sup>a</sup> Scattering factors from Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321. <sup>b</sup>  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>c</sup>  $Rw(F) = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ , where  $w = 1/(\sigma^2(F) + gF^2)$  with  $g = 0.0049$  (composition I) and  $g = 0.0073$  (composition II).

**Table 2.** Atomic Coordinates and Thermal parameters in  $K_6(\text{NaCd})_2\text{Ti}_{12}\text{Cd}^a$ 

atom	position	$x$	$y$	$z$	$M$	$B_{\text{eq}}$
$K_6(\text{Na}_{2.36}\text{Cd}_{1.64})\text{Ti}_{12}\text{Cd}$ , Composition I						
Tl	24( <i>g</i> )	0.6406(1)	-0.2577(1)	0.5	0.5	2.20(8)
Cd(1)	2( <i>a</i> )	0.0	0.0	0.0	0.0417	1.8(1)
Cd(2)	8( <i>c</i> )	0.25	0.25	0.25	0.068(4)	2.6(3)
Na	8( <i>c</i> )	0.25	0.25	0.25	0.099(4)	2.6(3)
K	12( <i>e</i> )	0.0	0.327(1)	0.5	0.25	3.0(5)
$K_6(\text{NaCd})_2\text{Ti}_{12}\text{Cd}$ , Composition II						
Tl	24( <i>g</i> )	0.5	-0.25678(8)	0.64086(9)	0.5	2.11(4)
Cd(1)	2( <i>a</i> )	0.0	0.0	0.0	0.0417	1.92(9)
Cd(2)	8( <i>c</i> )	0.25	0.25	0.25	0.080(3)	2.7(2)
Na	8( <i>c</i> )	0.25	0.25	0.25	0.086(3)	2.7(2)
K	12( <i>e</i> )	0.5	0.3279(8)	0.0	0.25	2.9(4)

<sup>a</sup> The general expression for the thermal parameter is  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}klb^{*}c^{*})]$ . The number of atoms in the unit cell = 48M.

like  $P4_232$  or lower symmetry  $Pn\bar{3}$  which would have split this position into individual ones to be separately occupied by cadmium and sodium atoms. Attempts in the  $R\bar{3}$  or  $R3$  rhombohedral space groups also failed. Careful examination of long exposure oscillation and Weissenberg photographs did not give evidence for a double cell, and reflections with  $h + k + l = 2n + 1$  that would indicate a primitive cell instead of the bcc one were not observed.

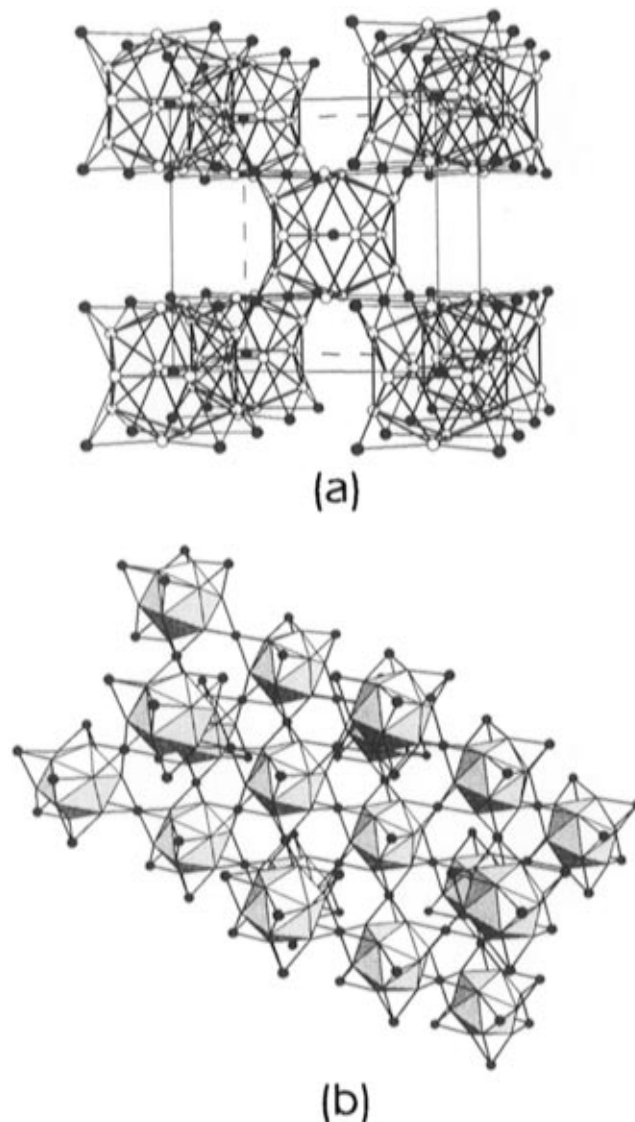
Refinement in the space group  $Im\bar{3}$  led to the formula  $K_6(\text{Na}_{2.36(9)}\text{Cd}_{1.64(9)})\text{Ti}_{12}\text{Cd}$  (composition I),  $Z = 2$ . Within standard deviations, the Na/Cd ratio (0.89(3)) was not far from that obtained from single crystal chemical analyses (0.85). The crystallographic formula corresponded to 49.6 electrons for a single icosahedral unit while that derived from the chemical analysis would give 49.7 electrons. This was already very close to the ideal VEC of 50 which fits the stoichiometry of  $K_6(\text{NaCd})_2\text{Ti}_{12}\text{Cd}$  with half occupations of the 8(*c*) position by Na and Cd.

However, a new synthesis of the compound was carried out starting from the ideal composition  $K_6\text{Na}_2\text{Cd}_3\text{Ti}_{12}$ . It yielded a homogeneous and well-crystallized shiny black product (composition II) with a smaller cubic cell ( $a = 11.321(2)$  Å) with respect to composition I ( $a = 11.352(2)$  Å) indicating a stoichiometry range for the compound. Refinement of the 8(*c*) site occupation gave 52(2)% Na (instead of 59(2)% in composition I) corresponding, within the  $3\sigma$  limit, to a balanced occupation of the site. Agreement factors  $R(F)$  and  $Rw(F)$  of 3.98% and 4.99% were obtained; refinement with fixed 50% occupations by sodium and cadmium atoms left these factors unchanged.

Data collection and refinement parameters are summarized in Table 1, final positional and thermal parameters are listed in Table 2, and main bond distances are given in Table 3. Two views of the polyhedral stacking within the structure are represented in Figure 1. The unit cell contains two formula units  $K_6(\text{NaCd})_2\text{Ti}_{12}\text{Cd}$ , and the structure is very close to those of the  $\text{NaK}_6\text{Ti}_{13}$  and  $\text{Na}_4\text{AgTi}_{13}$  compounds which contain Tl-centered thallium icosahedra. The thallium atom lies on the special position 24(*g*) and forms an icosahedron with  $\bar{3}m$  ( $T_h$ ) symmetry centered at the 2(*a*) position (0,0,0) by the cadmium atom Cd(1) (Figure 2). The distance between the Cd(1) centering atom and Tl is 3.181(1)

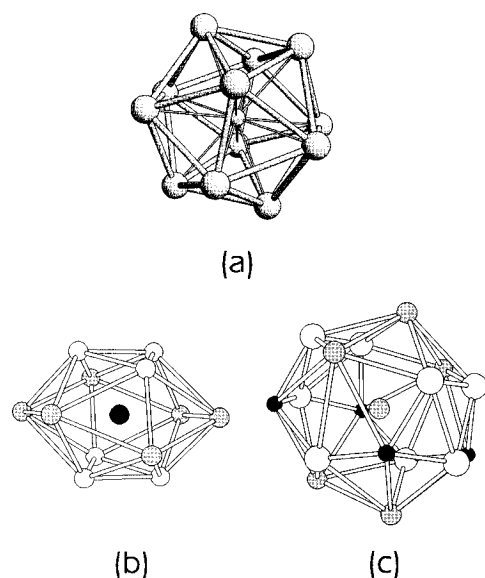
**Table 3.** Distances less than 5.0 Å in  $K_6(\text{NaCd})_2\text{Ti}_{12}\text{Cd}$ 

	$K_6(\text{Na}_{2.36}\text{Cd}_{1.64})\text{Ti}_{12}\text{Cd}$ composition I	$K_6(\text{NaCd})_2\text{Ti}_{12}\text{Cd}$ composition II
Tl–2Cd(2)/Na	3.0991(9)	3.0897(6)
Tl–Cd(1)	3.180(2)	3.181(1)
Tl–Ti	3.192(3)	3.186(2)
Tl–4Ti	3.383(2)	3.386(1)
Tl–K	3.614(6)	3.594(4)
Tl–2K	3.865(6)	3.848(4)
Tl–K	4.156(3)	4.145(2)
Cd(1)–12Ti	3.180(2)	3.181(1)
Cd(1)–8Cd(2)/Na	4.916(1)	4.9021(8)
Cd(2)/Na–6Ti	3.0991(9)	3.0897(6)
Cd(2)/Na–6K	4.109(2)	4.097(2)
Cd(2)/Na–2Cd(1)	4.916(1)	4.9021(8)
K–2Ti	3.614(6)	3.594(4)
K–4Ti	3.865(6)	3.848(4)
K–K	3.92(2)	3.91(1)
K–4Cd(2)/Na	4.109(2)	4.097(2)
K–2Ti	4.156(3)	4.145(2)
K–4K	4.202(5)	4.190(3)



**Figure 1.** Two views of atomic packing in the  $K_6(\text{NaCd})_2\text{Ti}_{12}\text{Cd}$  structure. (a) Cubic  $Im\bar{3}$  cell: blank circles represent thallium atoms and dark circles sodium and cadmium; for clarity, potassium atoms are omitted. (b) View along the [111] direction of the cubic cell of the icosahedral layers: potassium atoms are not represented.

Å and, owing to cadmium's size, is a little smaller than that in  $\text{Ti}_{13}^{10-}$  and  $\text{Ti}_{13}^{11-}$ , in Tl-centered clusters, in cubic  $\text{Na}_4\text{K}_6\text{Ti}_{13}$  (3.222(1) Å), and in rhombohedral  $\text{Na}_3\text{K}_8\text{Ti}_{13}$  (3.204(1) and 3.273(1) Å). The smaller size of the  $\text{Ti}_{12}\text{Cd}$  icosahedron is also reflected by atomic distances on the surface of the cluster, the Tl–Ti distances of 3.186(2) Å ( $\times 1$ ) and 3.386(1) Å ( $\times 4$ ) are slightly shorter than in  $\text{Na}_4\text{K}_6\text{Ti}_{13}$  (3.255(3) and



**Figure 2.** Cluster and coordination polyhedra in the  $K_6(NaCd)_2Tl_{12}$ -Cd structure. (a) Closed shell  $Tl_{12}Cd^{12-}$  anion. (b) Coordination around Cd(2)/Na atom (black circle): blank circles represent thallium, gray circles potassium. (c) Coordination around potassium atom.

3.241(2) Å). The icosahedron is surrounded by eight atoms, indistinctly Cd(2) or Na, at the apices of a regular cube. These eight atoms sit on the body diagonals of the cubic unit cell and are capping faces of two  $\bar{3}m$  inverted icosahedra (Figure 1). Since ionic radii are respectively 1.09 and 1.16 Å for six-coordinated  $Cd^{2+}$  and  $Na^+$ <sup>29</sup> and metallic radii are not very different, 1.41 (Cd) and 1.57 Å (Na),<sup>30</sup> these elements can easily substitute for each other on the site.

Owing to the stoichiometry range related to variations in  $\delta(c)$  site occupation, the cube around the icosahedron would be statistically composed of 3.3 Cd and 4.7 Na for composition I and of 4.0 Cd and 4.0 Na atoms in II. The Cd(2)/Na atom sits at the center of a distorted icosahedron which also can be envisioned as an elongated Tl trigonal antiprism encircled by a cyclohexane-like ring of potassium atoms (Figure 2).

The Cd(2)/Na–Tl distance of 3.0897(6) Å ( $\times 6$ ) (against 3.0991(9) Å in I) is smaller than the Na–Tl distance in  $Na_4K_6Tl_{13}$  (3.1380(4) Å). Potassium occupies the center of a 17-vertex polyhedral cavity bordered by 4 Cd(2)/Na, 5 K, and 8 Tl atoms (Figure 2). K–Tl distances range from 3.594(4) to 4.145(2) Å, K–K distances are 4.190(3) Å ( $\times 4$ ), 3.91(1) Å ( $\times 1$ ), and the Cd(2)/Na–K distance is 4.097(2) Å ( $\times 6$ ). K–Tl distances are within the limits of those observed in the other potassium–thallium intermetallic phases.<sup>21</sup>

**Electronic Structure and Band Calculations.** The  $K_6(NaCd)_2Tl_{12}$ -Cd is distinguishable from the compounds  $Na_4A_6Tl_{13}$ ,  $NaK_9Tl_{13}$ , and  $Na_3K_8Tl_{13}$  by replacement, in the first coordination shell of the centered icosahedron, of some  $Na^+$  cations by a divalent heteroatom (Cd). In such intermetallic phases, and in agreement with the Zintl–Klemm concept, alkali metals would transfer their electrons to the more electronegative elements to achieve electronic stabilization of clusters or frameworks they are forming. It is worth noting that alkali cation size (packing contribution) is also an important factor in the stabilization of these clusters and frameworks and that association of alkali cations with different sizes adds to the versatility of this chemistry. Stabilization of an empty icosahedron (closed shell configuration) requires an optimal valence electron count (VEC) of 50 of which 26 are skeletal electrons. Although the maximal stability for the centered icosahedron would be at 50 electrons, an open shell count of 49 has been recently found in  $NaK_9Tl_{13}$ <sup>20</sup> and in  $Na_4K_6Tl_{13}$ . This one-electron shortage has been imputed mainly to alkali metal packing limitations,<sup>21</sup> but the alternative would be to replace one Na atom by a two-valence-electron element (Ca, Cd, ...). Interesting questions then arise about the nature of interactions between the centered icosahedron and atoms in its first coordination shell: can the centered icosahedral cluster be really

considered as a naked polyanion? If not, are the interactions with the outer atoms mainly Coulombic or to what extent covalent? Obviously, nonnegligible covalent interactions would delocalize electrons from nonbonding (lone pair) orbitals of the naked cluster toward outer atoms and substitution of sodium by cadmium would help to answer these questions. Noteworthy is the fact that cadmium is electronegative enough to form mainly covalent bonding with gallium in some of their intermetallic phases with alkali metals, as it has been found to do with thallium in the ternary compound  $K_{14}Cd_9Tl_{21}$ .<sup>22</sup>

Extended Hückel molecular calculations<sup>23</sup> have been carried out to derive the electronic configuration of the  $Tl_{12}Cd$  cluster by using fragment analysis and perturbation techniques. The electronic structure of a boron regular icosahedron was investigated theoretically 40 years ago by Longuet-Higgins and Roberts on the basis of an LCAO-MO calculation.<sup>31</sup> Although qualitative in character, their results indicated 13 ( $n + 1$ ) bonding orbitals to be available for bonding within the icosahedron and 12 to be used for external bonding to neighboring atoms. Then 50 electrons are required for stabilization of the icosahedron (closed electron shell). The division of the ( $n + 1$ ) bonding MOs into a unique centering and  $n$  surface orbitals featured the rules which were later formulated by Wade for boranes and carboranes.<sup>32</sup> This concept also applies to non-exo-bonded (naked) clusters in which each atom bears a lone pair. Owing to the paucity of Hückel parameters for cadmium, we could only tune our calculations by testing two sets of parameters for thallium (see appendix). Although the two parameter sets gave results not significantly different for the empty  $Tl_{12}^{14-}$  cluster, the first set was not retained since it yielded unlikely, too high electron populations on the centering cadmium atom ( $\approx 4$  electrons) in the molecular cluster  $Tl_{12}Cd^{12-}$  as well as on the other cadmium atoms in the structure, associated with too large a depopulation of thallium atoms. The molecular orbital diagram of the  $Tl_{12}Cd$  icosahedron is built from the interaction of fragment molecular orbitals of an empty  $Tl_{12}$  icosahedron with the 5s and 5p orbitals of a cadmium atom. The cadmium 4d orbitals were used in a preliminary calculation and, owing to their strong localized character (high value of Slater exponent), the five resulting molecular levels stay at the same energy as the cadmium 4d ionization potential. Since these 4d atomic orbitals do not mix notably with thallium levels, they were not taken into account in further calculations.

The  $Tl_{12}$  icosahedron, slightly distorted from the icosahedral symmetry ( $I_h$ ), has been analyzed in its crystallographically imposed  $T_h$  symmetry. In a semilocalized description, it is possible to separate the orbitals into two sets: skeletal (endo) orbitals and external (exo) orbitals; assignments of the 48 molecular orbitals of the ideal icosahedron ( $I_h$  symmetry) are reported below.

MOs (4n MOs for n vertices)	exo	skeletal		total
		tangential	radial	
bonding	$a_g + t_{1u} + t_{2u} + h_g$	$t_{1u} + g_u + h_g$	$a_g$	$2n + 1$ (25)
antibonding	$n$ (12)	$t_{1g} + g_g + h_u$	$t_{1u} + t_{2u} + h_g$	$2n - 1$ (23)
		$2n$ (24)	$n$ (12)	$4n$ (48)

Encapsulation of a cadmium atom inside the icosahedron does not notably modify the molecular orbital diagram: 50 electrons are still required to fill levels up to the degenerate HOMO and to reach the stable closed shell configuration (Figure 3). The HOMO–LUMO separation remains unchanged (1.94 eV) after centering, but energetic stabilization by  $\approx 7$  eV in sum of one-electron energies mainly results from the interaction of the  $1a_g$  and  $2a_g$  molecular orbitals of the empty icosahedron with the 5s orbital of cadmium, and at least to some extent from the interaction of the  $1t_u$ ,  $3t_u$ , and  $4t_u$  molecular orbitals with the cadmium 5p orbitals (Figure 4). The results are in agreement with those recently published for the Tl-centered icosahedron.<sup>21</sup> The only difference between the  $Tl_{12}$  fragment diagrams lies in the energetic inversion of the very close  $e_g$  and  $t_g$  MOs at the HOMO level, but this is not significant since it depends mainly upon the deltahedral geometry (atomic coordinates from ref 20, 21, or this work) and also on the Hückel parameters used.

Our results also show that in  $Tl_{12}Cd$ , the HOMO (degenerate  $e_g$  level) and the three molecular orbital  $t_g$  lying just below are mainly

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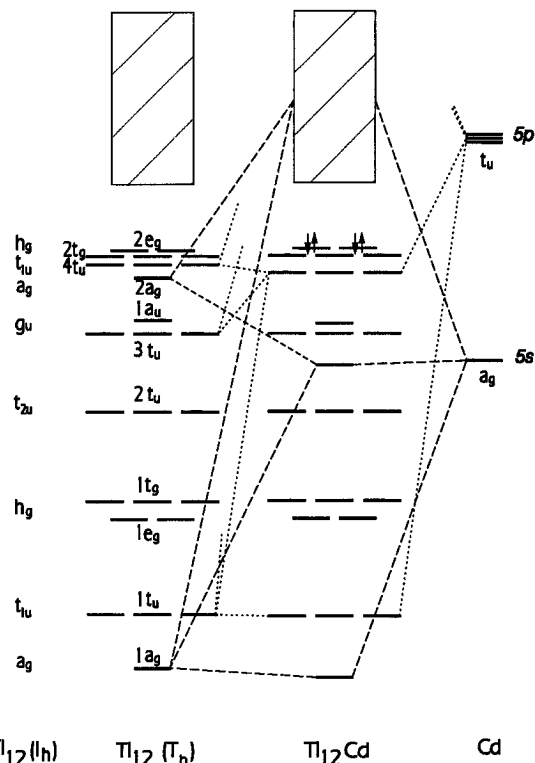


Figure 3. Extended Hückel MO diagrams for the empty  $Tl_{12}^{14-}$  cluster (symmetry  $T_h$ ) and the Cd-centered icosahedral anion  $Tl_{12}Cd^{12-}$  ( $T_h$ ).

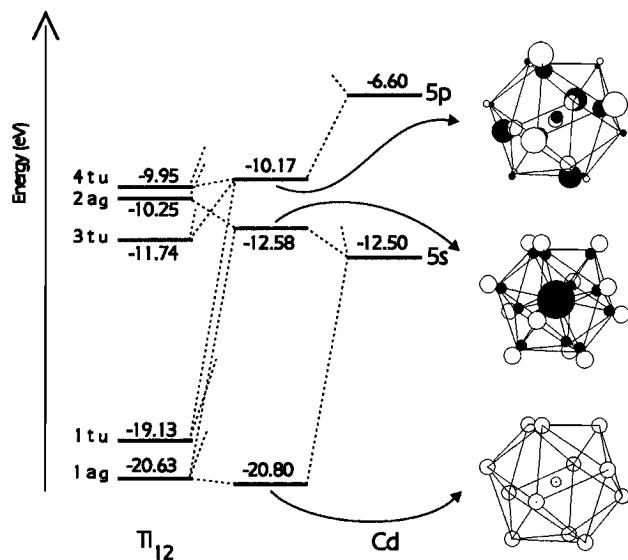


Figure 4. Schematic representation of the atomic orbital populations in the three MOs of  $Tl_{12}Cd$  most involved with cadmium centering.

nonbonding in character (lone pair orbitals) and are centered on the 6p thallium levels. These frontier orbitals should be very accessible to interact with outer atoms having close energy levels. With the Hückel parameters used (set no. 2), the surface thallium atoms of  $Tl_{12}Cd$  are found to be fairly reduced (-1), while the centering cadmium atom is very slightly oxidized (+0.14).

Interactions between icosahedra in the  $K_6(NaCd)_2Tl_{12}Cd$  compound have been investigated using the extended Hückel band method,<sup>24</sup> which is very useful to understand bonding and electronic properties. Our calculation used an effective Hamiltonian of the extended Hückel type.<sup>33</sup>

The major problem in this structure resulted from the occupational disorder within the first coordination shell of the centered icosahedron. The structure refinement shows the  $8(c)$  crystallographic site, for composition II, to be statistically occupied by 4 cadmium and 4 sodium atoms. Such a disordered situation seems quite reasonable judging from

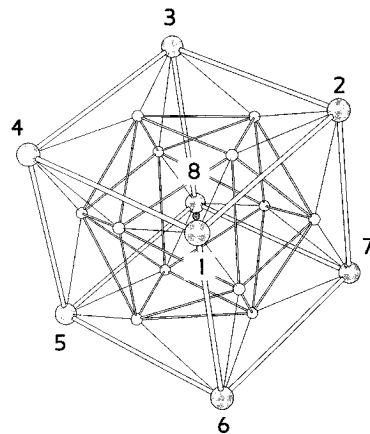


Figure 5. Cubic Cd/Na environment of the  $Tl_{12}Cd$  icosahedron: site  $8(c)$  can be filled either with four Cd (1,3,5,7) and four Na (2,4,6,8) tetrahedrally arranged or with only six Cd (2,3,4,5,6,7) within a trigonal antiprism, sites 1 and 8 are then left vacant. In both cases, the valence electron count remains the same.

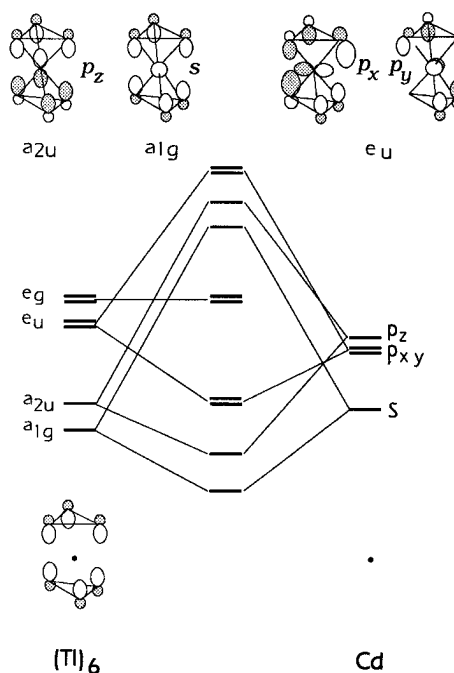
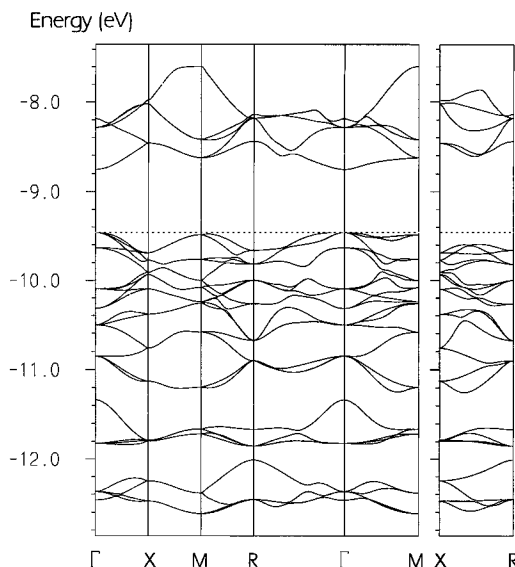


Figure 6. Localized scheme of the interaction of nonbonding pair orbitals of two facing  $Tl_{12}Cd$  icosahedra through the s and p orbitals of an outer Cd atom.

the tight packing attributed to  $Im\bar{3}$  structure but is difficult to manage with respect to the lattice periodicity. However, a periodic model can be achieved by partitioning sodium and cadmium atoms into the two distinct tetrahedra inscribed in the cube (Figure 5). We now have to deal with a primitive cell, instead of a body-centered one, which then contains two independent icosahedral units. The different wave vector labels are those usual for the primitive cubic irreducible Brillouin zone.

In a qualitative approach, we can analyze how a  $Tl_{12}Cd$  cluster would interact in the crystal with neighboring alike units through the surrounding sodium and cadmium atoms lying at the  $8(c)$  position. We can assume the 5s and 5p cadmium orbitals to interact mostly with the six radial outwardly directed orbitals of two neighboring  $Tl_{12}Cd$  units (three orbitals within each of the  $\bar{3}m$  inverted triangular faces) as shown in Figure 6. According to the local symmetry ( $D_{3u}$ ), the four cadmium orbitals combine with four  $(Tl)_6$  MOs into four bonding MOs ( $a_{1g}$ ,  $a_{2u}$ , and  $e_u$ ) leaving the two radial ( $e_g$ ) orbitals as nonbonding. This provides 3 filled (2 bonding and 1 nonbonding) levels for each  $(Tl)_3$  triangular unit, and since there are 4 outer cadmium atoms around  $Tl_{12}Cd$ , we still have 12 filled (8 bonding and 4 nonbonding) orbitals outside the icosahedral skeleton, hence the ideal count of 50 electrons is preserved.

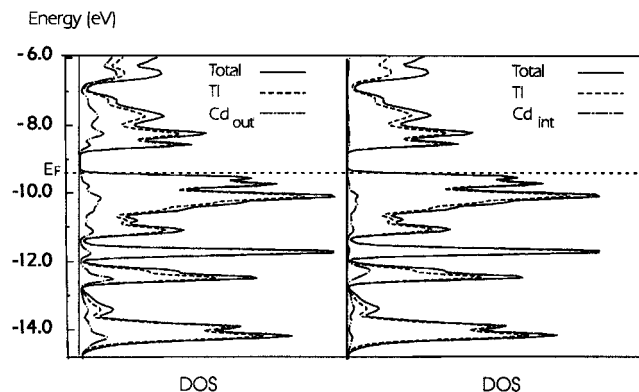
Things are not so straightforward in the three-dimensional lattice; electrons from lone pair orbitals may now be delocalized not only



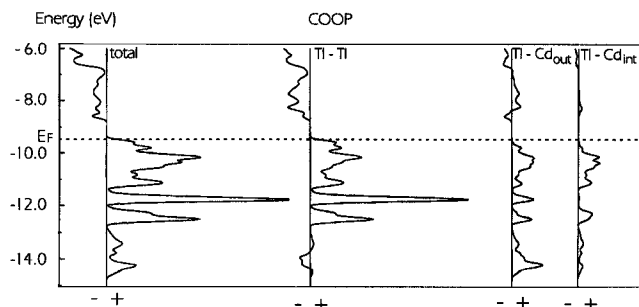
**Figure 7.** Band structure for the  $K_6(NaCd)_2Tl_{12}Cd$  stoichiometric compound, Na and K atoms have been considered as one-electron donors and neglected in the calculation. The dashed line marks the Fermi level ( $-9.46$  eV) for 100 electrons (2 icosahedral units). The irreducible part of the Brillouin zone is limited by the special  $k$  points  $\Gamma$  (0,0,0),  $X$  (1/2,0,0),  $M$  (1/2,1/2,1/2), and  $R$  (1/2,1/2,0).

toward cadmium but presumably at least to a degree onto sodium atoms. Band structure calculations for the  $K_6(NaCd)_2Tl_{12}Cd$  framework have been carried out in the full energy domain. Since the potassium atom sits in a large cavity, it has been considered as a one-electron donor and not taken into account in calculations. We have checked that sodium does not significantly modify the band structure; thus, like potassium, it will be considered as a cation and neglected in further calculations. For clarity, only the energy domain between  $-7.5$  and  $-13$  eV has been represented in Figure 7. The Fermi level is indicated for 100 electrons (50 per single icosahedral unit). There is a group of three bands almost flat around  $-11.8$  eV. Crystal orbital analysis at point  $\Gamma$  shows that these bands correspond to combinations of tangential thallium AOs on the surface of the icosahedron and have remained free from any combination with cadmium levels. A group of three bands near  $-9.45$  eV, just below the Fermi level, are not much dispersed. They essentially result from thallium radial AO combinations and have no contribution from cadmium atoms and correspond to unaltered nonbonding pairs of the molecular  $Tl_{12}Cd$  unit. However, the outer cadmium atoms ( $Cd_{out}$ ) contribute in the domain between  $-9.8$  and  $-11.2$  eV, which makes the bands a little bit more dispersive with a total width of less than  $0.6$  eV, the bonding and antibonding domains being separated by a substantial gap of  $\approx 0.6$  eV. Noteworthy is the  $Tl-Cd_{out}$  bonding contribution just above  $-8.5$  eV in the antibonding domain that results from overlapping of  $p_{x,y}$  orbitals (see Figure 6 for orientation) of the outer cadmium atom with tangential skeletal orbitals ( $p$  in character) of the icosahedral units. The strong  $Tl-Tl$  antibonding contribution is responsible for the destabilization of these levels. It has been shown that, up to the Fermi level, nearly half the  $Cd_{out}$  states are filled, and bonding around the outer cadmium atom may be schematically visualized as two  $4c-2e$  bonds. These findings are supported by the  $Cd_{out}$  electron population of 1.88 calculated at the Fermi level; for comparison, electron populations of 1.72 and 3.71 have been found for centering cadmium ( $Cd_{int}$ ) and thallium atoms, respectively. All these conclusions suggest that molecular features of the  $Tl_{12}Cd$  cluster are partially retained in the crystal band structure and that the compound looks like a semiconductor, this is in agreement with single crystal electrical resistivity measurements:  $\approx 2 \times 10^{-2} \Omega$  cm at 295 K, with a negative coefficient.

A simple but more informative description of the electronic structure of this compound is provided by the analysis of the densities of states (DOS)<sup>34</sup> which can be interpreted like an energy level diagram of a molecular system (Figure 8), these have been calculated with a set of 170  $k$  points. The Fermi level lies at a domain of nearly a zero density



**Figure 8.** Total DOS and projections of the atomic contributions within the  $K_6(NaCd)_2Tl_{12}Cd$  network.



**Figure 9.** COOP curves for  $Tl-Tl$  and  $Tl-Cd$  bonds in  $K_6(NaCd)_2Tl_{12}Cd$ : total COOP is also indicated.

of states, close in energy to the HOMO of the molecular cluster; the gap separating valence and conduction bands is about  $0.4$  eV,  $1.5$  eV less than the HOMO-LUMO separation of the isolated  $Tl_{12}Cd$  unit.

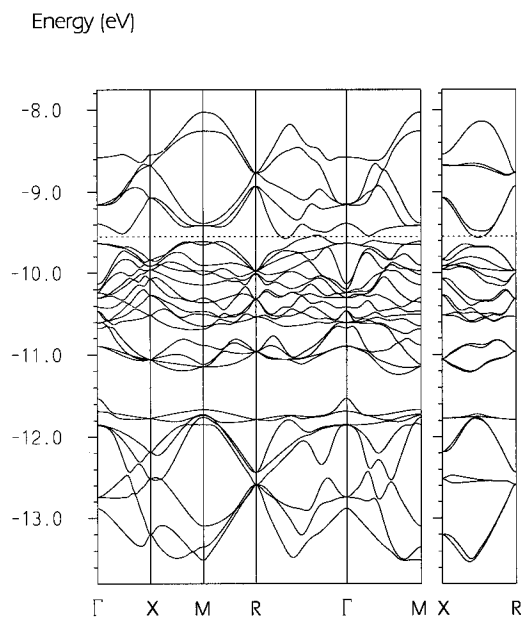
Comparison of partial and total DOS is also interesting; there is a good match of the partial DOS of the outer cadmium atom with the thallium projection, which indicates the presence of covalent interactions. The centering cadmium atom does not contribute very much in the domain just below the Fermi level, which confirms the band structure analysis.

We will now look at the crystal orbital overlap population (COOP)<sup>35</sup> for the different types of bonds in the structure; these curves tell us the bonding, nonbonding, or antibonding nature of the interactions. The results shown in Figure 9 are very clear since all types of bonds reach an optimal overlap population at the Fermi level with a large separation between bonding and antibonding domains indicating that addition of electrons would be very much destabilizing.

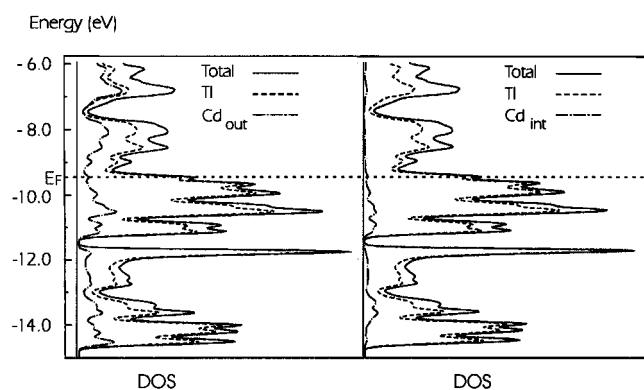
We can also imagine that a VEC of 50 would be reached with a partial filling of the  $8(c)$  site of the bcc ( $Im\bar{3}$ ) cell with only cadmium atoms; this could allow relaxation of the  $Im\bar{3}$  close packing to less tight atomic arrangements in primitive rhombohedral  $R\bar{3}m$  or  $R\bar{3}$  structures. In the former space group, the  $8(c)$  site would transform into the  $3(d)$  and  $1(b)$  positions. The  $1(b)$  position would remain unoccupied, and the  $3(d)$  site would be filled with cadmium atoms within a trigonal antiprismatic arrangement around the centered icosahedron as depicted in Figure 5; such an ordered compound could be formulated as  $K_6(Cd_3\Box)Tl_{12}Cd$ . The corresponding band structure shown in Figure 10 is slightly different from that of  $K_6(NaCd)_2Tl_{12}Cd$ , especially in the domain of the Fermi level in which more dispersion occurs and where a few bands now cut the Fermi level. The antibonding domain is lowered in energy so there is no perceptible gap as also indicated in the DOS (Figure 11) that contains more contributions of the outer cadmium atoms below the Fermi level. Examination of the COOP shows that, although the  $Tl-Tl$  contribution remains bonding up to nearly 52 electrons, the optimal situation in terms of  $Cd-Tl$  overlap is still provided for an electron count of 50. The 50-electron incomplete filling of the bands up to  $-9.5$  eV would provide this hypothetical compound with more metallic behavior compared to  $K_6(NaCd)_2Tl_{12}Cd$ .

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**Figure 10.** Band structure for the hypothetical  $K_6(Cd_3\Box)Tl_{12}Cd$  compound, K atoms have been considered as one-electron donors and neglected in the calculation. The dashed line marks the Fermi level ( $-9.55$  eV) for 100 electrons (2 icosahedral units).



**Figure 11.** Total DOS and projections of the atomic contributions within the hypothetical  $K_6(Cd_3\Box)Tl_{12}Cd$  compound.

## Conclusion

So far, an empty  $Tl_{12}$  icosahedral cluster has not been observed either in thallium–alkali metal binary compounds or in ternary compounds which can be tuned with different size alkali metals. Energetic stabilization and skeletal strengthening of this icosahedral cluster is favored by centering with thallium or, as found recently, by monovalent or divalent metals like sodium, magnesium, zinc, or cadmium.<sup>36</sup> Centering also reduces the global anionic charge of the cluster, thereby allowing alternative crystal packing and symmetry.

The valence electron count for this open or closed shell cluster does not seem to depend on the type of centering atom but mainly on the way (number and charge) electropositive elements can fill voids between clusters.

The peculiarity of the  $K_6(NaCd)_2Tl_{12}Cd$  structure is that smaller voids, which are occupied only by sodium in related phases ( $Na_4A_6Tl_{13}$  and  $Na_3K_8Tl_{13}$ ), are now half-occupied by cadmium. If these voids were entirely occupied by sodium cations ( $K_6Na_4Tl_{12}Cd$ ), the icosahedral centered cluster  $Tl_{12}Cd$  would have a charge of  $-10$  and a valence electron count of 48, which would be less favorable from a Jahn–Teller point of view. However, a 49-electron count might be provided by the composition  $K_6(Na_3Cd)Tl_{12}Cd$  in a rhombohedral cell ( $R\bar{3}m$ ) where the  $3(d)$  and  $1(b)$  positions would be occupied by sodium

and cadmium, respectively, whereas for the above-mentioned stoichiometry  $K_6(Cd_3\Box)Tl_{12}Cd$  (50 electrons) the  $3(d)$  site would be filled with cadmium and site  $1(b)$  left vacant.

Solvation by alkali cations seems to be merely a driving force in stabilization of these icosahedral units, but is it appropriate to speak of alkali cations? As is the case for bonds in molecules, bonds in crystals are usually of mixed type being neither purely covalent nor purely ionic, and it would be wise to better examine the average electron density of bonding electrons that should drop to zero in the vicinity of a pure cation. These considerations are particularly exemplified in the field of polar intermetallic phases (Zintl phases).

In  $K_6(NaCd)_2Tl_{12}Cd$ , the alkali metal valence electrons are unlikely to be completely localized on the icosahedral cluster but partly drawn back to the alkali metal as a consequence of the polarization effects. Factors that generally increase polarization are the high charge and small size of the cation as well as the high charge and large size of the anion. Increasing the polarization in salts provides some covalent character as indicated by lower solubility in polar solvents, and, to our knowledge, no solubility of a group 13 element–alkali metal phase in a polar basic solvent has ever been claimed. In spite of its low ionic potential,  $Na^+$  should be somewhat polarizing owing to the low electronegativity of thallium and the softness of the electronic cloud of the lone pairs in  $Tl_{12}Cd^{12-}$ .

On the other hand, much more covalency is achieved when sodium is replaced by cadmium, which has an electronegativity very close to that of thallium. This allows more delocalization from the lone pair orbitals of the cluster but does not greatly modify the initial molecular features since the anionic substructure still has a closed shell configuration. The valence Zintl phase character of the compound is supported by its brittleness and its electrical resistivity characteristic of a semiconductor; however, though limits are not yet thoroughly determined, the compound has a stoichiometry range permitting slight electron deficiency (49.7 electrons for composition I, instead of the closed shell 50 electrons for composition II) and hole formation in the valence band that would provide some metallic character.

In this study, the theoretical investigation is somewhat limited by the one-electron approximation of the extended Hückel theory and findings remain only qualitative. More sophisticated calculation methods (LMTO, DFT) would provide complementary information on the nature of these interactions.

**Acknowledgment.** We thank M. Köckerling for having kindly provided to us a PC adaptation of the extended Hückel band calculation program.

## Appendix

Exponents and parameters used in the calculations are as follows:

atom	orbital	$H_{ii}$ , eV	$\xi(C_1^a)$	$\xi(C_2^a)$
$Tl$ set 1 <sup>b</sup>	6s	-11.60	2.30	
	6p	-5.80	1.60	
$Tl$ set 2 <sup>c</sup>	6s	-16.20	2.37	
	6p	-9.00	1.97	
$Cd^d$	4d	-14.60	6.38(0.6404)	2.81(0.5203)
	5s	-12.50	2.30	
	5p	-6.60	2.10	

<sup>a</sup> Contraction coefficients used in the double- $\xi$  expansion. <sup>b</sup> From ref 37. <sup>c</sup> From ref 38. <sup>d</sup> From ref 39.

**Supporting Information Available:** Tables of data collection and refinement details and of anisotropic displacement parameters for  $K_6(Na_{2.36}Cd_{1.64})Tl_{12}Cd$  and  $K_6(NaCd)_2Tl_{12}Cd$  (2 pages). Ordering information is given on any current masthead page.

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