

# Synthesis and Characterization of the Largest Isolated Clusters of Tin, $[\text{Sn}_{12}]^{12-}$ , in $(\text{AE})\text{Na}_{10}\text{Sn}_{12}$ (AE = Ca or Sr)

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Reported are two isostructural Zintl compounds,  $\text{CaNa}_{10}\text{Sn}_{12}$  and  $\text{SrNa}_{10}\text{Sn}_{12}$ , with mixed alkali and alkaline-earth cations and isolated clusters of  $\text{Sn}_{12}^{12-}$  with the shape of giant truncated tetrahedra. The compounds were synthesized by heating the corresponding mixtures of elements at 950 °C. The structures were solved and refined from single-crystal X-ray diffraction data in the cubic space group  $I\bar{4}3m$  (No. 217), where  $Z = 2$  with  $a = 11.1847(6)$  and  $11.2176(4)$  Å for  $\text{CaNa}_{10}\text{Sn}_{12}$  and  $\text{SrNa}_{10}\text{Sn}_{12}$ , respectively. Both compounds are diamagnetic and therefore electronically balanced.

## Introduction

Isolated deltahedral clusters of group 14 in the solid state were, for many years, limited to only tetrahedral species,  $\text{Tt}_4^{4-}$  (Tt = Tetrel, an element of group 14, excluding carbon), found typically in binary compounds with alkali metals  $\text{A}_4\text{Tt}_4$  (A = alkali metal).<sup>1</sup> Larger homologues were discovered only very recently in the solid-state compounds  $\text{A}_4\text{Tt}_9$  and  $\text{A}_{12}\text{Tt}_{17}$ .<sup>2</sup> They are nine-atom clusters,  $\text{Tt}_9^{4-}$ , with a charge and geometry that correspond to *nido*-species according to Wade's rules developed for electron counting in deltahedral boranes.<sup>3</sup> Such clusters were known previously only in compounds crystallized from ethylenediamine or liquid ammonia solutions of  $\text{A}_x\text{Tt}_y$  precursors in which the countercations are alkali metals sequestered by large organic molecules such as 2,2,2-crypt (2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8,8,8]-hexacosane) or crown ethers.<sup>4</sup> Thus, it was found, for the first time, that exactly the same clusters exist in neat solids and in solids crystallized from solutions, and this established that Zintl phases and Zintl ions are indeed related. These findings have stimulated the search for other, yet to be discovered Zintl phases with possibly novel clusters.

In our search, we have studied quite extensively the binary A–Tt and pseudobinary A–A'–Tt systems. Especially interesting in the latter type are the systems in which a very small alkali metal is combined with a very large one. These produced the first *arachno*-clusters of group 14,  $\text{Sn}_8^{6-}$ , discovered in the Li-containing Zintl phases  $\text{A}_4\text{Li}_2\text{Sn}_8$  (A = K, Rb).<sup>5</sup> Similarly,

the use of Ge instead of Sn afforded giant isolated truncated tetrahedra of  $\text{Ge}_{12}^{12-}$  in  $\text{RbLi}_7\text{Ge}_8$ .<sup>6</sup> More intriguingly, both species, i.e., the *arachno*- $\text{Sn}_8^{6-}$  and  $\text{Ge}_{12}^{12-}$ , are "stabilized" as *closo*- $[\text{Li}_2\text{Sn}_8]^{4-}$  and *closo*- $[\text{Li}_4\text{Ge}_{12}]^{8-}$  by lithium that caps the open faces. Lead clusters,  $\text{Pb}_4^{4-}$  tetrahedra and *nido*- $\text{Pb}_9^{4-}$  deltahedra, are also found in similar mixed-cation systems.<sup>7</sup> Furthermore, some extended structures such as certain clathrates of Si, Ge, and Sn can form only with mixed cations of very different sizes and do not exist otherwise.<sup>8</sup> These examples illustrate clearly that there is a very delicate balance between packing and electronic requirements for the stabilization of such novel compounds that are otherwise inaccessible in simple binary systems.

We have now extended these systematic explorations into the analogous pseudobinary systems of mixed-alkali and alkaline-earth cations and report here the synthesis and characterization of the first two members of this new family of compounds,  $\text{CaNa}_{10}\text{Sn}_{12}$  (**1**) and  $\text{SrNa}_{10}\text{Sn}_{12}$  (**2**). They contain large isolated clusters of tin,  $\text{Sn}_{12}^{12-}$ , that are only the second example of isolated clusters with the geometry of a truncated tetrahedron.

## Experimental Section

**Synthesis.** All manipulations were performed in an inert atmosphere glovebox (moisture level at <1 ppm). Initially, the compounds were found as the major products of reactions with compositions of AE:A:Tt = 1.5:10:23 (AE = alkaline-earth) that were designed to produce the alkaline-earth analogues of the clathrate-like compounds  $\text{A}_3\text{Na}_{10}\text{Sn}_{23}$  (A = Cs, Rb, K).<sup>9</sup> Later, the compounds were synthesized in high yields from stoichiometric mixtures of Na (Alfa, 99.9%, sealed under Ar), Ca or Sr (Strem, granules 99.5%), and Sn (Alfa, ingot 99.999%) corresponding to the composition  $(\text{AE})\text{A}_{10}\text{Tt}_{12}$ . In a typical reaction, the mixture is loaded in a niobium tube that has been closed by arc welding at one end. Then, the other end is also sealed by arc welding under argon atmosphere, and the container is placed in a fused-silica ampule, which in turn is evacuated and flame-sealed. These assemblies were heated at 950 °C for 48 h and were cooled to room

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**Table 1.** Selected Data Collection and Refinement Parameters for  $\text{CaNa}_{10}\text{Sn}_{12}$  and  $\text{SrNa}_{10}\text{Sn}_{12}$ 

empirical formula	$\text{CaNa}_{10}\text{Sn}_{12}$	$\text{SrNa}_{10}\text{Sn}_{12}$
formula weight	1694.26	1741.80
space group, $Z$	$I\bar{4}3m$ (No. 217), 2	
radiation, $\lambda$ (Å)	Mo $K\alpha$ , 0.71073	
temperature (°C)	21(2)	
unit cell parameters:		
$a$ (Å)	11.1847(6)	11.2176(4)
$V$ (Å <sup>3</sup> )	1399.2(1)	1411.56(9)
$\mu$ (cm <sup>-1</sup> )	108.31	124.23
$\rho_{\text{calcd}}$ (g/cm <sup>3</sup> )	4.021	4.098
R1/wR2 (%), $I > 2\sigma_I$	1.31/2.93	2.19/4.40
R1/wR2 (%), all data	1.36/2.95	2.59/4.53

$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}$ , where  $w = 1/[\sigma^2 F_o^2 + (0.0083P)^2 + 0.1566P]$  for  $\text{CaNa}_{10}\text{Sn}_{12}$ ,  $w = 1/[\sigma^2 F_o^2 + (0.0196P)^2]$  for  $\text{SrNa}_{10}\text{Sn}_{12}$ , and  $P = (F_o^2 + 2F_c^2)/3$ .

**Table 2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for  $\text{CaNa}_{10}\text{Sn}_{12}$  and  $\text{SrNa}_{10}\text{Sn}_{12}$ 

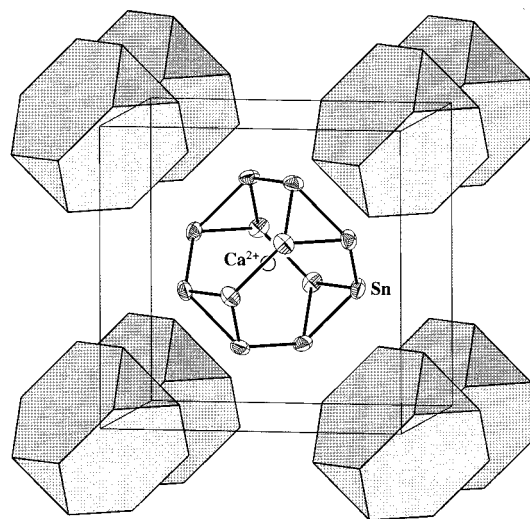
atom	site	$x$	$y$	$z$	$U_{\text{eq}}$
$\text{CaNa}_{10}\text{Sn}_{12}$					
Sn	24g	0.09068(2)	$x$	0.27800(3)	0.0267(1)
Na1	8c	0.3061(2)	$x$	$x$	0.0347(9)
Na2	12d	1/4	1/2	0	0.0404(7)
Ca	2a	0	0	0	0.0151(5)
$\text{SrNa}_{10}\text{Sn}_{12}$					
Sn	24g	0.09110(4)	$x$	0.27884(5)	0.0264(2)
Na1	8c	0.3059(3)	$x$	$x$	0.030(1)
Na2	12d	1/4	1/2	0	0.041(1)
Sr	2a	0	0	0	0.0177(5)

temperature at a rate of 5 °C/h. The products were phase analyzed by powder X-ray diffraction under vacuum in an Enraf–Nonius Guinier camera (Cu  $K\alpha$  radiation,  $\lambda = 1.540562$  Å). For this purpose, a finely ground sample is secured between pieces of scotch tape in order to avoid exposure to air during its transfer from the glovebox to the camera. The powder diffraction patterns showed negligible amounts of unreacted elemental Sn and sometimes contained the binaries NaSn,  $\text{CaSn}_3$ , or  $\text{SrSn}_3$  as impurities.

**Structure Determination.** Single crystals were selected from the initial reactions and were sealed in capillaries. They were checked for singularity, and for the best ones (dimensions of  $0.18 \times 0.16 \times 0.14$  mm for **1** and  $0.14 \times 0.10 \times 0.08$  mm for **2**), data were collected (an octant of a sphere) on an Enraf–Nonius CAD4 diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature with  $\omega$ - $2\theta$  scans ( $\theta_{\text{max}} = 30^\circ$ ). The data sets were corrected for absorption with the aid of the average of six  $\psi$ -scans for both compounds (min/max transmissions of 0.246/0.312 for **1** and 0.275/0.436 for **2**). The structures were solved and refined on  $F^2$  in the noncentrosymmetric body-centered space group  $I\bar{4}3m$  (No. 217) with the aid of the SHELXTL-V5.1 software package. Further details on the data collection and refinement are summarized in Table 1. The final positional and equivalent isotropic displacement parameters and important distances for the refined structures are listed in Tables 2 and 3, respectively.

**Magnetic Measurements.** Magnetizations of 24 mg of **1** and 21 mg of **2** were measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range of 10–280 K. Data were corrected for the holder contribution and for ion-core diamagnetism. The corrected magnetic susceptibility is negative, temperature independent, and varies from  $-7.8 \times 10^{-4}$  to  $-8.0 \times 10^{-4}$  emu/mol for **1** and from  $-4.5 \times 10^{-4}$  to  $-4.7 \times 10^{-4}$  emu/mol for **2**. This is consistent with diamagnetic compounds.

**Electronic Structure Calculations.** Extended-Hückel band calculations<sup>10</sup> were carried out within the tight-binding approximation with

**Figure 1.** General view of the body-centered cubic  $\text{CaNa}_{10}\text{Sn}_{12}$  (thermal ellipsoids at an 80% probability level). The  $\text{Sn}_{12}^{12-}$  clusters (shown in both polyhedral representation and ORTEP plots) are arranged at the center and corners of the body-centered unit cell. The sodium cations are omitted for clarity, while one  $\text{Ca}^{2+}$  is shown encapsulated in the central cluster.  $\text{SrNa}_{10}\text{Sn}_{12}$  adopts the same structure with interstitial  $\text{Sr}^{2+}$  instead of  $\text{Ca}^{2+}$ .**Table 3.** Important Distances (Å) in  $\text{CaNa}_{10}\text{Sn}_{12}$  and  $\text{SrNa}_{10}\text{Sn}_{12}$ 

		$\text{CaNa}_{10}\text{Sn}_{12}$		$\text{SrNa}_{10}\text{Sn}_{12}$	
Sn–	Sn	2.8686(7)	Sn–	Sn	2.890(1)
	$2 \times$ Sn	2.9631(6)	$2 \times$ Sn	$2 \times$ Sn	2.979(1)
	Na1	3.422(3)	Na1	Na1	3.421(5)
	$2 \times$ Na1	3.514(2)	$2 \times$ Na1	$2 \times$ Na1	3.532(3)
Ca–	$2 \times$ Na2	3.2201(3)	$2 \times$ Na2	$2 \times$ Na2	3.2212(4)
	Ca	3.4243(3)	Sr	Sr	3.4457(5)
	$12 \times$ Sn	3.4243(3)	$12 \times$ Sn	$12 \times$ Sn	3.4457(5)
	$4 \times$ Na1	3.756(3)	$4 \times$ Na1	$4 \times$ Na1	3.772(6)
Na1–	$3 \times$ Sn	3.422(3)	Na1–	$3 \times$ Sn	3.421(5)
	$6 \times$ Sn	3.514(2)	$6 \times$ Sn	$6 \times$ Sn	3.532(3)
	Ca	3.756(3)	Sr	Sr	3.772(6)
	$4 \times$ Sn	3.2201(3)	$4 \times$ Sn	$4 \times$ Sn	3.2212(4)
Na2–	$4 \times$ Na2	3.9544(2)	$4 \times$ Na2	$4 \times$ Na2	3.9660(1)

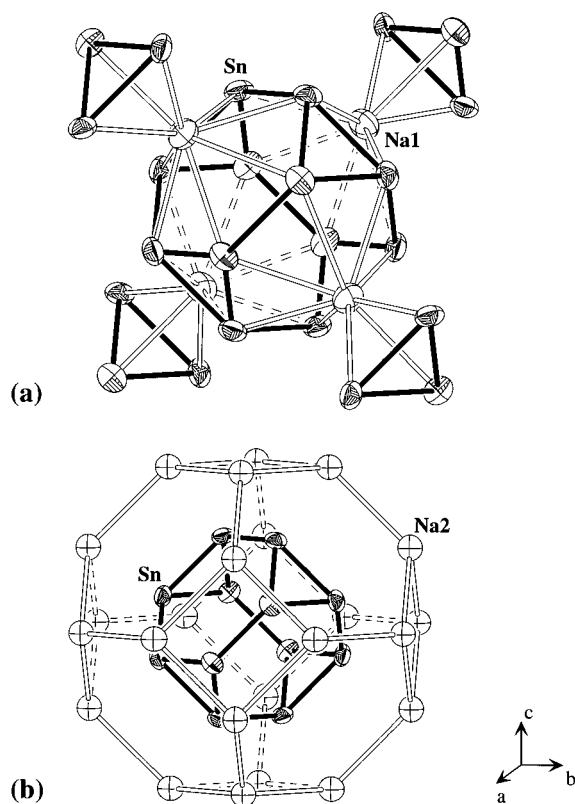
only the tin atoms included ( $H_{ii}/\zeta_i = -16.16/2.12$  and  $-8.32/1.82$  for the 5s and 5p orbitals, respectively). Density of states (DOS) and crystal orbital overlap populations (COOP) were calculated on the basis of 480  $k$ -points over the irreducible wedge of the Brillouin zone.

## Results and Discussion

The main structural element in the two isostructural compounds is the isolated giant truncated tetrahedra of twelve atoms of tin (Figure 1). They are positioned at the center and vertexes of the cubic cell, making it body centered, and their acentric shape is reflected in the acentric space group,  $I\bar{4}3m$ . The  $\text{Sn}_{12}$  cluster has four hexagonal and four triangular faces as a result of the truncation of the imaginary tetrahedron. Each tin atom is three-bonded and therefore carries a formal charge of  $-1$ , which gives the cluster a charge of  $-12$ , i.e.,  $\text{Sn}_{12}^{12-}$ . There are two different Sn–Sn distances in the cluster: longer distances within the triangular faces, 2.9631(6) Å for **1** and 2.979(1) Å for **2**, and shorter distances between them, 2.8686(7) Å for **1** and 2.890(1) Å for **2** (Table 3). They are quite longer than the distances in  $\alpha$ -Sn (diamond form), where each Sn atom has four equivalent neighbors at a distance of 2.810 Å and is, of course, also neutral.<sup>11</sup> The distances are also longer than those in  $\text{A}_8\text{Sn}_{44}$  and  $\text{A}_{30}\text{Na}_2\text{Sn}_{162}$  (clathrate compounds), where the three-

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**Figure 2.** Positioning of the two sets of sodium cations around the clusters of Sn<sub>12</sub><sup>12-</sup> (Sn, full ellipsoids; Na, crossed ellipsoids, all at an 80% probability level). (a) Na1 atoms cap the open faces of the Sn<sub>12</sub><sup>12-</sup> cluster, “completing” it to a *closo*-[Na<sub>4</sub>Sn<sub>12</sub>]<sup>8-</sup>, and also interact with triangular faces of tin atoms (shown) from neighboring clusters. (b) Na2 atoms form sodalitelike cages made of 24 atoms around the Sn<sub>12</sub><sup>12-</sup> clusters that shield the clusters from each other.

dimensional network of four-connected tin atoms is only mildly reduced, i.e., Sn<sub>44</sub><sup>8-</sup> and Sn<sub>162</sub><sup>32-</sup>, which provides formal charges of  $-0.18$  and  $-0.20$  per tin atom, respectively.<sup>8c,12</sup> On the other hand, they are shorter than the distances in deltahedral clusters such as Sn<sub>9</sub><sup>4-</sup> and Sn<sub>8</sub><sup>6-</sup> due to the delocalized bonding in these species.<sup>5,13</sup> As might be expected, the distances in Sn<sub>12</sub><sup>12-</sup> are very similar to the distances in tetrahedra of Sn<sub>4</sub><sup>4-</sup>, where the tin atoms are similarly three-bonded and equivalently reduced.<sup>1</sup>

The clusters are centered by the alkaline-earth cations, Ca<sup>2+</sup> and Sr<sup>2+</sup>, with distances to the tin atoms of 3.4243(3) and 3.4457(5) Å, respectively (Figure 1). One set of four sodium cations, Na1, caps the open hexagonal faces (Figure 2a) with distances of 3.514(2) and 3.532(3) Å for **1** and **2**, respectively, while the other set, Na2, screens the clusters from each other by “forming” sodalitelike cages around them (Figure 2b). The four Na1 atoms also cap triangular faces of the four neighboring clusters (Figure 2a) with distances of 3.422(3) and 3.421(5) Å for **1** and **2**, respectively. Since the two different alkaline-earth cations are encapsulated inside the tin clusters while the cations outside them are the same, the unit cell parameters for the two compounds differ only very slightly (Table 1). The clusters are very well separated, and as a result of these nearly equal lattice parameters, the shortest intercluster Sn–Sn distances are also very similar (5.0506(5) and 5.0827(8) Å in **1** and **2**, respectively).

Similar truncated tetrahedra of Al<sub>12</sub><sup>24-</sup> may exist in the metallic alloys “Mg<sub>17</sub>Al<sub>12</sub>” and “Mg<sub>17-x</sub>Li<sub>x</sub>Al<sub>12</sub>”, both modifications of the  $\alpha$ -Mn structure,<sup>14,15</sup> although this cannot be unequivocally established due to the similar scattering factors of Mg and Al. Thus, those compositions are only suggested. Besides, all conclusions for Mg<sub>17</sub>Al<sub>12</sub> were based on powder diffraction experiments, which, at the time, were not nearly as sophisticated as they are today.<sup>14</sup> There are also a few compounds such as As<sub>8</sub>Hg<sub>9</sub>S<sub>24</sub> (*galkhaite*) and M<sub>4</sub>SP<sub>6</sub>N<sub>12</sub> (M = Cd, Co, Fe, Mg, Mn) with atoms that occupy the same sites as in (AE)Na<sub>10</sub>Sn<sub>12</sub>, but they are completely unrelated structurally as well as in the chemical nature and connectivity of the constituting elements.<sup>16</sup> Furthermore, Mg<sub>17</sub>Al<sub>12</sub> and Mg<sub>17-x</sub>Li<sub>x</sub>Al<sub>12</sub> are not electronically balanced compounds but are rather metallic alloys with variable compositions and many extra electrons. The compositions of CaNa<sub>10</sub>Sn<sub>12</sub> and SrNa<sub>10</sub>Sn<sub>12</sub>, on the other hand, are easily rationalized with the aim of the Zintl concept since the formula provides twelve sodium and one alkaline-earth metal cations that balance exactly the charge of each cluster of Sn<sub>12</sub><sup>12-</sup>. The latter is supported by results from the extended-Hückel calculations, which show that both compounds are wide-band-gap semiconductors (estimated band gap of ca. 4 eV) with very narrow valence and conduction bands. This indicates electronically balanced, closed-shell compounds, which is also in agreement with the appearance of the crystals, which are black in color and very brittle. More importantly, the measured negative and temperature-independent magnetic susceptibilities confirm experimentally the saltlike nature of these Zintl phases.

If the four sodium atoms, Na1, capping the hexagonal faces of Sn<sub>12</sub><sup>12-</sup> are considered as part of the cluster (assuming some covalency of the Na–Sn interactions), it becomes a *closo* deltahedron with sixteen vertexes, i.e., *closo*-[Na<sub>4</sub>Sn<sub>12</sub>]<sup>8-</sup>. In addition to the *closo* shape, the number of bonding electrons in the cluster also satisfies the requirements for such a geometry. It is known that due to the *T<sub>d</sub>* symmetry, clusters such as the tetrahedron and the tetracapped truncated tetrahedron are hyperelectronic and violate Wade’s rules for *closo* species.<sup>3,17</sup> They require  $2n + 4$  electrons instead of  $2n + 2$  electrons for cluster bonding, and because of this, the tetrahedron is often considered to be a *nido* species despite the fact that its faces are triangular and, geometrically, it clearly is a *closo* cluster. This is also true for *closo*-[Na<sub>4</sub>Sn<sub>12</sub>]<sup>8-</sup>. The number of valence electrons provided by the four sodium and twelve tin atoms is  $(4 \times 1) + (12 \times 2) = 28$ . When combined with the charge of  $-8$ , this number totals 36 electrons, which equals exactly the number of required electrons,  $2n + 4 = (2 \times 16) + 4 = 36$ . The vertexes of such isolated species should also carry lone pairs of electrons (one per vertex). This, however, is not the case for the four capping sodium atoms since a lone pair of electrons would create a large negative charge on the alkali metal, which is clearly impossible. Instead, each of them interacts with a triangular face of tin atoms from a neighboring cluster and “shares” the three lone pairs from these atoms (Figure 2a). This can be readily described as a four-center six-electron configuration in a trigonal pyramid with an “open” base. A more comprehensive treatment of these interactions has been already debated in the similar case of *closo*-[Li<sub>4</sub>Ge<sub>12</sub>]<sup>8-</sup>, where

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the four lithium atoms cap the open faces of a truncated tetrahedron of germanium and also interact with triangular faces of germanium from neighboring tetrahedral clusters.<sup>6</sup> Similarly, the two lithium atoms in *closo*-[Li<sub>2</sub>Sn<sub>8</sub>]<sup>4-</sup> found in A<sub>4</sub>Li<sub>2</sub>Sn<sub>8</sub> (A = K, Rb) cap the open faces of a square antiprism of tin and also interact with the lone pairs of an edge of the tin of a neighboring cluster.<sup>5</sup>

In conclusion, CaNa<sub>10</sub>Sn<sub>12</sub> and SrNa<sub>10</sub>Sn<sub>12</sub> are two novel compounds with a specific structure that forms only when an alkali metal is mixed with an alkaline-earth metal. They contain the largest isolated clusters of group 14, Sn<sub>12</sub><sup>12-</sup>, which are only the second example of such clusters after Ge<sub>12</sub><sup>12-</sup> found in RbLi<sub>7</sub>Ge<sub>8</sub>. As such, these recent advances in the field of bare

metal clusters confirm the importance of the packing efficiency and electronic requirements as a very effective tool for the stabilization of novel and unprecedented cluster compounds in the solid state.

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**Supporting Information Available:** X-ray crystallographic file for the two structures in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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