Inorg. Chem. **2006**, *45*, 196–200

Inorganic Chemistry
Article

New Tetragonal Structure Type for $A_2Ca_{10}Sb_9$ (A = Li, Mg). Electronic Variability around a Zintl Phase

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Received September 8, 2005

The phases $LiMgCa_{10}Sb_9$ (**1**), $Mg_2Ca_{10}Sb_9$ (**2**), and $Li_{1.38(2)}Ca_{10.62}Sb_9$ (**3**) have been synthesized by high-temperature solid-state means and characterized by single-crystal means and property measurements. These occur in space group $P4_2/mnm$, $Z = 4$, with $a = 11.8658(5)$, $11.8438(6)$, $11.9053(7)$ Å and $c = 17.181(2)$, $17.297(2)$, $17.152(2)$ Å, respectively. The two types of A atoms occupy characteristic sites in a Ca–Sb network that contains a 5:2 proportion of (formal) Sb^{3-} and Sb_2^{4-} anions and can be described in terms of two slab types stacked along [001]. Bonding appears to be strong in these salts with generally normal distances and high coordination numbers except for the 4-bonded atoms in a C_{2v} position for the second type of A that is occupied by Li, Mg or $Ca_{0.62(2)}Li_{0.38}$, respectively. The three compounds are, respectively, an ideal electron-precise Zintl phase, one e^--rich and 0.40(4) e^--short per formula unit. The $LiMgCa_{10}Sb_9$ compound is correspondingly diamagnetic and presumably a semiconductor.

Introduction

Much of the development of solid-state inorganic chemistry derives from a plethora of new compositions and crystal structures together with the chemistry that these define for a large variety of possible elements, how all of these can be systematically categorized, the diverse properties that go with each compound or category, and how these may be "understood". The continued flow of unprecedented and inconceivable compounds makes clear how very difficult it still is to predict the unknown, namely the compositions and structures not yet defined, or even imagined. Thus, exploratory synthesis remains a vital and active component in expanding and defining the field. Still, reasons that led to the initiation of a series of reactions and thence to one or more discoveries are often left undescribed, so that some readers may be left to believe that chance or a random walk was the principal intellectual activity prior to a discovery.

The sequence of studies that led to the novel results reported here provide a useful counter example, namely an ongoing study that has been centered around an initial puzzle, a diverse exploration that has required chemical knowledge, intuition, imagination, and persistence and has in return resulted in a number of unusual and unexpected findings Our initial question concerned the nonexistence of Ca_5Sn_3 in the Cr_5B_3- or the Mn_5Si_3-type structures (or in any other structure, for that matter) even though analogous examples were known for many of its main group 14 (tetrel) congeners, both lighter and heavier, or with Sr or Ba. (A hydride-stabilized version, Ca_5Sn_3H, does however exist in a stuffed example of the Cr_5B_3 type.[2]) An example in yet a third W_5Si_3-type structure would seem even less likely on the basis of analogues, but it too turns out to be pertinent.

Repeated efforts to synthesize any binary Ca_5Sn_3 first led to the discovery of the nearby composition $Ca_{31}Sn_{20}$ with its remarkable tin oligomers.[3] This alone may be responsible for the instability of Ca_5Sn_3; analogues of $Ca_{31}Sn_{20}$ are known only for $A_{31}Pb_{20}$, A= Sr, Yb.[3] Recognition that cation sizes can be an important factor when different lattice sites are involved also led to attempts to dope or substitute other divalent cations into a Ca_5Sn_3 composition and to a number of surprises. The use of ~40% Mg gave the very remarkable $Ca_{6.2}Mg_{3.8}Sn_7$ containing infinite zigzag chains of interbonded square planar Sn_4 units, an arrangement evidently made

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(1) This research was supported in part by the Office of the Basic Energy Sciences, Materials Sciences Division, U. S. Department of Energy (DOE). The Ames Laboratory is operated for the DOE by Iowa State University under Contract No. W-7405-Eng-82.

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10.1021/ic051536u CCC: $33.50

possible by favorable packing of a particular combination of cations of two sizes.[4] In addition, a $Ca_{2-x}Mg_xSn$ phase with a Co_2Si-type structure was identified for x up to 1.0.[5] Moreover, doping of a Ca−Sn composition with less Mg (as well as with other smaller metals) has recently yielded the first W_5Si_3-type derivatives of the Ca−Sn binary system in, for example, $Ca_4Sn_{3.22}Mg_{0.78}$. In this case, the smaller Mg (and Sn), which substitute on a certain, evidently crowded Ca site, again appears to be of major importance in this stabilization.[6]

Analogous expansions of the neighboring binary Ca−Sb systems, with Mg in particular so as to follow the novel Ca−Mg−Sn findings above, have again proven profitable. An unusual example of even a new Ca−Sb binary phase beyond the common Mn_5Si_3 type was discovered earlier as $Ca_{16}Sb_{11}$, which has a distorted W_5Si_3-like structure.[7] Again, additions of the smaller Mg and/or Li atoms have stabilized the first entries into the new and novel network series that we report here, $Mg_2Ca_{10}Sb_9$ and the isostructural analogue $LiMgCa_{10}Sb_9$. Omission of Mg in the last yields a third isotype, $Li_{1.38}Ca_{10.62}Sb_9$, with a mixed Li/Ca site occupancy. All define a novel structural series in which the intermediate quaternary example is a confirmed Zintl phase.[8]

Experimental Section

Syntheses. The compounds were synthesized by means of high-temperature reactions of the high-purity elements in sealed refractory metal containers, and the new phases were first recognized via high-quality Guinier patterns secured with the aid of a Huber 670 powder camera. Details of these procedures have been described before.[6,9] In contrast to the successful use of Ta in many other intermetallic systems, this container always yielded appreciable amounts of byproduct Ta_5Sb_4 from well-reduced Ca−Sb systems, but such a side reaction disappeared when Nb was used as the container. Dendritic Ca (99.8%, Alfa-Aesar), Li ribbons (99.9%, Alfa-Aesar), Sb chunks (6−9's Alfa-Aesar), and Mg turnings (99.99%, Ames Laboratory) were used for the syntheses. In most cases, stoichiometric amounts of the elements were loaded into Nb tube containers inside a He-filled glovebox. The tubes were welded on the second end, jacketed in evacuated and baked fused-silica containers, and heated in resistance furnaces. The only other reported ternary (or higher) phases in these systems are evidently the fairly normal $CaMg_2Sb_2$ (inverse La_2O_3 type),[10] LiCaSb (Co_2Si),[11] and Li_2MgSb (inverse BiF_3).[12]

Initial reactions of the compositions $LiMgCa_2Sb_3$ and $CaMgSb_3$ (in Ta) both yielded $CaMg_2Sb_2$ plus recognizable amounts of what turned out to be the isostructural gray-black $LiMgCa_{10}Sb_9$ (**1**) and $Mg_2Ca_{10}Sb_9$ (**2**), respectively. Single crystals from both gave the earliest indications of the related stoichiometries. A reaction loaded with the refined composition of the former yielded 95% of the targeted phase plus ∼5% $CaMg_2Sb_2$. (All reactions were cooled from 850 °C and held at 750° for 4 days, after which they were slowly cooled to 400° or below.) Products of the syntheses of Li−Mg samples from both Mg-richer and -poorer compositions yielded diffractometer lattice constants that varied only in the hundredths figure, meaning that a significant nonstoichiometry seems unlikely. The highest yield of **2** under parallel conditions was 70% (plus $CaMg_2Sb_2$), but 80% was obtained after cooling directly from a 5-day equilibration at 850 °C. Several samples of the Li-saturated $Li_{1.38}Ca_{10.62}Sb_9$ compound (**3**) (according to powder data and single-crystal refinements) were obtained in about 40% yield from the starting composition $Li_2Ca_{10.6}Sb_9$, $Ca_{16}Sb_{11}$[7] (plus presumably some $LiSb_x$ or its derivative according to the loaded composition) being the other product. These reactions were cooled from either 850 or 1000 °C and equilibrated for several days at either 750 or 500 °C. A sample that was slowly cooled from 750 to 250 °C yielded lattice constants that were about 0.2 Å less in a and b and 0.1 Å less in c than did the single crystal sample (below), presumably because of a higher Li content. Lower Li contents are probably also accessible.

Structural Studies. Several irregular crystals from the synthesis reactions were selected and saved in thin-wall glass capillaries in a glovebox designed for this purpose. Several were examined, and data sets were collected at room temperature, on a Bruker APEX CCD diffractometer with the aid of monochromated Mo Kα radiation. The later took place over ranges of ∼2.08−28.27° in Θ and substantially a whole sphere of reciprocal space. The detector was placed at a distance of 5.995 cm from the crystal. Three sets of 606 frames were collected for each with a scan width of 0.3° in ω and an exposure of 10 s per frame. The frames were integrated with the SAINT program in the SMART software package.[13] Data were corrected for absorption effects using the multiscan techniques in SADABS.[13] All of the structures were solved by direct methods and refined by full matrix least-squares on F_0^2 with the SHELXTL Version 6.1 program package.[14]

For **1**, the systematic extinctions were consistent with space groups $P\bar{4}n2$ (No. 118), $P4_2nm$ (No 102), and $P4_2/mnm$ (No. 136), and selection of the last, centrosymmetric group was affirmed by the subsequent successful solution of the structure by direct methods and its final refinement. This choice was also made on the basis of the mean $<E^2 - 1>$ value, close to the expected value for a centrosymmetric structure, and a better combined figure of merit. No violations of the systematic absences or inconsistent equivalents were observed in any of the data sets. All of the positional coordinates for Sb and Ca were correctly given in the initial solution for **1,** whereas five possible Mg positions were all deleted during subsequent isotropic refinements of the initial model. The most intense difference peak at this stage was assigned to Mg, and the model refined for a few more cycles. At this stage, anisotropic refinement led to well-behaved ellipsoids for all atoms. Finally, a clear residual of ∼9 $e^-/Å^3$ indicated another atom, and this was subsequently refined as Li. The final anisotropic refinement with 65 variables converged at R1 = 3.46% for observed ($I > 2\sigma(I)$) data and wR2 = 5.59% for all data. The subsequent solution and refinement of diffraction data for the isostructural $Mg_2Ca_{10}Sb_9$ was uneventful.

The successful analysis of the structure of the Mg-free $Li_{2-x}Ca_{10+x}Sb_9$ (**3**) required more effort because of the low scattering

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Table 1. Some Crystal and Refinement Data for the Tetragonal $A_2Ca_{10}Sb_9$ Phases

composition	$LiMgCa_{10}Sb_9$ (**1**)	$Mg_2Ca_{10}Sb_9$ (**2**)	$Li_{1.38}Ca_{10.62}Sb_9$ (**3**)
space group, Z	$P4_2/mnm$, 4	$P4_2/mnm$, 4	$P4_2/mnm$, 4
a(Å)[a]	11.8658(5)	11.8438(6)	11.9053(7)
c(Å)	17.181(2)	17.297(2)	17.152(2)
V(Å^3)	2419.0(3)	2426.3(3)	2431.1(3)
d_{calc}(g/cm^3)	4.195	4.230	4.236
abs. coeff. (mm^{-1})	12.013	12.003	12.138
R1/wR2 [$I > 2\sigma(I)$]	0.0260, 0.0538	0.0288, 0.0606	0.0421, 0.0918

[a] Diffractometer data.

power of Li and the presence of some appreciable residuals close to heavy atoms. Confirmation of the same heavy-atom structure followed readily, but location of the Li positions required some care. Fourier peaks remaining before assignment of any Li were an isolated one of 6.12 e$^-$/Å^3, one of 5.8 e$^-$/Å^3 that was 2.2 Å from Ca4, more than 1 Å too close, and three that were close to Sb atoms, namely 8.21, 5.58, and 2.77 e$^-$/Å^3 at 0.8, 0.7, and 0.75 Å from Sb4, Sb6, and Sb5, respectively. In addition, the noteworthy Ca4, now located in the same position as Li and Mg2 atoms in the two earlier structural solutions, exhibited a larger than normal displacement ellipsoid ($U_{11} = U_{22} = 56(2)$, $U_{33} = 41(3)$ Å^2 × 10^3). This was refined to fit better relative to the rest of the parameters as the constrained mixture 62(2)% Ca5, 38% Li2. Thereafter, the 5.8 e$^-$/Å^3 residual that had been close to Ca4 disappeared. Assignment of Li1 to the above-isolated residual, which was close to the sites occupied by Mg and Mg1 in the two earlier results, gave reasonable results, but the 8.92 e$^-$/Å^3 residual close to Sb4 remained, and a new residual of 5.8 e$^-$/Å^3 now appeared near 0.16, 0.16, 0, which was only 1.2 Å from Li1. This potential Li site was ultimately concluded to be spurious because it not only was 2.2 Å from Ca5/Li2 but it also had only two reasonable Sb(3) neighbors at 2.58 Å. Its presence precluded anisotropic refinement of Li1, which process is a marginal one in any case. Alternate unconstrained refinements in triclinic symmetry also proceeded reasonably well, but the large residual near Sb4 still remained, and the same was true utilizing a data set collected at 100 K. Errors in the absorption correction seem to be the most reasonable explanation.

Some collection and refinement parameters in the standard settings for all three structures are given in Table 1, and more complete details, as well as the final anisotropic displacement parameters, are contained in the Supporting Information. The final positional parameters and isotropic-equivalent displacement ellipsoids for all atoms in the three structures are collected in Table 2 arranged according to equivalent positions. The two sites at which Li, Mg, etc. may be substituted are designated M1 and M2 in later sections. Additional crystal and refinement data and the anisotropic displacement parameters are contained in the Supporting Information.

Physical Properties. Resistivities of powdered $LiMgCa_{10}Sb_9$ sieved to a grain size of 150−250 μm and dispersed in chromatographic Al_2O_3 were examined by the Q method[15] over 123−223 K. Magnetic susceptibilities of the same compound were measured at 10 and 30 kOe and over a range of 6−350 K with the aid of a Quantum Design MPMS SQUID magnetometer. A weighed sample was held between two fused silica rods within a tightly fitting outer silica tube that was sealed under helium.[16] The raw data were corrected for the susceptibility of the container and for the diamagnetic contributions of the atom cores. M vs H data at 2 K indicated the absence of significant paramagnetic impurities. These graphical data are included in the Supporting Information.

Table 2. Atom Coordinates in the Three $A_2Ca_{10}Sb_9$ Structures

atom	str.	Wyckoff			x	y	z	U(iso)
Ca1	**1**	16	k	1	.0126(1)	.2515(1)	.1893(1)	16(1)
Ca1	**2**				.0128(1)	.2515(1)	.1885(1)	17(1)
Ca1	**3**				.0145(2)	.2495(2)	.1866(1)	17(1)
Ca2	**1**	16	k	1	.0153(1)	.3384(1)	.3967(1)	15(1)
Ca2	**2**				.0150(1)	.3391(1)	.3964(1)	17(1)
Ca2	**3**				.0175(2)	.3415(2)	.3960(1)	15(3)
Sb1	**1**	8	j	m	.2237(1)	.2237(1)	.3188(1)	15(1)
Sb1	**2**				.2228(1)	.2228(1)	.3198(1)	15(1)
Sb1	**3**				.22295(5)	.22295(5)	.31951(6)	15(2)
Sb2	**1**	8	j	m	.3128(1)	.3128(1)	.1725(1)	15(1)
Sb2	**2**				.3107(1)	.3107(1)	.1751(1)	17(1)
Sb2	**3**				.31325(6)	.31325(6)	.17449(6)	19(2)
Sb3	**1**	8	i	m	.0314(1)	.3341(1)	0	13(1)
Sb3	**2**				.0297(1)	.3362(1)	0	16(1)
Sb3	**3**				.02945(8)	.33386(8)	0	18(2)
Ca3	**1**	4	g	mm	.1821(1)	.8179(1)	0	18(1)
Ca3	**2**				.1824(1)	.8176(1)	0	18(1)
Ca3	**3**				.1739(3)	.8261(3)	0	23(1)
Sb4	**1**	4	g	mm	.3729(1)	.6271(1)	0	18(1)
Sb4	**2**				.3763(1)	.6237(1)	0	29(1)
Sb4	**3**				.3753(1)	.6247(1)	0	27(1)
Mg	**1**	4	f	mm	.1041(2)	.1041(2)	0	22(1)
Mg1	**2**				.1104(3)	.1104(3)	0	28(1)
Li1	**3**				.096(2)	.096(6)	0	12(6)
Li	**1**	4	f	mm	.3072(13)	.3072(13)	0	16(4)
Mg2	**2**				.3166(3)	.3166(3)	0	31(1)
Ca5[a]	**3**				.2949(5)	.2949(5)	0	23(2)
Sb5	**1**	4	e	mm	0	0	.1327(1)	13(1)
Sb5	**2**				0	0	.1307(1)	13(1)
Sb5	**3**				0	0	.13322(8)	15(1)
Ca4	**1**	4	e	mm	0	0	.3547(1)	21(1)
Ca4	**2**				0	0	.3504(2)	22(1)
Ca4	**3**				0	0	.3416(3)	27(1)
Sb6	**1**	4	d	−4	0	1/2	1/4	13(1)
Sb6	**2**				0	1/2	1/4	11(1)
Sb6	**3**				0	1/2	1/4	10(3)

[a] Ca5/Li2 = 62(2)/38 occupancy.

Results and Discussion

Structures. All three new phases, $LiMgCa_{10}Sb_9$, $Mg_2Ca_{10}Sb_9$, and $Li_{1.38(2)}Ca_{10.62}Sb_9$ (**1, 2, 3)**, exist in a novel tetragonal structure type in which isolated cations of the active metals are interbonded with 5:2 proportions of (formal) Sb^{3-} and Sb_2^{4-} dimers, the latter with typical bond lengths close to 2.91 Å. The somewhat complex overall arrangement in the unit cell is shown in a ∼[010] view in Figure 1 with the atom legend listed below. The structure can be readily broken down into two types of layer sequences normal to $\vec{c}$. The Sb_2 dimers (dark red) plus four types of single Sb anions (red) are interspersed with Ca1 ions (dark blue) in layers centered around $z = {}^1/_4, {}^3/_4$, Figure 2a. These alternate with planes containing Li (yellow), Mg (orange), Ca3, Sb3, and Sb4 cations that are surrounded by Ca2 (light blue) atoms at $z = 0, {}^1/_2$, Figure 2b. (The orientations of the respective layers alternate out c according to the 4_2 axes that lie in the cell faces.) The light green and light blue bonds in these

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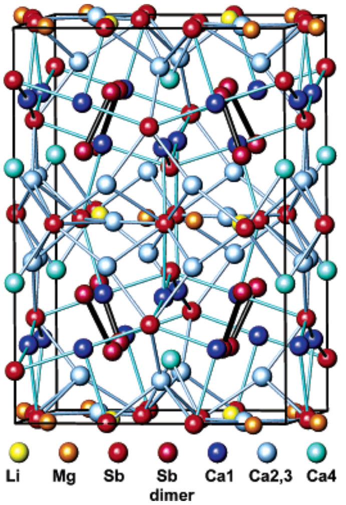

Figure 1. ~[010] projection of the unit cell of $LiMgCa_{10}Sb_9$ and its isotypes. The atom legend is given below the figure.

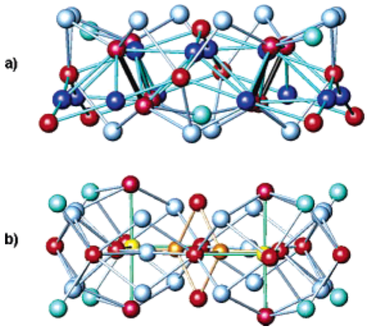

Figure 2. ~[010] views of the two slab types in $LiMgCa_{10}Sb_9$ (**1**) and its isotypes (see the color legend in Figure 1.) (a) The layer around $z = {}^{1}/_{4}, {}^{3}/_{4}$ that contains the Sb1−Sb2 dimers (dark red), Ca1 (dark blue), single Sb5, Sb6 (red), and the surrounding Ca2 (light blue) atoms. (b) The slab around $z = 0, {}^{1}/_{2}$ composed of a layer of M1 (orange, Mg), M2 (yellow, Li), Ca3, Sb3, and Sb4. The surrounding Ca2 (light blue) and Ca4 (blue green) are common to both slabs.

two emphasize the Ca−Sb networks. The bonded antimony neighbors of Li and Mg are also included in Figure 2b, so that this illustration includes Sb2 and Sb5 atoms from the first layer. The (lighter blue) Ca2 ions constitute common features of both layer types in Figure 1 inasmuch as these lie in general positions in layers around about $z = 0.1$, 0.4, 0.6, and 0.9. All Ca atoms are bonded to the dimers at 3.12−3.49 Å, Ca1 (dark blue) within the dimer layers forming three such bonds, and the rest, two. Only Ca4 atoms (colored blue-green) have four rather than five or six Sb neighbors and, reasonably, somewhat larger U(iso) values (Table 2). In contrast, all Sb atoms have six to nine cation neighbors, most of these being calcium.

The environment of Mg (M1) in the first phase consists of four isolated Sb atoms at ~2.86 Å that come close to describing a tetrahedron. On the other hand, the Li (M2) surroundings are more irregular and unusual (Figure 3), a strongly flattened tetrahedron, or a "teeter-totter" defined by two Sb3 plus two Sb2 (dimer ends) that are nearly collinear with Li. This arrangement also "sits on" a rectangle of Ca2 atoms that are each 3.50 Å from Li. This irregular cation site is very similar in all three compounds, as will be considered a bit more below.

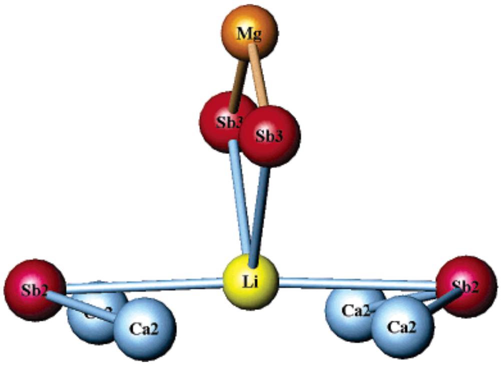

Figure 3. The unusual environment about the M2 site, Li in this example.

Table 3. Bond Distances (Å) in the $A_2Ca_{10}Sb_9$ Phases **1**, **2**, and **3**

M1 M2		Mg Li	Mg1 Mg2	Li1 Ca5/Li2
Ca1	Sb1	3.355(1)	3.384 (1)	3.386(2)
Ca1	Sb1	3.431(1)	3.452(1)	3.488(2)
Ca1	Sb2	3.428 (1)	3.440 (1)	3.463(2)
Ca1	Sb3	3.388 (1)	3.417 (1)	3.357(2)
Ca1	Sb5	3.132(1)	3.146 (1)	3.124(2)
Ca2	Sb1	3.116(1	3.115 (1)	3.115(2)
Ca2	Sb2	3.216 (1)	3.245 (1)	3.282(2)
Ca2	Sb3	3.176 (1)	3.181(1)	3.213(2)
Ca2	Sb3	3.392 (1)	3.379(1)	3.365(2)
Ca2	Sb6	3.163(1)	3.174(1)	3.144(2)
Ca2	M2	3.486(4)	3.484(1)	3.584(2)
Ca3	Sb1 × 2	3.474 (1)	3.499(1)	3.550(3)
Ca3	Sb3 × 2	3.1020(7)	3.1025(6)	3.081(1)
Ca3	Sb4	3.189(2)	3.249(2)	3.391(5)
Ca4	Sb2 × 2	3.1677(7)	3.2013(7)	3.157(1)
Ca4	Sb4 × 2	3.268 (2)	3.315(2)	3.434(4)
M1	Sb3 × 2	2.850(2)	2.840(2)	2.94(2)
M1	Sb5 × 2	2.867(3)	2.921(3)	2.80(2)
M1	M2	3.37(2)	3.454(7)	3.35(3)
M2	Sb2	2.950(1)	3.0308(6)	3.009(1)
M2	Sb3	3.276(1)	3.406(3)	3.195(5)
Sb1	Sb2	2.9107(9)	2.9033(8)	2.916(1)

The other two isotypes, $Mg_2Ca_{10}Sb_9$ and $Li_{1.38}Ca_{10.62}Sb_9$, are generally indistinguishable from the first at the resolution of Figures 1−3 except for differences in the first two elements on their respective sites. The first 4f site (M1) is successively occupied by Mg, Mg1, and Li1 in compounds **1**, **2**, **3** and the second (M2) by Li, Mg2, and Ca4/Li2, respectively (Table 3). The last member is the only one with a detectable mixed occupancy, Ca4/Li2 = 0.62(2)/0.38 in the presence of excess Li. (Lesser amounts are presumably possible too.) (One can even imagine some distance correlations between the disk-shaped thermal ellipsoids refined for the mixed Ca4/Li2 site and the bonded Sb3 around site M2 if these are taken literally.) Overall, both the positional parameters (Table 2) and the distances (Table 3) demonstrate how very similar these two sites are in all three phases at a semiquantitative level. The environment around site M2 (Li) in phase **1** was illustrated in Figure 3; again, the arrangements around this position in the other two structural versions are substantially identical visually. This distorted result must represent one of the many compromises necessary in a complex polar structure such as this; this particular assembly may be close to the least important energetically.

Overall, this rather complex structure containing three or four atom types reveals an effective way of providing all

Table 4. Nearest-Neighbor Distances (Å) around M2 Positions

phase	**1**	**2**	**3**
M2 atom	Li	Mg2	Ca4/Li2
crystal radius[a]	0.90	0.86	1.05
	Neighbors		
2 Sb2[b]	2.95	3.03	3.01
2 Sb3	3.28	3.41	3.20
avg	3.11	3.22	3.10
Ca2	3.50	3.48	3.58
M1	3.37 (Mg)	3.45 (Mg1)	3.35 (Li1)

[a] Reference 17. [b] Dimer atoms exhibit the expected smaller effective radii.

cations with a good environment of bonded anions, and vice versa, while at the same time minimizing close contacts between like-charged species. Obviously the choice serves to maximize both Coulombic and covalent types of interactions in this fairly complex "salt". The partial formation of antimony dimers affords a ready buffer in reducing the overall anion charge to some degree and thence the number of cations necessary.

The unusual M2 atom environments illustrated in Figure 3 also contain the closest approaches by other M-site cations (since these are all organized in layers at $z = 0, {}^1/_2$) as well as some seemingly irregular distance trends. The distances about the M2-sited cations are collected in Table 4. To gain some measure of relative sizes, the CN6 crystal radii[17] for Li, Mg, and Ca/Li (weighted) are also listed. On comparison, the Mg−Sb distances in the table appear to be disproportionately large in compound **2**, perhaps because of Mg1−Mg2 repulsions reflecting their higher effective charges (or because of other less-simple effects in this complex structure). The separations between neighboring cations of course involve relatively large distances, around 1.5 Å greater than crystal radius sums. Even so, the relative intercation distances in phase **3** around the mixed Ca/Li appear to be the shortest by ca. 0.15−0.2 Å.

Properties. This series of compounds is particularly interesting regarding their valence properties. Phase **1** with atom dispositions $LiMgCa_{10}(Sb)_5(Sb_2)_2$ counts out as a valence compound and therefore as a ideal Zintl phase according to customary oxidation state assignments; viz., $1 + 2 + 10(2) + 5(-3) + 2(-4) = 0$. Of course, anion−cation covalency is expected to be appreciable, but this need not upset the oxidation state assignments or the closed shell implication for **1**. Although many supposed Zintl phases do not actually meet such literal ideal assignments when definitive properties such as conductivity and magnetic susceptibility are considered (particularly with alkaline-earth or rare-earth metal cations or less tightly bound anions[18,19]), the present phase (**1**) does appear to meet these tests. Its resistivities at 123−223 K were generally too large to be measured by the Q method, i.e., some hundred $\mu\Omega$ cm. However, magnetic susceptibility data (Supporting Information) indicate this phase is diamagnetic (rather than Pauli-paramagnetic as found for metallic examples,[8]) with M/H at 30 kOe equal to about -2.3×10^{-4} emu/mol over ~100−350 K. The three phases of course nicely demonstrate that it is possible to vary the overall electron population via small cation alterations, making **2** 1 e^- rich per formula unit and **3** about 0.4 e^- poor, both presumably behaving as relatively electron-poor metals. There is no good evidence that the electronic differences in **2** and **3** are localized in the dimer bonding, these varying only between 2.903(1) and 2.916(1) Å in length, respectively, and in the "wrong" direction as well.

Acknowledgment. We are indebted to Serge Bud'ko for the susceptibility data.

Supporting Information Available: Tables of more-detailed crystal and structural refinement data and anisotropic displacement ellipsoids for the three structures; one figure of magnetic susceptibility data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051536U

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