Synthesis and Structural Characterization of $L^{1,2}\text{Mg}$ -substituted Polystibides, $[(L^{1,2}\text{Mg})_4\text{Sb}_8]$

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Dedicated to Prof. Dr. H. W. Roesky on the occasion of his 80th birthday

Abstract: Redox reactions of $[\text{L}^{1,2}\text{Mg}]_2$ and Sb_2R_4 ($\text{R} = \text{Me}, \text{Et}$) yielded the first Mg-substituted realgar-type Sb_8 polystibides, $[(\text{L}^{1,2}\text{Mg})_4(\mu_4, \eta^{2,2,2,2}\text{-Sb}_8)]$ $\{\text{L}^1 = \text{HC}[\text{C}(\text{Me})\text{N}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)]_2$ (**1**), $\text{L}^2 = \text{HC}[\text{C}(\text{Me})\text{N}(2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)]_2$ (**2**)\}. $[\text{L}^{1,2}\text{Mg}]_2$ serve as reducing agents, initiating the cleavage of the Sb-C bonds, and as stabilizer for the resulting Sb_8 polyanion. **1** and **2** were characterized by NMR, IR, elemental analysis and X-ray structure analysis. In addition, results from quantum chemical calculations are presented.

Metal-metal bonded compounds have attracted tremendous attention in recent years due to their fundamental appeal and their unique combination of properties, which facilitate their use in catalysis and small molecule activation.^[1] Spectacular examples of the d-block elements are the quadruple bonded dianion $[\text{Re}_2\text{Cl}_8]^{2-}$ and the quintuple bonded Cr(I) dimer $[\text{Ar}^*\text{CrCrAr}^*]$ $\{\text{Ar}^* = 2,6\text{-(Dipp)}_2\text{C}_6\text{H}_3$; Dipp = 2,6-diisopropylphenyl\} as well as Carmona's dizincocene $\text{Cp}^*\text{Zn-ZnCp}^*$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$).^[2] Inspired by this report, theoretical calculations predicted the existence of chemically relevant Mg(I) dimers^[3] and "bottleable" derivatives $[\text{L}^{2,3}\text{Mg}]_2$ $\{\text{L}^2 = \text{HC}[\text{C}(\text{Me})\text{N}(\text{Dipp})]_2$, $\text{L}^3 = (\text{NPr}_2)\text{C}(\text{N}(\text{Dipp}))_2\}$ were reported in 2007 by Green, Jones and Stasch.^[4] Since then, the number of Mg(I) dimers, which are typically stabilized by bulky, often chelating organic ligands, steadily increased.^[5]

Mg(I) compounds are soluble and selective two-electron reducing agents.^[6] Their promising potential for the synthesis of unusual complexes was demonstrated in reduction reactions of carbodiimide, azobenzene, cyclooctatetraene, azides, isocyanates, CO_2 , N_2O and SO_2 .^[5a,7,8] In addition to their widespread reactivity toward small organic molecules, Mg(I) dimers also function as "soft reductants" in the synthesis of low-valent p-block derivatives such as $[(^t\text{BuMes})\text{Sn}]_2$ ($^t\text{BuMes} = \text{HC}[\text{C}(\text{Bu})\text{N}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)]_2$),^[9] $[(\text{IPr})\text{M}=\text{M}(\text{IPr})]$ ($\text{M} = \text{Ge}, \text{Sn}, \text{AlH}_2$; IPr = $:\text{C}(\text{N}(\text{Dipp})\text{C}(\text{H}))_2$),^[10] L^*SnSnL^* ($\text{L}^* = \text{-N}(\text{Ar})(\text{SiPr}_3)$, $\text{Ar} = \text{C}_6\text{H}_2[\text{C}(\text{H})\text{Ph}_2]_2\text{-Pr-2,6,4}$),^[11] $[(\text{Butiso})\text{M}]_2$ $\{\text{M} = \text{Si}, \text{Ge}, \text{Sn}$; Butiso = $(\text{DippNH})(\text{DippN})\text{C}(\text{C}_6\text{H}_4\text{-Bu-4})$ \},^[12] $[(^t\text{BuNac})\text{Ge}]$ ($^t\text{BuNac} = \text{HC}[\text{C}(\text{Bu})\text{N}(\text{Dipp})]_2$),^[13] and $[(\text{Et}_3\text{P})_2\text{Pt}(\text{B}_2\text{Dur}_2)]$ ($\text{Dur} = 2,3,5,6\text{-tetramethylphenyl}$),^[14] respectively. The Mg(I) dimers were found

to behave superior compared to the traditional heterogeneous reductants such as Na, K and KC_8 .

As part of our general interest in the chemistry of heavier group 13/15 elements, we recently described reactions of group 13 diyls L^2M ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) with Et_3E and Et_4E_2 ($\text{E} = \text{Sb}, \text{Bi}$), which proceeded with insertion of L^2M into the E-C, E-E bonds and subsequent formation of $\text{L}^2\text{M}(\text{Et})\text{BiEt}_2$ and $\text{L}^2\text{M}(\text{EEt}_2)_2$.^[15] The organic substituents at E were shown to have a subtle influence on the outcome of these reactions. A notable example is the reaction of L^2Ga and $\text{Sb}(\text{NMe}_2)_3$, which afforded a Ga-substituted distibene, $\text{L}^2(\text{Me}_2\text{N})\text{GaSb}=\text{SbGa}(\text{NMe}_2)\text{L}^2$ and the first example of a Sb analogue of bicyclo[1.1.0]butane, $[\text{L}^2(\text{Me}_2\text{N})\text{Ga}]_2\text{Sb}_4$.^[16] In this context, we now report on the formation of $[(\text{L}^{1,2}\text{Mg})_4\text{Sb}_8]$ $\{\text{L}^1 = \text{HC}[\text{C}(\text{Me})\text{N}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)]_2$ (**1**); $\text{L}^2 = \text{HC}[\text{C}(\text{Me})\text{N}(\text{Dipp})]_2$ (**2**)\} from the reactions of Sb_2R_4 ($\text{R} = \text{Me}, \text{Et}$) with $[\text{L}^{1,2}\text{Mg}]_2$.

Scheme 1. Synthesis of **1** and **2**.

The reactions of Sb_2R_4 ($\text{R} = \text{Me}, \text{Et}$) with $[\text{L}^{1,2}\text{Mg}]_2$ in 2:5 molar ratio, which are accompanied by gradual color changes from pale yellow to red-orange, led to the formation of $[(\text{L}^{1,2}\text{Mg})_4\text{Sb}_8]$ ($\text{L}^1 = \textbf{1}$; $\text{L}^2 = \textbf{2}$) in 27-30% yield. At ambient temperature, the reactions were completed after 1 (**1**) or 3 (**2**) days, whereas at 80 °C, the starting reagents Sb_2R_4 , $[\text{L}^{1,2}\text{Mg}]_2$ were consumed completely after 4h (**1**) and 18h (**2**), respectively. Similar to the scrambling reaction of $\text{L}^2\text{Ga}(\text{I})$ with Sb_2Et_4 , which led to the insertion compound $\text{L}^2\text{Ga}(\text{SbEt}_2)_2$,^[15b] the reaction may proceed with initial formation of $\text{L}^{1,2}\text{Mg-SbR}_2$, which is then reduced by $[\text{L}^{1,2}\text{Mg}]_2$ to afford the polystibides **1** and **2** as well as $\text{L}^{1,2}\text{MgR}$ ($\text{R} = \text{Me}, \text{Et}$). However, *in situ* NMR experiments gave no evidence for the formation of $\text{L}^{1,2}\text{Mg-SbR}_2$. Equimolar reaction of $[\text{L}^{1,2}\text{Mg}]_2$ and Sb_2Et_4 also did not produce $\text{L}^{1,2}\text{Mg-SbEt}_2$, instead only the formation of **1** and **2** and excess of Sb_2Et_4 along with $\text{L}^{1,2}\text{MgEt}$ were observed in the ^1H NMR spectra. For the synthesis of **2**, Sb_2Me_4 was preferred over Sb_2Et_4 due to the poor solubility of L^2MgMe in aromatic solvents, which makes it easier to separate **2** from the reaction mixture. A similar reaction of $[\text{L}^{1,2}\text{Mg}]_2$ with Bi_2Et_4 at room temperature immediately resulted in the formation of a metallic mirror and $\text{L}^{1,2}\text{MgEt}$.

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1 and **2**, which have to be handled with care since they quickly turn into black precipitates upon treatment with trace of air and water, are stable in solution and in the solid state at ambient temperature under argon atmosphere in a glovebox. They are sparingly soluble in benzene and toluene at ambient temperature, but dissolve well upon heating. The ^1H NMR spectrum of **1** in C_6D_6 shows eight resonances at ambient temperature. The C_2 rotation axis of L^1 ligand is lost by coordination to the Sb_8 moiety. Therefore two sets of ^1H NMR signals are detected compared to L^1H or $[\text{L}^1\text{Mg}]_2$ (see ^1H signal sets of **1**, L^1H and $[\text{L}^1\text{Mg}]_2$ in SI). $o\text{-CH}_3$ groups of $o\text{-CH}_3$ pairs surprisingly display only one signal at 2.20 ppm, while two separate signals appear in the $^{13}\text{C}\{^1\text{H}\}$ NMR at 20.94, 20.51 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** at room temperature shows 17 signals including the characteristic resonances due to the $\gamma\text{-CH}$ (94.59 ppm), the remaining two $\text{C}_3\text{N}_2\text{Mg}$ ring carbons (168.97, 168.23 ppm) and the methyl carbon atoms of mesityl groups {22.59 ($p\text{-CH}_3$), 21.99 ($p\text{-CH}_3$), 20.94 ($o\text{-CH}_3$), 20.51 ($o\text{-CH}_3$) ppm} as well as the $\text{C}_3\text{N}_2\text{Mg}$ ring (23.76, 23.57 ppm). The remaining signals are from the phenyl carbon atoms {144.97, 144.06, 133.97, 133.50, 132.35, 131.79, 130.60 ($m\text{-C}$), 130.46 ($m\text{-C}$) ppm}.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral patterns of **2** are similar to **1**. The ^1H NMR spectrum of **2** in toluene- d_8 exhibits single resonances for the $\gamma\text{-H}$ and two methyl groups of the $\text{C}_3\text{N}_2\text{Mg}$ ring at 4.74, 1.60 and 1.54 ppm, respectively. The methyl protons of the isopropyl substituents broaden from 1.50 to 0.95 ppm, whereas the methine protons appear as a two overlapping septets at 2.99 ppm. Similar broad signals have also been observed in the aromatic and aliphatic regions of **2** in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, however, the observed signals are in consistence with the characteristic resonances of the organic substituents. Although **1** and **2** were reproducibly isolated in pure forms from both reactions, additional peaks were observed in the ^1H NMR spectra of the crude reaction mixtures. Unfortunately, all our efforts to isolate other components of the reaction mixture failed, to date.

Crystals of **1** and **2** were obtained from a saturated benzene solution at ambient temperature after storage for several days.^[17] **1** crystallizes in the triclinic space group $P\bar{1}$. In the molecular structure of **1**, the unit cell consists of two independent molecules with almost identical conformations and structural parameters. One of these is depicted in Figure 1 and described (*vide infra*). **2** crystallizes in the tetragonal space group $P4/ncc$ with the molecule placed on Wyckoff-position 4a. The 2.22 symmetry of this position leads to a quarter of the molecule forming the asymmetric unit. The crystals of **2** showed severe degradation of quality and signs of modulation upon cooling to 100 K. Therefore, the crystal was measured at 200 K. The quality of the resulting model is still limited but good enough to give a realistic view of the connectivity, while quantitative results should be carefully accessed (Fig. S16).

The structures of **1** and **2** each consist of a Sb_8 unit stabilized by four chelating $\text{L}^{1,2}\text{Mg}$ moieties. Each Mg center is fourfold-coordinated by a chelating β -diketiminato ligand and two Sb atoms with distorted tetrahedral geometry. The mean Mg-N bond distances (2.026 Å **1**, 2.063 Å **2**) within the almost

planar the $\text{C}_3\text{N}_2\text{Mg}$ heterocycles of **1** and **2** are comparable to those reported for β -diketiminato magnesium complexes with fourfold coordinated Mg atom such as $\text{L}^1\text{Mg}(\text{OEt}_2)$ [2.031(2); 2.036(2) Å], $\text{L}^1\text{Mg}(\text{THF})$ [2.026(2); 2.036(2) Å], $[\text{L}^1\text{Mg}]_2$ [2.004(2); 2.001(2) Å], $[\text{L}^1\text{MgH}]_2$ [2.0219(14); 2.0226(13) Å]^[10c] and to those reported for $(\text{L}^1)_2\text{Mg}$ [2.0796(17); 2.0579(17); 2.0738(17) Å].^[5c] The Mg-Sb bond lengths of **1** (2.8459(10) Å - 2.9007(10) Å) are slightly shorter compared to those of **2** (2.882(3) - 3.007(3) Å), but for both compounds the sum of the covalent radii (Mg = 1.39 Å; Sb = 1.40 Å) is slightly exceeded.^[18] The Sb-Mg-Sb angles of **1** (87.07(3)° - 88.68(3)°) and **2** (84.76(8)°) are similar. The only structurally characterized magnesium stibide, $[\text{Me}_2\text{SiSi}(\text{SiMe}_3)_2\text{SbMgBr}(\text{OEt}_2)_2]$ shows a slightly shorter Mg-Sb bond distance of 2.7806(13) Å.^[19] The eight Sb atoms in **1** can be divided into tricoordinated (Sb') and tetracoordinated (Sb'') atoms (Fig. 2). The Mg-Sb''-Mg units are almost linear [174.45(3)° - 178.17(3)°], while the butterfly shaped $\text{Mg}_4\text{Sb}''_4$ unit has a dihedral angle of 29.35° (Mg1-Mg4-Mg3-Mg2). The angles within the Sb_8 cluster of **1** range from 89.449(11)° to 103.226(11)° and the Sb-Sb distances range from 2.7974(4) Å to 2.8582(4) Å, which agrees to those observed in $[(\text{Me}_3\text{Si})_2\text{CH}]_4\text{Sb}_8$ (2.784(4)-2.8618(4) Å).^[20] Note that the Sb'1-Sb'2 (2.8580(4) Å) and Sb'3-Sb'4 (2.8582(4) Å) bond distances of **1** are slightly longer than the other Sb-Sb bonds, which range from 2.7974(4) to 2.8209(4) Å. Comparable findings were observed for **2**, which also shows a long Sb'-Sb' bond (2.8616(12) Å) and shorter Sb'-Sb'' bonds (2.7820(8) - 2.8084(7) Å).

Figure 1. Molecular structure of $[(\text{L}^1\text{Mg})_4\text{Sb}_8]$ **1**. H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths and angles in Å and °: Mg1-Sb5 2.8459(10), Mg1-Sb6 2.9007(10), Mg2-Sb6 2.8958(11), Mg2-Sb7 2.8603(10), Mg3-Sb7 2.8627(9), Mg3-Sb8 2.8663(10), Mg4-Sb5 2.8521(9), Mg4-Sb8 2.8855(10), Sb1-Sb2 2.8580(4), Sb1-Sb5 2.8130(4), Sb1-Sb6 2.8113(4), Sb2-Sb7 2.7974(4), Sb2-Sb8 2.8209(4), Sb3-Sb4 2.8582(4), Sb3-Sb5 2.8083(4), Sb3-Sb8 2.8082(4), Sb4-Sb6 2.8174(4), Sb4-Sb7 2.8056(4), Sb5-Mg1-Sb6 87.43(3), Sb6-Mg2-Sb7 87.69(3), Sb7-Mg3-Sb8 88.68(3), Sb5-Mg4-Sb8 87.07(3), Sb1-Sb5-Sb3 101.109(12), Sb1-Sb6-Sb4 99.422(10), Sb2-Sb7-Sb4 100.821(11), Sb2-Sb8-Sb3 99.378(10), Mg1-Sb6-Mg2 174.45(3), Mg2-Sb7-Mg3 178.17(3), Mg3-Sb8-Mg4 175.40(3), Mg1-Sb5-Mg4 177.32(3). Data of the second independent molecule are given in the cif file.

The solid state structures of **1** and **2** are very similar to those of analogous polyphosphides, i. e. $[(L_2M)_4P_8]$ $\{L = Cp^*, M = Sm; L_2 = 1,1'-fc(NSi^tBuMe_2)_2, M = Sc\}$,^[21] which were obtained from redox reactions of white phosphorous P_4 with divalent Cp^*_2Sm or the scandium naphthalene complex $[(NN^{f6})Sc]_2(\mu-C_{10}H_8)$,^[22] as well as of $Cp'_4Fe_4(CO)_6P_8$, $Cp'_4Fe_6(CO)_{13}P_8$ ($Cp' = \eta^5-C_5H_4Me$)^[23] and alkyl-substituted P_8R_4 clusters.^[24] Since the dimerization of two P_4 molecules to a P_8 unit is enthalpically disfavored,^[25] their formation was explained by the electron transfer from the reducing agent to the P_4 molecule, subsequently yielding tetraanionic polyphosphides P_8^{4-} , which adopt realgar-type structures, also called α - P_8 structure. According to quantum chemical calculations, the neutral P_8 molecule should adopt the cuneane structure, which shows two additional P-P bonds compared to the α - P_8 structure, which are replaced by four lone pairs in the polyphosphides.^[26]

In analogy to these phosphorus compounds, the central Sb_8 unit in **1** and **2**, which also adopt the realgar-type homoatomic structure, can be described as Sb_8^{4-} unit. Even though homoatomic Zintl-type polystibides including Sb_4^{2-} , Sb_5^{5-} , Sb_7^{3-} and Sb_{11}^{3-} are well known,^[27] to the best of our knowledge, **1** and **2** represent the first examples containing a $[Sb_8]^{4-}$ polyanion. However, Korber et al. reported on the structure of a $[Sb_8]^{8-}$ Zintl anion, which adopts a ring structure as observed for S_8 .^[28] In addition, Breunig et al. synthesized the polystibine $Sb_8[CH(SiMe_3)_2]_4$, a metal organic derivative containing an analogous Sb_8 core as observed for **1** and **2**, by reduction of $(SiMe_3)_2HCSbCl_2$ with Mg ,^[20] while von Hähnisch et al. successfully prepared $[Sb_4(PSiMe_2Thex)_4]$ (Thex = CMe_2Pr) and $[Sb_4(AsSiPr_3)_4]$ with central Sb_4E_4 ($E = P, As$) realgar-type core structures.^[29] The Sb-Sb bond lengths in $[Sb_4(PSiMe_2Thex)_4]$ (2.879 Å) and $[Sb_4(AsSiPr_3)_4]$ (2.881–2.890 Å) are slightly elongated compared to those in **1**.

Figure 2. Mg_4Sb_8 skeleton of **1**. L^1 ligands are omitted for clarity, ellipsoids are drawn at 30% probability level.

Very recently, Roesky et al. reported the first examples of Sm substituted polyarsenides, $[(Cp''_2Sm)(\mu, \eta^4-\eta^4-As_4)(Cp^*Fe)]$ and $[(Cp''_2Sm)_2As_7(Cp^*Fe)]$ ($Cp'' = \eta^5-1,3-(tBu)_2C_5H_3$) from the redox reactions of $[Cp^*Fe(\eta^5-As_5)]$ and $[Cp''_2Sm(thf)]$. $[(Cp''_2Sm)(\mu, \eta^4-\eta^4-As_4)(Cp^*Fe)]$ is a first d/f-triple decker sandwich complex containing a central As_4^{2-} unit, whereas $[(Cp''_2Sm)_2As_7(Cp^*Fe)]$ consist of a norbornadiene-type As_7^{3-}

cage structural motif.^[30a] $[L^2MgBu]$ is also known to activate white phosphorus and afforded the dianions $[nBu_2P_4]^{2-}$ and $[nBu_2P_8]^{2-}$ from 2:1 and 1:1 molar reactions of P_4 and $[L^2MgBu]$.^[30b] In addition, a cuneane-type complex $\{[Cp^*IrCO]_2-P_8[Cr(CO)_5]_3\}$ was obtained by reaction of white phosphorus with $[Cp^*Ir(CO)_2]$ under thermal and photochemical conditions.^[30c]

To gain further insight into the interatomic interactions, electronic structure calculations were performed for **1** with an emphasis on the bonding situation in the Mg_4Sb_8 skeleton (Figure 3a).^[31]

Figure 3. Atomic labeling for the Mg_4Sb_8 skeleton (a) and ELF distribution in $[(L^1Mg)_4Sb_8]$ complex in the $Sb_5-Sb_6-Sb_7$ (b), $Mg_1-Sb_1-Sb_2$ (c), and $Sb_4-Sb_7-Sb_2$ (d) planes. $V(Mg,Sb)$, $V(Sb)$, and $V(Sb,Sb)$ basins are indicated by white (b), red (c), and black (c, d) arrows.

BP86-D3BJ/def2-SVP computation^[32] converged to a D_{2d} -symmetrical structure of $[(L^1Mg)_4Sb_8]$. The calculated geometric parameters agree well with the experimental values (deviations from exp. bond lengths range within 0.03–0.08 Å for Mg_4Sb_8 core). The $(L^1Mg)^+$ moiety was found to rather strongly bind to $[(L^1Mg)_3Sb_8]^-$ ($\Delta G_{298}^\circ = 136.9$ kcal/mol, Table S1). The ΔG_{298}° value for the dissociation of $[(L^1Mg)_4Sb_8]$ into four $(L^1Mg)^+$ and one Sb_8^{4-} ions is equal to 989.4 kcal/mol at B3LYP-D3BJ/def2-TZVP/BP86-D3BJ/def2-SVP level of theory (Table S1).^[33] According to the energy decomposition analysis (Table S2),^[34] electrostatic interaction (ΔE_{elstat} , 44%) between $(L^1Mg)^+$ and $[(L^1Mg)_3Sb_8]^-$ is dominated over orbital interaction (ΔE_{orb} , 32%). It is important to note that the dispersion term (ΔE_{disp} , 24%) also gives noticeable contribution to the total attractive interactions. Computed atoms in molecules (AIM) parameters (Table S3) indicate an *intermediate* character for the Mg–Sb and Sb–Sb bonds ($\nabla^2\rho(r_b) > 0$; $1 < |V(r_b)|/G(r_b) < 2$, $H(r_b) < 0$).^[35] However, the Mg–Sb bonds have a high ionic contribution, while the Sb–Sb bonds are rather covalent, as can be seen from the corresponding values of AIM parameters. Natural population analysis (NPA) partial charges on Mg and Sb (+1.16 |e| vs. -0.54/-0.55 |e|; Table S3) imply highly polarized Mg–Sb bonds. Additionally, natural bond orbital analysis (NBO)^[36] reveals no covalent Mg–Sb bonds, which is in line with results of quantum chemical calculations on a Li_4Sb_8 cluster with realgar-

type $[\text{Sb}_8]^{4-}$ skeleton,^[37] for which ionic interactions between the Li and Sb atoms were found. The chemical bonding pattern for the Sb_8 fragment in $[(\text{L}^1\text{Mg})_4\text{Sb}_8]$ complex is analogue to the $[\text{Sb}_8]^{4-}$ core of the Li_4Sb_8 cluster.^[37] It includes eight s-type lone pairs (occupation number (ON)=1.9 |e| for Sb1, Sb2, Sb3, Sb4; ON=1.7 |e| for Sb5, Sb6, Sb7, Sb8), four p-type lone pairs (ON=1.9 |e|), and ten covalent two-center two-electron Sb–Sb bonds (ON=1.9 |e|). Electron localization function (ELF)^[38] (Figure 3b) reveals eight valence basins between Mg and Sb atoms with a population of 2.5 e (Table S3), indicating some extent of covalent bonding. However, these V(Mg,Sb) basins are displaced from the corresponding bond lines, which is not typical for covalent bonds. Moreover, Mg contributes into V(Mg,Sb) basin only 0.1 e, as calculated by ELF/AIM intersection procedure (Table S3).^[39] So, these objects can be attributed to the lone pairs of Sb $[\text{V}(\text{Mg,Sb}) \approx \text{V}(\text{Sb})]$. As shown in Figure 3c, each inner Sb atom (Sb1, Sb2, Sb3, Sb4) have one V(Sb) valence monosynaptic basin populated by 2.7 e, which is associated with the lone pair localized on Sb. The presence of V(Sb,Sb) basins ($\bar{N}[\text{V}(\text{Sb,Sb})]=1.4\text{--}1.6$ e; Figures 3c, d) suggests a covalent bonding between these atoms. Thus, on the basis of the AIM, EDA, ELF, and NBO analyses one can conclude that the Sb–Sb bonds possess a covalent nature, whereas the Mg–Sb bonds have a mixed character with a dominant ionic contribution. In other words, bonds between Mg and Sb atoms are highly polar covalent.

In summary, the first magnesium polystibides containing realgar-type clusters of the general type $[(\text{L}^{1,2}\text{Mg})_4\text{Sb}_8]$ were obtained in two-centered/two electron reduction reactions of $[\text{L}^{1,2}\text{Mg}]_2$ with Sb_2R_4 (R = Me, Et). In spite of their different steric environments, both mesityl and diisopropylphenyl derivatives of $[\text{L}^{1,2}\text{Mg}]_2$ gave similar clusters. Compounds **1** and **2** are presumably the orthogonally fused version of the two bicyclo[1.1.0]butane type Sb_4 units. Such dimerizations have been observed in As derivatives. For example, stirring the solution of $[(\text{Cp}^*\text{Cr}(\text{CO})_3)_2(\mu_4, \eta^{1:1:1:1}\text{-As}_8)]$ under ambient conditions led to $[(\text{Cp}^*\text{Cr}(\text{CO})_3)_4(\mu_4, \eta^{1:1:1:1}\text{-As}_8)]$. Similarly, UV irradiation of $[(\text{Cp}^*\text{Fe}(\text{CO})_2)_2(\mu, \eta^{1:1}\text{-As}_4)]$ ($\text{Cp}^* = 1,2,4\text{-}(\text{tBu})_3\text{C}_5\text{H}_2$) for 2 h produced $[(\text{Cp}^*\text{Fe}(\text{CO})_2)_2(\text{Cp}^*\text{Fe}(\text{CO}))_2(\mu_4, \eta^{1:1:2:2}\text{-As}_8)]$.^[40] We are currently looking at the possibilities of synthesizing lower aggregated complexes ($\text{Sb} < 8$) such as the hypothetical molecules $\text{L}^{1,2}\text{MgSb}=\text{SbMgL}^{1,2}$, $(\text{L}^{1,2}\text{Mg})_2\text{Sb}_4$ and $(\text{L}^{1,2}\text{Mg})_3\text{Sb}_7$, which would give an insight into the formation of polymeric aggregates from simple monomers in such redox reactions.^[16] The use of $[\text{L}^{1,2}\text{Mg}]_2$ as facile two-electron reductants toward other heavier main group elements may offer unprecedented molecules and clusters stabilized by LMg^+ units.

Experimental Section

¹H, ¹³C NMR and IR spectra of **1** and **2** as well as quantum chemical details are given in the electronic supplement.

Synthesis of 1. A mixture of $[\text{L}^1\text{Mg}]_2$ ($\text{L}^1 = \text{HC}[\text{C}(\text{Me})\text{N}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)]_2$) (0.492 g, 0.688 mmol) and Sb_2Et_4 (0.099 g, 60 μL , 0.275 mmol) was dissolved in 1 mL of benzene and heated at 80 °C for 4 h. The reaction mixture was cooled to ambient temperature and the red solution was separated from the white precipitate, L^1MgEt . Storage of the red solution

at room temperature for 5 days yielded red crystals of **1**. Yield: **1**: 50 mg (0.0208 mmol, 30 %), L^1MgEt : 0.404 g (1.044 mmol, 95 %). Anal. Calcd. for $\text{C}_{92}\text{H}_{116}\text{Na}_8\text{Mg}_4\text{Sb}_8$: C, 45.94; H, 4.86; N, 4.66. Found: C, 46.10; H, 4.80; N, 4.70%. IR (neat): ν 3001, 2911, 2849, 1544, 1522, 1443, 1375, 1263, 1190, 1145, 1010, 954, 920, 853, 824, 740, 627, 565, 498 cm^{-1} . ¹H NMR (C_6D_6 , 300 MHz, 25 °C): δ 7.11 (s, 2 H, $\text{C}_6\text{H}_2(\text{Me})_3$), 7.04 (s, 2 H, $\text{C}_6\text{H}_2(\text{Me})_3$), 4.79 (s, 1 H, $\gamma\text{-CH}$), 2.73 (s, 3 H, $p\text{-CH}_3$), 2.56 (s, 3 H, $p\text{-CH}_3$), 2.20 (s, 12 H, $o\text{-CH}_3$), 1.66 (s, 3 H, ArNCCH_3), 1.61 (s, 3 H, ArNCCH_3). ¹³C{¹H} NMR (C_6D_6 , 75.5 MHz, 25 °C): δ 168.97, 168.23 (ArNCCH_3), 144.97, 144.06, 133.97, 133.50, 132.35, 131.79, 130.60 ($m\text{-C}$), 130.46 ($m\text{-C}$) (C_6H_2), 94.59 ($\gamma\text{-CH}$), 23.76, 23.57 (ArNCCH_3), 22.59 ($p\text{-CH}_3$), 21.99 ($p\text{-CH}_3$), 20.94 ($o\text{-CH}_3$), 20.51 ($o\text{-CH}_3$).

Synthesis of 2. $[\text{L}^2\text{Mg}]_2$ ($\text{L}^2 = \text{HC}[\text{C}(\text{Me})\text{N}(\text{Dipp})]_2$) (0.746 g, 0.844 mmol) was suspended in 10 mL of fluorobenzene and Sb_2Me_4 (0.102 g, 50 μL , 0.338 mmol) was added. The reaction mixture was stirred at 80 °C for 18 h. The resulting red solution was separated from the white precipitate L^2MgMe , and stored at room temperature for 15 days to afford analytically pure red crystals of **2**. The manipulation of the reaction products was performed inside the glove box in order to avoid forming the black precipitate. Yield: **2**: 62.4 mg (0.0228 mmol, 27 %), L^2MgMe : 0.565 g (1.236 mmol, 92 %). Anal. Calcd. for $\text{C}_{116}\text{H}_{164}\text{Na}_8\text{Mg}_4\text{Sb}_8$: C, 50.81; H, 6.03; N, 4.09. Found: C, 50.90; H, 6.08; N, 4.15%. IR (neat): ν 2959, 2924, 2863, 1520, 1393, 1309, 1255, 1177, 1099, 1021, 925, 847, 787, 757, 703, 619, 523, 487, 445 cm^{-1} . ¹H NMR (Toluene- d_8 , 300 MHz, 25 °C): δ 7.30–7.14 (m, 6 H, $\text{C}_6\text{H}_3(\text{Pr})_2$), 4.74 (s, 1 H, $\gamma\text{-CH}$), 2.99 (two sept, 4 H, $-\text{CH}(\text{CH}_3)_2$), 1.60 (s, 3 H, ArNCCH_3), 1.54 (s, 3 H, ArNCCH_3), 1.50–0.95 (br m, 24 H, $-\text{CH}(\text{CH}_3)_2$). ¹³C{¹H} NMR (Toluene- d_8 , 150 MHz, 25 °C): δ 169.67, 169.65 (ArNCCH_3), 146.40, 145.36, 143.00, 126.28, 126.24, 125.13 (C_6H_3), 96.25 ($\gamma\text{-CH}$), 28.26 (br s, $-\text{CH}(\text{CH}_3)_2$), 25.99, 25.63 (ArNCCH_3), 25.61, 25.17 (br s), 21.33 ($-\text{CH}(\text{CH}_3)_2$).

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Keywords: Main group elements • Metal-metal interactions • Cluster compounds • Subvalent compounds

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- 1:** [C₉₂H₁₁₆Mg₄N₈Sb₈], M = 2405.16, orange crystal, (0.184×0.166×0.076 mm); triclinic, space group $P-1$; a = 15.3947(18) Å, b = 21.451(3) Å, c = 30.779(4) Å; α = 98.574(6)°, β = 102.194(6)°, γ = 95.022(6)°, V = 9749(2) Å³; Z = 4; μ = 2.253 mm⁻¹; ρ_{calc} = 1.639 g cm⁻³; 260201 reflexes (θ_{max} = 33.338°), 73624 unique (R_{int} = 0.0371); 2081 parameters; largest max./min in the final difference Fourier synthesis 1.696 e⁻ Å⁻³/ -1.021 e⁻ Å⁻³; max./min. transmission 0.40/0.50; R_1 = 0.0337 ($I > 2\sigma(I)$), wR_2 = 0.0878 (all data). **2:** [C₁₁₆H₁₆₄Mg₄N₈Sb₈], M = 2741.78, orange crystal, (0.444 × 0.090 × 0.075 mm); tetragonal, space group $P4/ncc$; a = 24.3186(7) Å, b = 24.3186(7) Å, c = 25.7075(7) Å; α = 90°, β = 90°, γ = 90°, V = 15203.3(10) Å³; Z = 4; μ = 1.453 mm⁻¹; ρ_{calc} = 1.198 g cm⁻³; 161781 reflexes (θ_{max} = 30.576°), 11652 unique (R_{int} = 0.0729); 318 parameters; largest max./min in the final difference Fourier synthesis 4.740 e⁻ Å⁻³/ -1.745 e⁻ Å⁻³; max./min. transmission 0.59/0.75; R_1 = 0.0986 ($I > 2\sigma(I)$), wR_2 = 0.3485 (all data). The crystallographic data (without structure factors) was deposited as „supplementary publication no. CCDC-1436397 (1)“ and CCDC-1448391 (2) at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).
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Entry for the Table of Contents

Polystibides

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Synthesis and Structural Characterization of $L^{1,2}Mg$ -substituted Polystibides, $[(L^{1,2}Mg)_4Sb_8]$

Reduction reactions of distibines Sb_2R_4 ($R = Me, Et$) with monovalent magnesium complexes $[L^{1,2}Mg]_2$ yielded the first tetraanionic polystibides $[(L^{1,2}Mg)_4Sb_8]$ $\{L^1 = HC[C(Me)N(2,4,6-Me_3C_6H_2)]_2$ (**1**), $L^2 = HC[C(Me)N(2,6-i-Pr_2C_6H_3)]_2$ (**2**)}, in which the central Sb_8 cores adopt realgar-type structures.

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