Mixed Lithium Magnesium Aryl Oxides Derived from Cresol: Crystal Structures and Solution NMR Studies of an Unexpected, Magnesium-Rich Oxo Product with a Trigonal Bipyramidal $LiMg_4$ Cage and an Expected Lithium-Rich Product with a More Familiar Li⋯Mg⋯Li Chain

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Intermetallic organoelement compounds of lithium and magnesium, lithium magnesiates, are still numerically rare, even though over 40 years has passed since their initial synthesis.[1−3] Reported herein is the extension of this class of compound to aryl oxides, derived from *o*-cresol. One of the two new cresylates, $[LiMg_4O(R)_7{\cdot}4THF]$ [R = *o*-$Me(C_6H_4)O^-$], **1**, is without precedent in composition, stoichiometry, and structure when compared against lithium magnesiates generally. An oxo (O^{2-}) anion is its unexpected constituent. It appears to be the first Mg-rich lithium magnesiate, as a consequence of its strange 1:4 Li:Mg stoichiometry, which is totally out of line with previously reported Li:Mg ratios (e.g., 1:1 in $[LiMg\{N(CH_2Ph)_2\}_3{\cdot}pyridine]$,[4] 2:1 in $(Li_2MgMe_4{\cdot}2TMEDA)$,[5] and 2:2 in $(Li_2Mg_2Ph_6{\cdot}2TMEDA)$[6]). X-ray crystallographic studies and ^1H NMR spectroscopic studies establish **1** to be a unique $LiMg_4$ cage species, in both the crystal and the solution phase. In stark contrast, the other cresylate, $(Li_2MgR_4{\cdot}2TMEDA)$, **2**, conforms to a well-established type of alkali metal magnesiate, though the participation of anionic oxygen ligands is a new feature.

Serendipitously prepared, but in a significant yield, **1** was produced by a method which, as yet, cannot be explained. A Schlenk tube under argon was charged with an *n*-butyllithium (in hexane)/dibutylmagnesium (in heptane) (5 mmol of each) mixture. Hydrocarbon solvents removed in vacuo were replaced by toluene (10 mL), and then *o*-cresol (40 mmol) was introduced, giving a white precipitate. A further portion of the metal alkyl solution (again, 5 mmol of each) was added, followed by *n*-butyllithium (10 mmol) on its own, so that the final Li:Mg:cresol ratio was 2:1:4. THF (5 mL) was subsequently added to the mixture, which became homogeneous on warming. Finally, some solvent was removed in vacuo to leave a solution which deposited colorless, crystalline **1**[8] on standing at ambient temperature for 12 h. As yet, the source of the oxo contaminant is still not known. Treating another 2:1:4 *n*-butyllithium:dibutylmagnesium:cresol combination with TMEDA (2 equiv or more) had a more straightforward outcome, in the stoichiometry-correct crystalline **2**.[7]

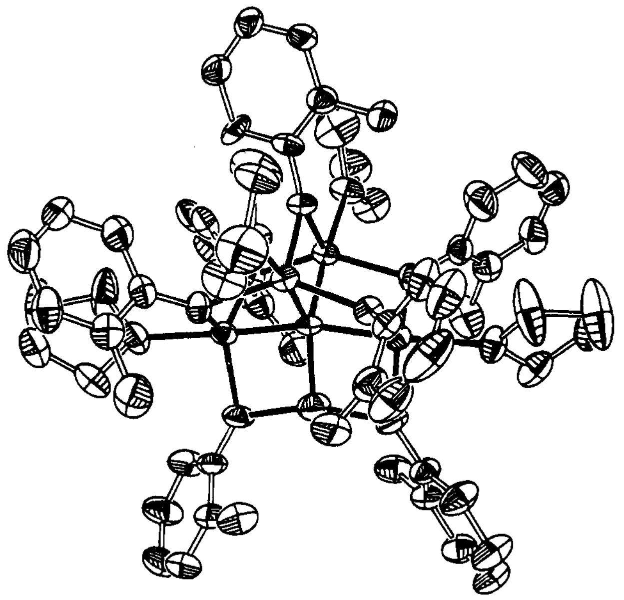

Figure 1. Thermal ellipsoid plot (40% probability) of the structure of **1**. Hydrogen atoms and second components of disordered groups are omitted for clarity.

The principal feature of the molecular structure of **1**[8] (Figure 1) is its oxo-centered, pseudo trigonal bipyramidal $LiMg_4$ core (Figure 2), which has crystallographic C_2 symmetry. Rare in Mg organoelement derivatives generally,[9] a select few cages have emerged recently where the metallic frameworks are supported by N[10] or C[11] ligands. Only one magnesium organo oxygen cage has so far been crystallographically characterized: the alkoxy metallocene $[(\eta^5\text{-}C_5H_5)MgOEt]$[12] displays a $(MgO)_4$ cubane architecture. Turning to the specifics of **1**, equatorial Mg(2) forms a marginally shorter contact to oxo O(4) than does apical Mg(1) [i.e., 2.002(4) Å, cf. 2.041(2) Å], but the Li−O(4) contact is significantly shorter than both [1.89(2) Å]. Here, the lower coordination of Li (i.e., 3 vs. 5 for Mg)

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(7) Melting points: for **1**, > 360 °C; for **2**, 140 °C. Satisfactory analyses (C, H, Li, Mg, N) were obtained.

(8) Crystal data for **1**: $C_{65}H_{81}LiMg_4O_{12}$, $M = 1158.5$, monoclinic, $C2/c$, $a = 13.343(5)$ Å, $b = 21.793(13)$ Å, $c = 21.356(12)$ Å, $\beta = 90.73(6)°$, $V = 6209(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.239$ g cm^{-3} λ(Mo Kα) = 0.710 73 Å, $\mu = 0.119$ mm^{-1}, $F(000) = 2472$. Measurements were made at 160 K on a Stoe-Siemens diffractometer with an Oxford Cryostream cooler from a crystal of size 0.40 × 0.30 × 0.20 mm^3. Structure solution was by direct methods, and all 4072 independent reflections were used for full-matrix least-squares refinement on F^2. H atoms were constrained; other atoms were assigned anisotropic atomic displacement parameters, and restraints were imposed on one disordered *o*-cresylate and one THF. At convergence, $R_w = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2} = 0.2229$, conventional R [on F values for 2374 reflections with $F^2 > 2\sigma(F^2)$] = 0.0660, goodness of fit on $F^2 = 1.057$ for 408 parameters and 106 restraints. All features in a final difference synthesis were within ±0.74 e Å^{-3}. Program systems: SHELXTL/PC, SHELXL−93 (F. M. Sheldrick, University of Göttingen, Germany). Key dimensions: (Å) Mg(1)−O(4) 2.041(2), Mg(2)−O(4) 2.002(4), Li−O(4) 1.89(2), Mg(1)−O(1) 2.012(4), Mg(2a)−O(1) 2.021(4), Mg(1)−O(3) 2.014(4), Mg(2)−O(3) 2.032(4), Mg(2)−O(5) 2.019(4), Mg(1)−O(2) 1.954(4), Li−O(2) 1.822(5), Mg(1)−O(7) 2.116(5), and Mg(2)−O(6) 2.084(4); (deg) LiO(4)Mg(1) 83.23(13), Mg(1)O(4)Mg(1a) 166.5(3). Crystal data for **2**: $C_{40}H_{60}Li_2MgN_4O_4$, $M = 699.1$, monoclinic, $P2_1/n$, $a = 10.687(2)$ Å, $b = 18.455(4)$ Å, $c = 21.952(4)$ Å, $\beta = 101.28(2)°$, $V = 4245.9(14)$ Å^3, $Z = 4$, $D_{calcd} = 1.094$ g cm^{-3}, μ(Mo Kα) = 0.082 mm^{-1}, $F(000) = 1512$. Data collection and structure determination were as for **1**, with crystal size 0.50 × 0.40 × 0.20 mm, 6281 independent reflections, no disorder or restraints, $R_w = 0.1607$, conventional $R = 0.0515$ (for 4466 observed F values), goodness of fit = 1.051, 472 parameters, final difference synthesis within ±0.71 e Å^{-3}. Key dimensions: (Å) Mg−O(1) 1.946(2), Mg−O(2) 1.938(2), Mg−O(3) 1.916(2), Mg−O(4) 1.953(2), Li(1)−O(1) 1.930(5), Li(1)−O(2) 1.917(5), Li(2)−O(3) 1.921(5), Li(2)−O(4) 1.964(5), Li(1)−N(1) 2.147(5), Li(1)−N(2) 2.148(5), Li(2)−N(3) 2.116(5), Li(2)−N(4) 2.212(5).

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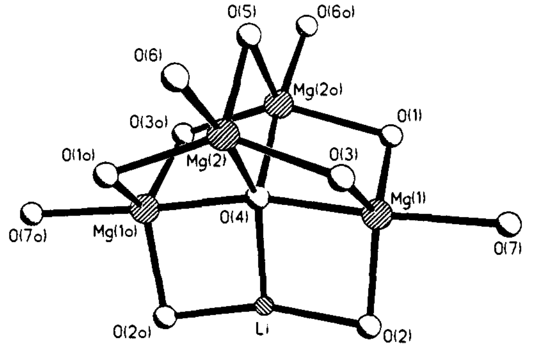

Figure 2. The oxo-centered trigonal bipyramidal core of **1** showing the local coordination geometries of the Li and Mg atoms.

exaggerates the difference in size between the two metal atoms. Seven cresyl ligands maintain the electroneutrality of the intermetallic cage of **1**, bonding through their oxygen atoms to pairs of metal centers. These μ_2-O atoms (and therefore the cresyl ligands themselves) fall into three chemically distinct groups: O(2) and O(2a) bridge Li/Mg mixed pairs; O(1), O(1a), O(3), and O(3a) bridge $(Mg)_2$ pairs and straddle the LiMg(2)-Mg(2a) trigonal plane; unique O(5) bridges the $(Mg)_2$ pair in this plane. Atoms of the first group approach the metal centers more closely, partly due to having fewer THF molecules nearby, with the Li−O bonds again being shorter than their Mg counterparts [i.e., 1.822(5) Å, cf. 1.954(4) Å]. Significantly longer, the remaining μ_2-O−Mg interatomic distances span a relatively narrow range (2.012−2.032 Å). Completing the cage, each Mg is solvated by a peripheral THF molecule which, though terminally bound, forms longer bonds [2.084(4) Å; 2.116(5) Å] than any of the μ_2-O−Mg type. Contrastingly, the Li atom remains THF-free. Overall, the local geometries of the Li and Mg sites can be approximately described as planar T-shaped [e.g., O(2)LiO(2a) = 161.9(10)°] and trigonal bipyramidal [e.g., O(4)Mg(1)O(7) = 175.8(2)°; O(4)Mg(1)O(2) = 90.1(2)°], respectively.

Critical to establishing **1** as an authentic compound rather than a rogue nonrepresentative crystal, further characterization of the bulk sample was achieved by ^{1}H NMR spectroscopy. The Me arm of the cresyl ligands proved useful in identifying the cage nature of **1** in THF-d_8 solution. Three distinct, well-separated singlets at 1.99, 2.43, and 2.80 ppm in the correct 2H:4H:1H ratio can be assigned to the Me groups of the three different cresyl ligands present associated with O(2) and O(2a), with O(1), O(1a), O(3), and O(3a), and with O(5), respectively, in the crystal structure. The complexity observed in the Ph region (a plethora of signals, some of which overlap, covering 6.33−7.25 ppm) provides additional confirmation.[13]

The crystal structure of **2**[8] (Figure 3) belongs to a familiar structural type[2] with two oppositely disposed lithium cations connected to a tetrahedral, tetraorganomagnesiate center by bridging of the organic groups. **2** is unusual in that its central, fused four-membered rings are almost square (mean endocyclic angles: at Li, 88.2°; at Mg, 87.9°; at O, 91.4°), and not rhomboidal as in the carbon and nitrogen analogs (e.g., corresponding angles in (Li_2MgMe_4·2TMEDA),[5] at Li, 107.1°; at Mg, 108.7°; at C, 70.3°; in [$Li_2Mg\{N(CH_2Ph)_2\}_4$],[4] at Li, 103.0°; at Mg, 96.0°; at N, 80.5°).

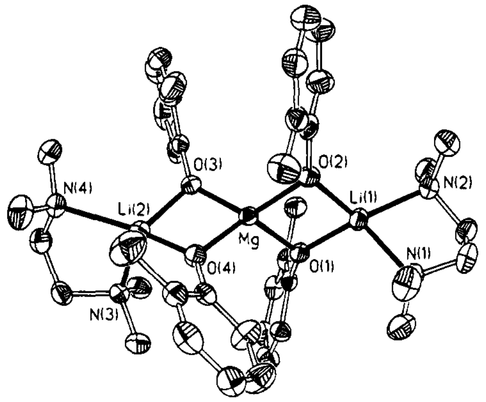

Figure 3. Thermal ellipsoid plot (40% probability) of the structure of **2**. Hydrogen atoms are omitted for clarity.

Effort is now being directed at developing a rational synthesis of the mixed anion complex **1**. Cases of adventitious oxygen have long been known in organometallic chemistry, but it is clear that the interaction of oxygen (irrespective of its source) with organomagnesium compounds is poorly understood and demands a proper systematic study. For example, why in our case should an oxide be formed, whereas insertion of O_2 into the Mg complexes [$Me_2Al\{\mu$-N(i-Pr)$_2\}_2$Mg(μ-Me)]$_4$[14] and [η^3-HB(3-Bu-t-Pz)$_3$}MgMe][15] produces alkoxide and peroxide derivatives, respectively, as recently reported? In conclusion, there is an urgent need for precise elaboration of what is meant by the description "oxygen sensitive", especially with regard to systems devoid of moisture (i.e., safe from hydrolysis) or lean in oxygen.

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Supplementary Material Available: Details of the X-ray analyses and tables of atomic coordinates, bond lengths and angles, and atomic displacement parameters for **1** and **2** (14 pages); listing of observed and calculated structure factors for **1** and **2** (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) ^{1}H NMR spectra (400 MHz; THF-d_8 solution; 298 K): **1**, other signals not discussed in text; ligand THF (CH_2), 16H, m, 1.78 ppm; impurity, <1H, 2.15 ppm; ligand THF (CH_2O), 16H, m, 3.62 ppm. **2**, TMEDA (*Me*), 12H, s, 2.15 ppm; TMEDA (CH_2), 8H, s, 2.36 ppm; Ph, 4H, t, 6.35 ppm, 4H, d, 6.66 ppm, 4H, t, 6.76 ppm, 4H, d, 6.87 ppm (relative to TMS, 0.00 ppm).

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