Experimental Section

1a: In analogy to the known synthesis of $Na_2[M(CO)_5]$ (M = Cr, W)[12] a solution of $[Me_3NCr(CO)_5]$ (1.21 g, 4.82 mmol) in THF (30 mL) was cooled to −78 °C, and a solution of $NaC_{10}H_8$ (57.8 mL, 0.20 M in THF were added dropwise over a period of 20 min. When the addition was complete all volatile materials were removed under high vacuum (0 °C/0.001 Torr). The remaining yellow solid was treated with Et_2O (50 mL) at 0 °C, filtered, and washed with Et_2O (2 × 10 mL). The light yellow product was dried briefly under high vacuum and subsequently suspended in toluene (30 mL) at 0 °C. $Br_2BN(SiMe_3)_2$[13] (1.36 g, 4.00 mmol) was added dropwise by a syringe, and the color of the suspension quickly turned from orange to dark brown. After the reation mixture was stirred for 30 min at 0 °C, it was warmed to ambient temperature and all volatile materials were removed under high vacuum. The dark brown residue was suspended in hexane (30 mL) and filtered, and the remaining solid was rinsed with hexane (10 mL). The filtrate was concentrated under vacuum to 20 mL and stored at −30 °C. After 72 h $[(Me_3Si)_2NBCr(CO)_5]$ (0.35 g, 36.7 %) was obtained as light brown crystals. All NMR spectra were recorded in in $[D_6]$benzene at 25 °C. ^1H NMR (500 MHz, TMS): $\delta = 0.14$ (s, $SiMe_3$); ^{11}B NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 92.3$; ^{13}C NMR (126 MHz, TMS): $\delta = 2.6$ ($SiMe_3$), 217.6 (CO_{eq}), 218.0 (CO_{ax}); IR (toluene): $\tilde{\nu} = 2064$ (w), 1981 (m), 1942 (vs) cm^{-1} (CO); elemental analysis calcd for $C_{11}H_{18}CrNBO_5Si_2$: C 36.37, H 5.00, N 3.86; found: C 35.47, H 5.10, N 3.72.

1b: As described for **1a** $[Me_3NW(CO)_5]$[14] (0.85 g, 2.22 mmol) was treated with a solution of $NaC_{10}H_8$ (26.7 mL, 0.20 M) and then with $Br_2BN(SiMe_3)_2$ (0.68 g, 2.00 mmol). $[(Me_3Si)_2NBW(CO)_5]$ (0.24 g, 24.3 %) was obtained as light brown crystals. All NMR spectra were recorded in $[D_6]$benzene at 25 °C. ^1H NMR (500 MHz, TMS): $\delta = 0.12$ (s, $SiMe_3$); ^{11}B NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 86.6$; ^{13}C NMR (126 MHz, TMS): $\delta = 2.9$ ($SiMe_3$), 196.5 (CO_{ax}), 197.2 (CO_{eq}); IR (toluene): $\tilde{\nu} = 2075$ (w), 1967 (m), 1941 (vs) cm^{-1} (CO); elemental analysis calcd for $C_{11}H_{18}NBO_5Si_2W$: C 26.68, H 3.66, N 2.83; found: C 26.29, H 3.59 N 2.72.

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Remarkable Reaction of Hetero-S-Block-Metal Amides with Molecular Oxygen: Cationic $(NMNMg)_2$ Ring Products (M = Li or Na) with Anionic Oxo or Peroxo Cores

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René B. Rowlings

Intensively studied since the early 1980s, the structural chemistry of lithium and sodium amides is based predominantly on $(NM)_n$ rings (M = Li or Na) which can remain discrete or self-associate by “ring-laddering”.[1] Lithium 2,2,6,6-tetramethylpiperidide (LTMP) is representative of the former type as highlighted in a recent textbook:[2] two-coordinate Li centers bridge pairs of amide N centers in a tetrameric octagonal ring core. Considerably less work has been carried out on heterometallic amide systems where lithium or sodium is combined with a second metal. Recently

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we have turned our attention to synthesizing heterodimetallic Li–Mg and Na–Mg amides.[3] These mixed-metal compounds can be formally regarded as alkali metal amide derivatives in which a proportion of M^+ ions have been replaced by $[\{Mg(NR_2)\}^+]$ units. Such substitutions should encourage a modification in chemical structure, which, in turn, could translate into a modification in chemical reactivity. Hence the heterodimetallic system may exhibit a chemical behaviour distinct from that of the homometallic amide. The widespread use of lithium amide reagents throughout synthetic chemistry provides a major incentive for pursuing this interesting topic. Herein we report how this heterodimetallic approach can be used to create a truly remarkable new piece of chemistry. Thus, octagonal $(N\text{-}M\text{-}N\text{-}Mg)_2$ mixed-metal ring systems closely related to the LTMP original but with oxo or peroxo cores are readily preparable. The core atoms are introduced into the molecular frameworks by deliberately exposing reaction solutions to molecular oxygen—a manoeuvre normally unthinkable in s-block organometallic chemistry, where generally every effort is made to avoid hydrolytic and oxidative decomposition by working in an oxygen-free inert atmosphere.

We still use such an atmosphere (argon) in the initial stages of the preparations described here. Subsequently, however, the Schlenk tube is opened to the atmosphere, and a drying tube filled with fresh $CaCl_2$ is placed at the inlet. This allows atmospheric oxygen to enter, but not moisture. Alternatively, dry compressed oxygen can be directly passed through the liquid amine for several minutes immediately prior to carrying out the preparation. Both methods have proved successful, and reproducibly so, in the synthesis of the heterodimetallic oxo variant of the classic LTMP system **1**.

$[\{C(Me_2)CH_2CH_2CH_2C(Me_2)N\}_4Li_2Mg_2(O)]$ **1**

Compound **1** is produced by mixing *n*-butyllithium with *n*,*s*-dibutylmagnesium in hydrocarbon solution, then adding enough amine to convert all the butyl groups to butane. X-ray crystallographic studies[4] reveal that the colorless, needle-shaped, single crystals of **1** are contaminated with some molecules of conventional LTMP, presumably as a consequence of the two octagonal ring systems having a similar, but not identical molecular shape (see below). Complete refinements on several different crystals show that the relative amount of LTMP contamination can be greatly reduced (e.g., from 39 to 7%) by increasing the Mg:Li stoichiometry used in the reaction from 1:1 to 2:1. Figure 1 shows the molecular structure of **1**. The core oxo atom occupies a square-planar site binding to all four metal atoms. Due to mutual substitution disorder the two Li and two Mg sites are indistinguishable. Their three-coordinate geometry is completed by two amido N atoms, which bridge to the metal atoms to produce the eight-membered ring. Though the disorder prejudices discussion of specific dimensions within the structure, it is still clear that the $(N_4Li_2Mg_2)$ ring takes on a star-shaped appearance with the N atoms located at the tips (evidenced by acute M-N-M bond angles of about 76°). This feature can be attributed to the additional pull on the metal atoms by the core oxo dianion, as it is not observed in the oxo-free structure of conventional LTMP, which has more open M-N-M bond angles of 101.5°.

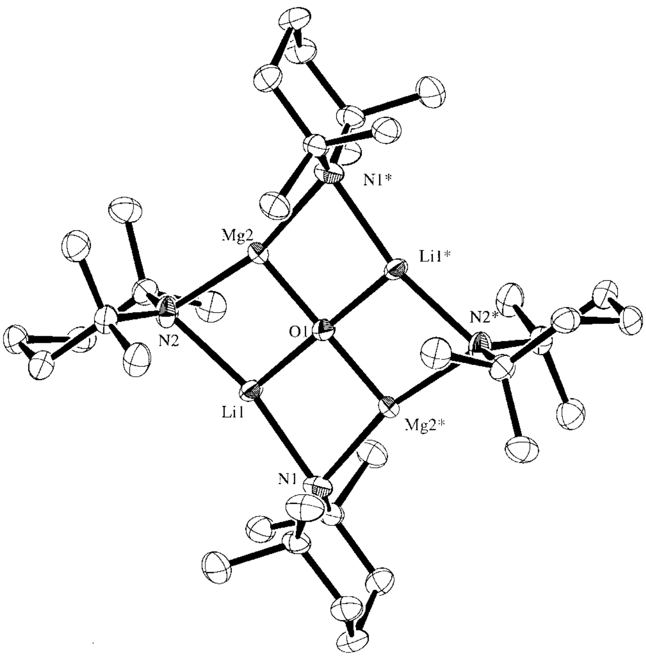


Figure 1. Molecular structure of **1** without hydrogen atoms and disorder component.

In an effort to circumvent the complication of Li/Mg substitutional disorder and to test the heterodimetallic strategy with a second amine, we tried the same reaction with *n*-butylsodium and 1,1,1,3,3,3-hexamethyldisilazane in place of *n*-butyllithium and tetramethylpiperidine, respectively. To our delight it proved successful and reproducible, yielding the desired complex **2**.

$[\{(Me_3Si)_2N\}_4Na_2Mg_2(O_2)_x(O)_y]$ **2**

The structure of **2** (Figure 2)[4] resembles that of **1**, though the octagonal ring has a more asymmetrical (but still planar) shape due to the significant size differential between Na and Mg atoms. For this reason there is no Na/Mg substitutional disorder in **2**; however, site disorder is found at the center of the structure, refined to 32% peroxide and 68% oxide for the specific crystal reported here. These appear to represent the kinetic and thermodynamic products, respectively, of the oxygen incorporation process. As such, a comparison can be made with reactions of alkyllithium compounds and molecular oxygen which produce alkoxides via unstable alkylperoxo intermediates.[5] Presumably steric shielding by the bulky amide ligand increases the stability of the peroxo component of **2**. Previously, we noted that the lithium analogue of **2** could be obtained as an unwanted by-product during the synthesis of mixed Li–Mg hexamethyldisilazide,[6] but at that time failed to recognize that it could be made by the rational method described here.

Oxygen incorporation in s-block compounds is not a new phenomenon. In 1964, the structure of the contaminated “Grignard reagent” $Mg_4Br_6(O)\cdot 4Et_2O$ was reported.[7] More recent examples include the tetradecalithium amide $[\{(c\text{-}C_5H_9)N(H)Li\}_{12}Li_2O]$[8] and the octadecalithium phos-

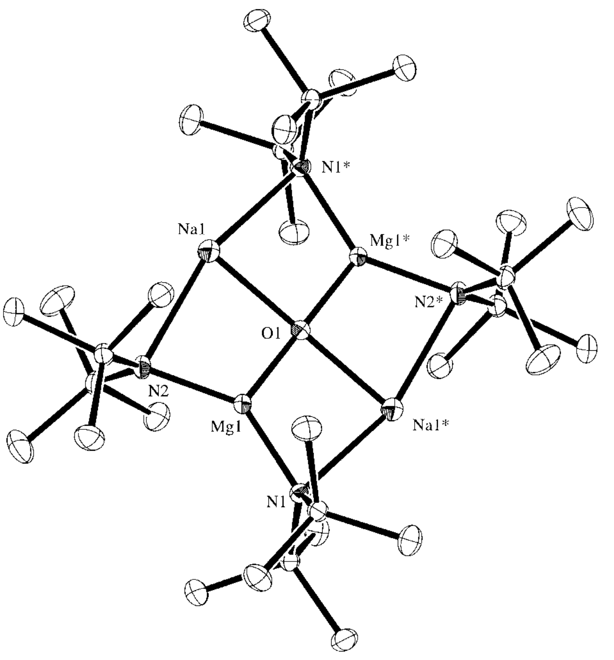
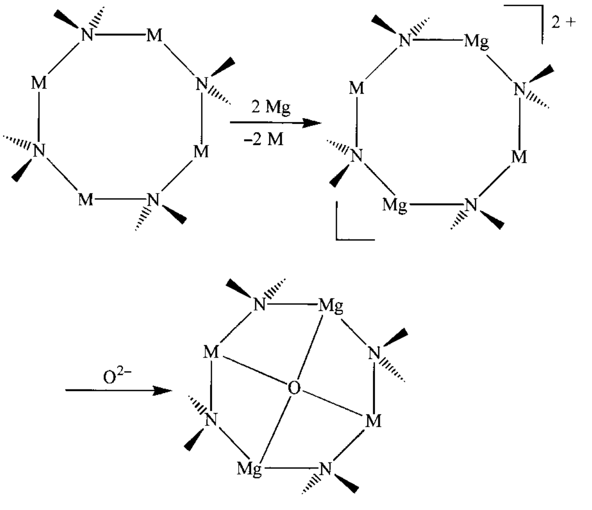


Figure 2. Molecular structure of **2** without hydrogen atoms and disorder component. Selected bond lengths [Å] and angles [°]: Mg1 ··· Na1 3.0099(7), Mg1 ··· Na1* 2.9459(8), Mg1–O1 1.8575(4), Na1–O1 2.3278(7), Mg1–N1 2.054(1), Mg1–N2 2.049(1), Na1–N1* 2.549(1), Na1–N2 2.595(1); N1-Mg-N2 141.60(5), N1*-Na1-N2 159.84(2), Mg-N1-Na1* 78.76(4), Mg1-N2-Na1 79.86(4). (*) = $-x, 1-y, 1-z$.

phanediide $[\{[i\mathrm{Pr}_2(\mathrm{Mes})\mathrm{Si}]\mathrm{P}\}_8\mathrm{Li}_{16}\cdot\mathrm{Li}_2\mathrm{O}]$.[9] However, such compositions are usually not planned, but obtained serendipitously, by reactions which cannot always be repeated. Furthermore, the source of the oxygen contamination is rarely, if ever, known with certainty, and is often vaguely attributed to Li_2O-containing butyllithium. Clearly by comparison, our rational, reproducible method, where oxygen is delivered into the system in a controlled, deliberate manner, represents a fundamental advance. In a *formal* sense, it can be regarded as a charge balance driven process (Scheme 1; though in reality it could be a one-step concerted mechanism): substituting two Mg^{2+} ions for two M^+ ions creates a cationic ring with a 2+ charge, the hole at the center of which is organized to capture small O^{2-} or O_2^{2-} ions to attain charge neutrality. Intriguingly this could be viewed, in effect, as the antithesis of a crown ether complex where a ring containing a series of oxygen atoms is used to capture a M^+ ion. While the principle of the methodology is all important, much work remains to be done to optimize the synthesis as present yields of **1** and **2** are modest (typically 5–12 %), and to ascertain the fate of the amide anions formally displaced by the oxo ones (we suspect the other products of the redox reactions are hydrazines R_2NNR_2). But the key question our future research will address is “how widely applicable is this oxygen incorporation strategy?”



Scheme 1. Formal course of the introduction of oxygen in the synthesis of **2**.

Experimental Section

1: A solution of *n*-butyllithium (5 mmol) in hexane was mixed with a solution of dibutylmagnesium (10 mmol) in heptane. (The possibility that the solutions contain a trace of moisture cannot be completely ruled out.) Oxygenated tetramethylpiperidine (25 mmol) was then introduced dropwise, resulting in an exothermic reaction. Turning orange in color, the solution deposited a precipitate which redissolved by adding oxygenated toluene and warming. This orange color deepened on standing. Allowing the solution to cool to ambient temperature on the bench afforded a crop of colorless needle crystals of **1**. M.p. 192–194 °C (decomp), c.f. 165–167 °C (decomp for LTMP).

2: *n*-Butylsodium (10 mmol) was placed in hexane (10 mL) and mixed in an ultrasonic bath until a fine suspension was obtained. The addition of dibutylmagnesium (10 mmol) in heptane resulted in a congealed brown mass. Oxygenated hexamethyldisilazane (30 mmol) was then introduced, causing the formation of a white precipitate which redissolved by adding oxygenated toluene and warming. On leaving the pale yellow solution to cool to ambient temperature, a batch of crystalline material was obtained. This was found to be a mixture of NaHMDS and **2**. Separation proved straightforward, since the former is significantly more soluble. Hence, several washings with hot toluene on a filter stick left pure **2**, which crystallized as distinctive colorless square-tipped needles. M.p. 224–226 °C (decomp) c.f. 175 °C for NaHMDS. Satisfactory C,H,Li,Mg,N,Na analyses for both compounds. Both readily hydrolyze in moist air, but remain crystalline under dry oxygen.

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0.61: 0.39 Mg_2Li_2:Li_4 ratio had unit cell dimensions, $a = 16.832(5)$, $b = 16.828(9)$, $c = 15.728(5)$ Å, $\beta = 118.45(2)^\circ$). For **2**, $C_{24}H_{72}Mg_2Na_2N_4O_{1.32}Si_8$; ($0.7 \times 0.4 \times 0.4$ mm^3), triclinic, $P1$, $a = 10.778(2)$, $b = 12.695(4)$, $c = 8.8511(14)$ Å, $\alpha = 108.03(2)$, $\beta = 99.49(2)$, $\gamma = 95.21(2)^\circ$, $V = 1122.8$ (5) Å^3, $\rho_{calcd} = 1.120$ g cm^{-3}, $\mu = 0.310$ mm^{-1}; $2\theta_{max} = 58^\circ$, 6266 data measured, 5966 unique, $R_m = 0.020$. H atoms and the peroxide O were refined isotropically and all other atoms anisotropically. Final refinement with 5100 observations ($I > 2\sigma(I)$) on F with Texsan.[12] $R = 0.0295$, $R_w = 0.0426$, GOF = 1.573, max/min residual electron density = 0.457/ − 0.330. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, as supplementary publications no. CCDC-101597 and 101598. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ. (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Novel Cyanide Coordination Models in Layer-Type Hydrated Double Salts of AgCN and AgF[**]

Guo-Cong Guo and Thomas C. W. Mak*

Dedicated to Professor James Trotter on the occasion of his 65th birthday

The chemistry of cyanide-bridged compounds has undergone quite spectacular advances in the last decade, especially in regard to one-, two-, and three-dimensional complexes that exhibit unusual magnetic and electrical properties.[1] Furthermore, the syntheses of oligonuclear cyanide-bridged complexes and investigation of the electronic interactions between their metal centers have been pursued by several research groups.[2] Recently another incentive to study bimetallic cyano complexes has emerged from finding that the enzyme cytochrome c oxidase is poisoned by cyanide.[3] During the course of our current study on the bonding interaction between the acetylenediide anion, C_2^{2-}, and silver(I) ions in various double salts of silver acetylide with other soluble silver salts,[4] we also explored the possibility of stabilizing the related isoelectronic diatomic species CN^- by coordination to multiple silver(I) sites in a crystalline environment. Herein we report two new double salts, $3\,AgCN \cdot 2\,AgF \cdot 3\,H_2O$ (**1**) and $AgCN \cdot 2\,AgF \cdot 3\,H_2O$ (**2**), which exhibit novel layer-type structures and bonding interaction between the cyanide anion and adjacent silver ions.

The coordination modes of the cyanide group in their metal complexes show considerable diversity (Figure 1). By far the two most commonly observed modes are the terminal C-bound mode (a) and the linear-bridged arrangement (b), which are based on the well-known fact that the cyanide ion possesses a donor electron pair at both its C and N terminals.[5] Modes (c)–(g) are much less common,[6] and to our knowledge modes (h) and (i) are found for the first time in compound **1**.

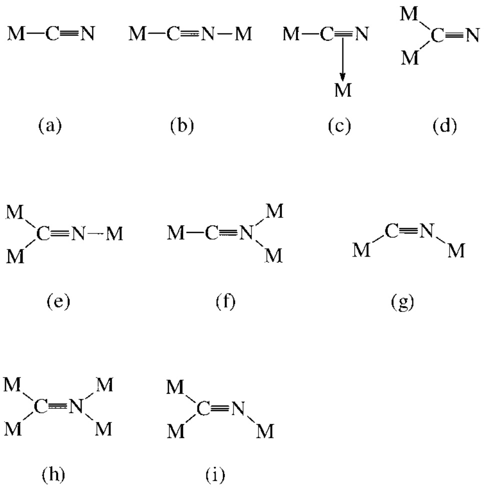

Figure 1. Coordination modes of the cyanide ion.

The layer-type structure of **1** can be regarded as constructed from two basic building blocks, namely a nonlinear dimeric Ag_2F_2 unit and the first edge-bridged triangular silver(I) cluster core $[Ag_3(\mu\text{-}CN)_3(H_2O)_3]$ (Figure 2). The Ag–Ag distances, which range from 2.8110(8) to 2.9189(8) Å in the Ag_3 cluster, are comparable to the interatomic contact of 2.89 Å in silver metal,[7] and hence suggestive of the existence of weak interactions of the same order of magnitude. The Ag–Ag distance of 2.7484(9) Å in the Ag_2F_2 unit (Ag–F 2.316(4) – 2.422(4) Å) is significantly shorter than those in the Ag_3 cluster. To our knowledge the $\mu_4\text{-}\eta^1\kappa C\text{:}\eta^1\kappa N$ and bent $\mu_3\text{-}\eta^1\kappa C\text{:}\eta^1\kappa N$ coordination modes observed for the cyanide group, as well as their coexistence in the same complex, are both unprecedented. Each of the two independent μ_3-cyanide groups is symmetrically bridged to an edge of the Ag_3 triangle through its N terminal and also bonded to one Ag atom of an adjacent Ag_2F_2 unit through its C terminal. The μ_4-cyanide group bridges an edge of the Ag_3 triangle through its N

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