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Low-coordinate calcium peroxide and oxide complexes†

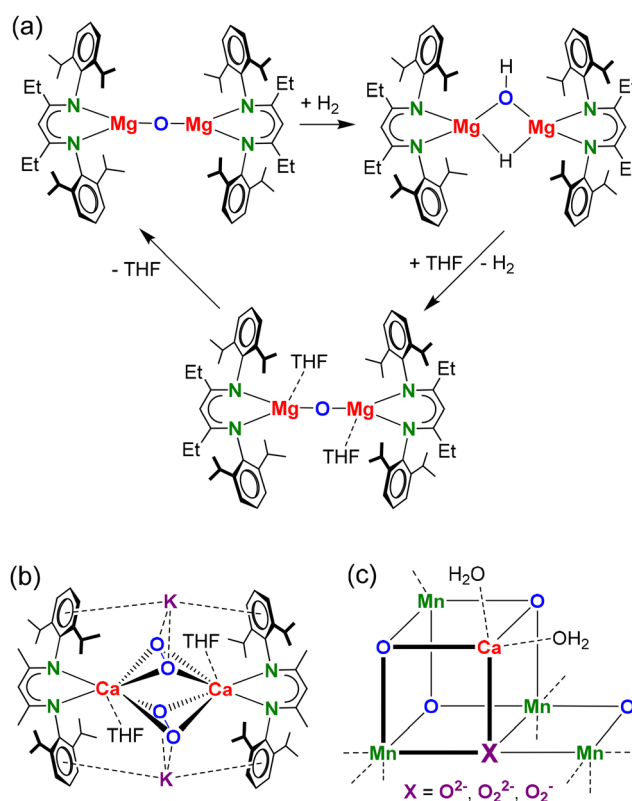
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A Ca^I synthon with superbulky β -diketiminate ligands (BDI*) and a N₂^{2−} dianion, [(BDI*)Ca]₂(N₂), is key to the synthesis of binuclear (BDI*)Ca(μ_2 -O₂)Ca(BDI*) and (BDI*)Ca(μ_2 -O)Ca(BDI*) complexes. The Ca oxide complex is particularly unstable in solution and was only accessible by a solvent-free reaction between solid [(BDI*)Ca]₂(N₂) and N₂O gas.

From a historical perspective, the alkaline earth (Ae) metal oxides beryllia, magnesia, lime, strontia and baria are among the oldest known group 2 metal compounds. In fact, most of the alkaline earth metal's names originate from these rock salt minerals. Solid MgO or CaO are often used as supports for catalysts¹ but also alone can be catalytically active.^{2,3} Their ionic nature combines a Lewis acidic Ae²⁺ cation with a Brønsted basic O^{2−} anion, which is a perfect combination for small molecule activation by an FLP-type mechanism.⁴ As the reactive cationic and anionic centres should be accessible for substrates, low-coordination numbers are a requirement. This was most recently elegantly demonstrated by Stasch and coworkers who showed that a hydrocarbon-soluble Mg oxide complex is able to split the strong H–H bond (Scheme 1a).⁵ A THF-solvate of this Mg oxide complex, for which a first example was reported earlier by Jones,⁶ only reacted with H₂ after prior elimination of the THF ligands.⁵ In fact, addition of THF to the mixed Mg hydride/hydroxide complex, the product of H₂ activation, reversed the reaction and led to Mg oxide formation under H₂ release (Scheme 1a). The reaction of the Mg oxide complex with H₂ can also be seen as a deprotonation of H₂ which is known to have a very high pK_a value of *circa* 49.⁷ This underscores the extreme basicity of low-coordinate Mg oxides. In contrast, the high-coordinate μ_4 -O or μ_3 -O arrangements in early main group metal

complexes^{8–26} are much less reactive than rare low-coordinate μ_2 -O compounds.^{5,6,27}

Herein, we report our investigations towards low-coordinate Ca oxide and peroxide complexes. Considering that the reactivity of Ae metal complexes rapidly increases with metal size,²⁸ we anticipate that the isolation of low-coordinate Ca oxide or peroxide complexes will be challenging. Lewinsky and co-workers recently isolated a first example of a heterobimetallic



Scheme 1 (a) Low-coordinate Mg oxide complex reacting with H₂ and H₂ release by addition of THF.⁵ (b) Heterobimetallic Ca/K peroxide complex.²⁹ (c) Mn₄CaO₄X cluster in photosystem II.

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Ca/K peroxide complex²⁹ (Scheme 1b) which, although not intended, incorporated K⁺ originating from KCl salt eliminated in an previous salt-metathesis step. This demonstrates the difficulty in making low-coordinate (per)oxide complexes.

Our interest in Ca oxide and peroxide chemistry is also motivated by the prominent role of the Ca²⁺ cation in the O₂ evolving Photosystem II which is used by nature for water splitting: 2H₂O → 4H⁺ + 4e⁻ + O₂. The Lewis-acidic Ca²⁺ cation is essential for catalytic activity of the central Mn₄CaO₅ cluster by stabilizing the oxide anion and transient peroxide species³⁰ (Scheme 1c) and also serves as a “taxi-stand” for incoming H₂O before moving into the active site.³¹

The key to well-defined Ca (per)oxide complexes is a recently isolated Ca dinitrogen complex, [(BDI*)Ca]₂(N₂) (**I**, Scheme 2, BDI* = HC[C(Me)N-(DIPEP)]₂, DIPEP = 2,6-(CHEt₂)-phenyl).³² This complex can be obtained in good yield, either ether-free or as THF or THP (tetrahydropyran) adduct, and was shown to react as a Ca^I synthon by release of N₂ and 2e⁻.^{32–35} Reaction of dry air with a suspension of ether-free **I** in hexanes at –85 °C led to a rapid color change from red-brown to yellow but all attempts to crystallize the product failed. However, after the addition of a few drops of THP the Ca peroxide complex **1** started to crystallize rapidly (yield: 53%). Alternatively, the complex can also be prepared by oxidation of **I**-THP with dry air. The raw product of this latter reaction is nearly pure (>95%, Fig. S9, ESI†). ¹H and ¹³C NMR spectra of **1** (Fig. S1–S3, ESI†) show one benzylic quintet and one Me-backbone signal, indicative of high average symmetry. ¹H NMR monitoring shows that a benzene-*d*₆ solution of **1** decomposes at 65 °C (Fig. S10, ESI†). We were not able to crystallize the decomposition product but, as observed by Lewinsky and coworkers,²⁹ we propose formation of a HOO⁻ complex. This is in agreement with appearance of signals around –0.5 ppm indicating deprotonation of alkyl arms.

Calcium peroxide **1** crystallized as a centrosymmetric, dinuclear complex in which the peroxide dianion O₂²⁻ bridges the pentacoordinated Ca²⁺ centres in a μ₂-η²:η²-fashion (Fig. 1a). The Ca–O distances (2.1911(8)–2.2132(9) Å) are shorter than those in the only other known Ca peroxide complex (Scheme 1b: 2.315(2)–2.328(2) Å)²⁹ which shows a higher coordination number at the Ca nuclei and additional O₂²⁻ ··· K⁺ interactions. The Ca–O distances in **1** are comparable to those reported for [(^{DIPP}BDI)Ca(THF)]₂(OH)₂ (2.224(2) Å and 2.218(2) Å).³⁶ The peroxide anion in **1** shows an O–O bond distance of 1.593(2) Å which is exceptionally long when compared to the only other reported Ca peroxide complex (Scheme 1b, O–O: 1.550(3) Å)²⁹ or to a Ca/V peroxide complex (O–O: 1.466(1)–1.482(1) Å).³⁷ Hill and coworkers reported pyridine and DMAP stabilized Mg peroxide complexes with longer O–O distances than that in **1** (1.625(1)–1.638(5) Å).³⁸ Samarium peroxide complexes show shorter O–O distances ranging from 1.509(4)–1.538 Å.^{39,40}

The remarkable reactivity of a low-coordinate Mg oxide complex⁵ prompted us to isolate a similar but even more reactive Ca oxide complex. Reactions of **I** or **I**-THP in alkanes with N₂O are fast but, independent of the temperature (–70 °C/+20 °C), highly unselective. This was concluded from appearance of several ¹H NMR signals for the CH backbone in the BDI* ligand (Fig. S11, ESI†). Cooling the concentrated reaction mixture led to crystallization of a decomposition product in which the backbone Me group has been deprotonated (**II**, Scheme 2). The same complex was formed upon decomposition of **I** and has been fully characterized.³² A solid-state reaction turned out to be more successful. Crystalline **I**-THP was cooled to –70 °C and the protective N₂ atmosphere was replaced with N₂O. Slowly warming the solid to 0 °C led to a colour change from red-brown to off-white. Rapid recrystallization from pentane at –25 °C allowed for isolation of [(BDI*)Ca(THP)]₂(μ₂-O) (**2**) in 27% yield. Its high reactivity and very high solubility both contribute to the moderate yield.

Dissolving crystalline **2** in benzene-*d*₆ or methylcyclohexane-*d*₁₄ led to immediate decomposition in several species. A solution of **2** in methylcyclohexane-*d*₁₄ decomposed even at –80 °C. The low temperature ¹H NMR spectrum showed several CH-backbone signals and signals at negative ppm values (Fig. S14, ESI†) which indicate the typical deprotonation of a –CHEt₂ arm. Similar alkyl deprotonations occurred upon attempted isolation of a (BDI)MgO⁻ anion.¹⁸ This illustrates the highly basic character of the oxide anion in **2**.

The crystal structure of **2** (Fig. 1b) shows a centrosymmetric dinuclear complex with perfectly linear Ca–(μ₂-O)–Ca bridging. Coordination of THP results in 4-coordinate Ca centres. Attempts to synthesize and crystallize ether-free Ca oxide complexes with 3-coordinate Ca centres failed, possibly due to extreme reactivity. The low coordination number for the bridging μ₂-O results in very short Ca–O distances of 2.0478(3) Å. Calcium complexes with μ₃-O or μ₄-O oxide ligands show much longer Ca–O distances: 2.223(9)–2.292(8) Å,¹⁴ 2.187(2)–2.265(8) Å,¹¹ or 2.128(2)–2.138(2) Å.¹²

Alkane solutions of the Ca oxide complex **2** react even at –80 °C instantaneous with H₂ but due to its instability in



Scheme 2 Synthesis of low-coordinate Ca peroxide (**1**) and Ca oxide (**2**) complexes.





Fig. 1 Crystal structures of **1** (a) and **2** (b); H atoms and CHEt_2 groups omitted for clarity. (c) The HOMO–3 and HOMO–4 for Ca oxide complex **2**.

solution such reactivity studies gave only complicated mixtures of products. A similar observation was made for reaction with CO_2 . Although **2** is reasonably stable in the solid crystalline state, even solid-state reactions of crystalline **2** with H_2 or CO_2 led to unselective product formation. Note that the similar Mg oxide complex only reacts with H_2 when ether-free (Scheme 1a) whereas the Ca oxide complex also reacts in presence of THP. This underscores the extreme reactivity of calcium complexes with μ_2 -bridging oxide ligands.

A DFT study sheds light on bonding and electron distribution in **1** and **2**. The optimized structures (B3PW91-GD3BJ/def2tzvp//B3PW91-GD3BJ/def2svp) fit reasonably well with the experimentally determined molecular structures (Fig. S17 and S18, ESI†), indicating a sufficient level of theory.

The formation of the Ca oxide or peroxide complexes from the ether-free Ca^{I} synthon **I** is thermodynamically highly favoured. Oxidation of $[(\text{BDI}^*)\text{Ca}]_2(\text{N}_2)$ (**I**) with N_2O to form $[(\text{BDI}^*)\text{Ca}](\mu_2\text{-O})$ was calculated to be exergonic by $\Delta G_{298\text{K}} = -109.8 \text{ kcal mol}^{-1}$ (Fig. S25, ESI†). Reaction of **I** with O_2 to form a Ca peroxide complex is even more exergonic ($\Delta G_{298\text{K}} = -150.0 \text{ kcal mol}^{-1}$). This underscores the highly reducing nature of Ca^{I} synthon **I** caused by the facile $2e^-$ -oxidation of the bridging dianion: $\text{N}_2^{2-} \rightarrow \text{N}_2 + 2e^-$.

Natural Population Analysis (NPA) confirms essentially ionic $\text{Ca}-(\text{O}_2)$ or $\text{Ca}-\text{O}$ bonds with highly positive charges on the Ca centres (**1**: +1.79, **2**: +1.79) and negative charges on the bridging (per)oxide dianions (O_2^{2-} : -1.78, O^{2-} : -1.74) (Fig. S19 and S20, ESI†). Ionic bonding is in agreement with Atoms-In-Molecules (AIM) analysis which shows low electron densities $\rho(\mathbf{r})$ and positive Laplacian $\nabla^2\rho(\mathbf{r})$ in the $\text{Ca}-\text{O}$ bond-critical-points (bcp's); Fig. S21 and S22 (ESI†). The Wiberg Bond Index (WBI) of 0.99 for the $\text{O}-\text{O}$ bond in the O_2^{2-} anion confirms single bond character for the peroxide anion in **1**. AIM analysis also shows that bridged O_2^{2-} in **1** and O^{2-} in **2** are involved in weak $\text{O} \cdots \text{H}-\text{C}$ bonding with organic fragments of the BDI^* ligand (Fig. S21 and S22, ESI†). These non-classical hydrogen bonds are typical for low-coordinate ligands.⁴¹

An interesting aspect of bonding in the central $\text{Ca}-(\mu_2\text{-O})-\text{Ca}$ of **2** is Ca d-orbital participation which is currently

controversially discussed. While the HOMO, HOMO–1 and HOMO–2 are mainly centred on the O^{2-} and BDI^* ligands (Fig. S24, ESI†), the HOMO–3 combines 84.8% $\text{O}(2p_z)$ with 7.9% $\text{Ca}(3d_{xz})$ character (Fig. 1c). For HOMO–4 following contributions are calculated: 77.9% $\text{O}(2p_z)$ with 11.2% $\text{Ca}(3d_{xz})$.

In summary, first Ca (per)oxide complexes with low-coordinate $\mu_2\text{-O}_2$ or $\mu_2\text{-O}$ dianions are accessible from the Ca^{I} synthon $[(\text{BDI}^*)\text{Ca}(\text{THP})]_2(\text{N}_2)$ and O_2 or N_2O , respectively. The very high reactivity and instability of the Ca oxide complex in solution required a solid-state synthesis. The low-coordinate number of the peroxide and oxide dianions result in numerous non-classical $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds but also cause instability. Facile decomposition likely proceeds through deprotonation of the ligand's alkyl groups, impeding selective reactivity. However, the reactivity of the low-coordinate Ca peroxide complex **1** as an oxidizing reagent is currently under investigation.

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Conflicts of interest

There are no conflicts to declare.

Data availability

X-ray crystallographic data have been deposited in the Cambridge Crystallographic Data Centre with reference numbers: CCDC 2427514–2427515. Complex syntheses and analyses, NMR spectra, crystallographic details including ORTEP representations, details for the DFT calculations including XYZ-files have been included as part of the ESI.†

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