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# Low-coordinate calcium peroxide and oxide complexes†

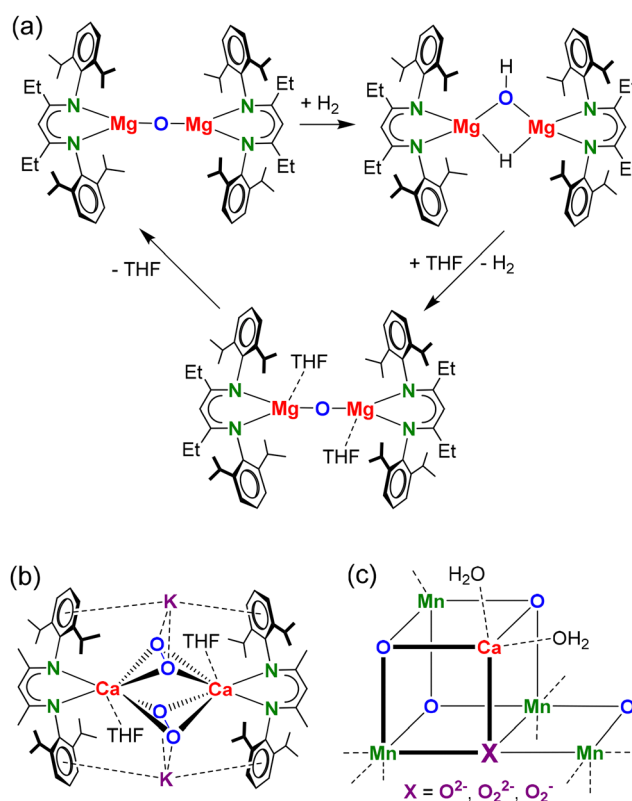
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A  $\text{Ca}^{\text{I}}$  synthon with superbulky  $\beta$ -diketiminate ligands (BDI\*) and a  $\text{N}_2^{2-}$  dianion,  $[(\text{BDI}^*)\text{Ca}]_2(\text{N}_2)$ , is key to the synthesis of binuclear  $(\text{BDI}^*)\text{Ca}(\mu_2\text{-O}_2)\text{Ca}(\text{BDI}^*)$  and  $(\text{BDI}^*)\text{Ca}(\mu_2\text{-O})\text{Ca}(\text{BDI}^*)$  complexes. The Ca oxide complex is particularly unstable in solution and was only accessible by a solvent-free reaction between solid  $[(\text{BDI}^*)\text{Ca}]_2(\text{N}_2)$  and  $\text{N}_2\text{O}$  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  $\text{MgO}$  or  $\text{CaO}$  are often used as supports for catalysts<sup>1</sup> but also alone can be catalytically active.<sup>2,3</sup> Their ionic nature combines a Lewis acidic  $\text{Ae}^{2+}$  cation with a Brønsted basic  $\text{O}^{2-}$  anion, which is a perfect combination for small molecule activation by an FLP-type mechanism.<sup>4</sup> 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).<sup>5</sup> A THF-solvate of this Mg oxide complex, for which a first example was reported earlier by Jones,<sup>6</sup> only reacted with  $\text{H}_2$  after prior elimination of the THF ligands.<sup>5</sup> In fact, addition of THF to the mixed Mg hydride/hydroxide complex, the product of  $\text{H}_2$  activation, reversed the reaction and led to Mg oxide formation under  $\text{H}_2$  release (Scheme 1a). The reaction of the Mg oxide complex with  $\text{H}_2$  can also be seen as a deprotonation of  $\text{H}_2$  which is known to have a very high  $\text{pK}_\text{a}$  value of *circa* 49.<sup>7</sup> This underscores the extreme basicity of low-coordinate Mg oxides. In contrast, the high-coordinate  $\mu_4\text{-O}$  or  $\mu_3\text{-O}$  arrangements in early main group metal

complexes<sup>8–26</sup> are much less reactive than rare low-coordinate  $\mu_2\text{-O}$  compounds.<sup>5,6,27</sup>

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,<sup>28</sup> 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  $\text{H}_2$  and  $\text{H}_2$  release by addition of THF.<sup>5</sup> (b) Heterobimetallic Ca/K peroxide complex.<sup>29</sup> (c)  $\text{Mn}_4\text{CaO}_4\text{X}$  cluster in photosystem II.

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Ca/K peroxide complex<sup>29</sup> (Scheme 1b) which, although not intended, incorporated K<sup>+</sup> 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 Ca<sup>2+</sup> cation in the O<sub>2</sub> evolving Photosystem II which is used by nature for water splitting: 2H<sub>2</sub>O → 4H<sup>+</sup> + 4e<sup>-</sup> + O<sub>2</sub>. The Lewis-acidic Ca<sup>2+</sup> cation is essential for catalytic activity of the central Mn<sub>4</sub>CaO<sub>5</sub> cluster by stabilizing the oxide anion and transient peroxide species<sup>30</sup> (Scheme 1c) and also serves as a “taxi-stand” for incoming H<sub>2</sub>O before moving into the active site.<sup>31</sup>

The key to well-defined Ca (per)oxide complexes is a recently isolated Ca dinitrogen complex, [(BDI\*)Ca]<sub>2</sub>(N<sub>2</sub>) (**I**, Scheme 2, BDI\* = HC[C(Me)N-(DIPEP)]<sub>2</sub>, DIPEP = 2,6-(CHEt<sub>2</sub>)-phenyl).<sup>32</sup> 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<sup>I</sup> synthon by release of N<sub>2</sub> and 2e<sup>-</sup>.<sup>32–35</sup> 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†). <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** (Fig. S1–S3, ESI†) show one benzylic quintet and one Me-backbone signal, indicative of high average symmetry. <sup>1</sup>H NMR monitoring shows that a benzene-*d*<sub>6</sub> 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,<sup>29</sup> we propose formation of a HOO<sup>-</sup> complex. This is in agreement with appearance of signals around –0.5 ppm indicating deprotonation of alkyl arms.

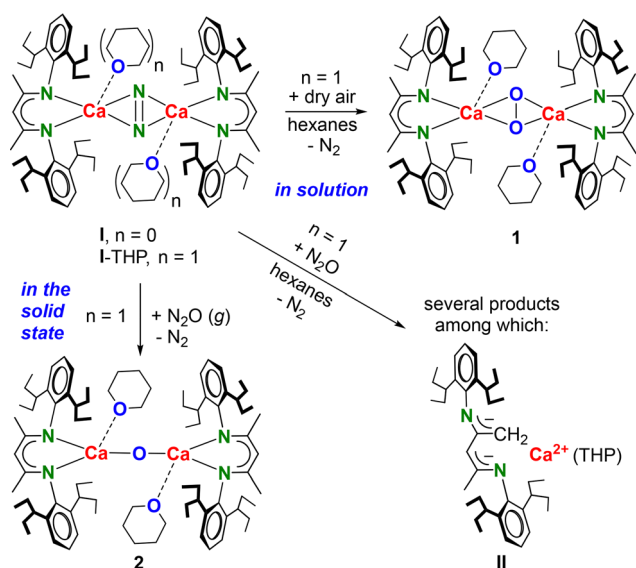
Calcium peroxide **1** crystallized as a centrosymmetric, dinuclear complex in which the peroxide dianion O<sub>2</sub><sup>2-</sup> bridges the pentacoordinated Ca<sup>2+</sup> centres in a μ<sub>2</sub>-η<sup>2</sup>:η<sup>2</sup>-fashion (Fig. 1a). The Ca–O distances (2.1911(8)–2.2132(9) Å) are shorter than those in the only other known Ca peroxide complex (Scheme 1b: 2.315(2)–2.328(2) Å)<sup>29</sup> which shows a higher coordination number at the Ca nuclei and additional O<sub>2</sub><sup>2-</sup> ··· K<sup>+</sup> interactions. The Ca–O distances in **1** are comparable to those reported for [(<sup>DIPP</sup>BDI)Ca(THF)]<sub>2</sub>(OH)<sub>2</sub> (2.224(2) Å and 2.218(2) Å).<sup>36</sup> 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)<sup>29</sup> or to a Ca/V peroxide complex (O–O: 1.466(1)–1.482(1) Å).<sup>37</sup> 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).<sup>38</sup> Samarium peroxide complexes show shorter O–O distances ranging from 1.509(4)–1.538 Å.<sup>39,40</sup>

The remarkable reactivity of a low-coordinate Mg oxide complex<sup>5</sup> prompted us to isolate a similar but even more reactive Ca oxide complex. Reactions of **I** or **I**-THP in alkanes with N<sub>2</sub>O are fast but, independent of the temperature (–70 °C/+20 °C), highly unselective. This was concluded from appearance of several <sup>1</sup>H 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.<sup>32</sup> A solid-state reaction turned out to be more successful. Crystalline **I**-THP was cooled to –70 °C and the protective N<sub>2</sub> atmosphere was replaced with N<sub>2</sub>O. 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)]<sub>2</sub>(μ<sub>2</sub>-O) (**2**) in 27% yield. Its high reactivity and very high solubility both contribute to the moderate yield.

Dissolving crystalline **2** in benzene-*d*<sub>6</sub> or methylcyclohexane-*d*<sub>14</sub> led to immediate decomposition in several species. A solution of **2** in methylcyclohexane-*d*<sub>14</sub> decomposed even at –80 °C. The low temperature <sup>1</sup>H NMR spectrum showed several CH-backbone signals and signals at negative ppm values (Fig. S14, ESI†) which indicate the typical deprotonation of a –CHEt<sub>2</sub> arm. Similar alkyl deprotonations occurred upon attempted isolation of a (BDI)MgO<sup>-</sup> anion.<sup>18</sup> 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–(μ<sub>2</sub>-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 μ<sub>2</sub>-O results in very short Ca–O distances of 2.0478(3) Å. Calcium complexes with μ<sub>3</sub>-O or μ<sub>4</sub>-O oxide ligands show much longer Ca–O distances: 2.223(9)–2.292(8) Å,<sup>14</sup> 2.187(2)–2.265(8) Å,<sup>11</sup> or 2.128(2)–2.138(2) Å.<sup>12</sup>

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



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



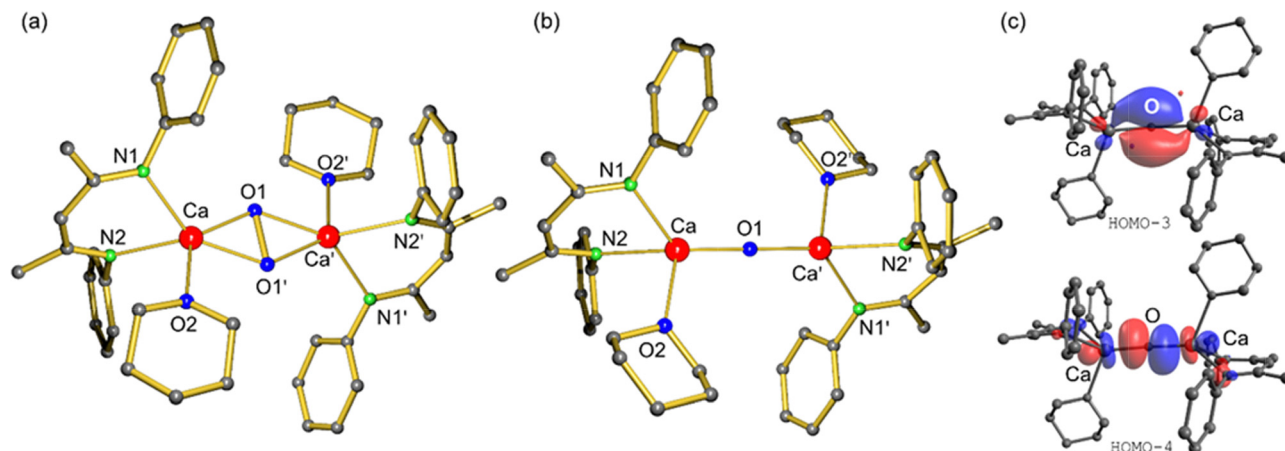


Fig. 1 Crystal structures of **1** (a) and **2** (b); H atoms and  $\text{CHEt}_2$  groups omitted for clarity. (c) The HOMO–3 and HOMO–4 for Ca oxide complex **2**.

solution such reactivity studies gave only complicated mixtures of products. A similar observation was made for reaction with  $\text{CO}_2$ . Although **2** is reasonably stable in the solid crystalline state, even solid-state reactions of crystalline **2** with  $\text{H}_2$  or  $\text{CO}_2$  led to unselective product formation. Note that the similar Mg oxide complex only reacts with  $\text{H}_2$  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  $\mu_2$ -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  $\text{Ca}^{\text{I}}$  synthon **I** is thermodynamically highly favoured. Oxidation of  $[(\text{BDI}^*)\text{Ca}]_2(\text{N}_2)$  (**I**) with  $\text{N}_2\text{O}$  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  $\text{O}_2$  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  $\text{Ca}^{\text{I}}$  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 ( $\text{O}_2^{2-}$ : -1.78,  $\text{O}^{2-}$ : -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  $\text{O}_2^{2-}$  anion confirms single bond character for the peroxide anion in **1**. AIM analysis also shows that bridged  $\text{O}_2^{2-}$  in **1** and  $\text{O}^{2-}$  in **2** are involved in weak  $\text{O}\cdots\text{H}-\text{C}$  bonding with organic fragments of the  $\text{BDI}^*$  ligand (Fig. S21 and S22, ESI†). These non-classical hydrogen bonds are typical for low-coordinate ligands.<sup>41</sup>

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  $\text{O}^{2-}$  and  $\text{BDI}^*$  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  $\text{Ca}^{\text{I}}$  synthon  $[(\text{BDI}^*)\text{Ca}(\text{THP})]_2(\text{N}_2)$  and  $\text{O}_2$  or  $\text{N}_2\text{O}$ , 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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