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Chromium Complexes

A Heterobimetallic Superoxide Complex formed through O_2 Activation between Chromium(II) and a Lithium Cation**

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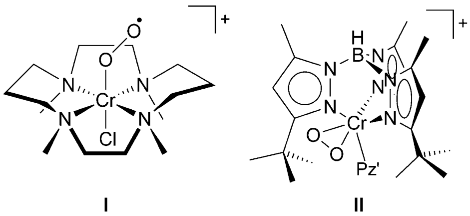
Dedicated to Professor Konrad Seppelt on the occasion of his 70th birthday

Abstract: *The reaction of 1,1,3,3-tetraphenyl-1,3-disiloxandiol (LH_2) with n-butyllithium and $CrCl_2$ results in a mononuclear chromium(II) complex (**1**) that further reacts with O_2 at low temperatures to yield a mononuclear chromium(III) superoxide complex $[L_2CrO_2(THF)][Li_2(THF)_3]$ (**2**). The crystal structure revealed that the chromium superoxido entity is stabilized by the coordination to an adjacent lithium cation. Complex **2** thus contains an unprecedented heterobimetallic $[Cr^{III}(\mu\text{-}O_2)Li^+]$ core; beyond this it is the first chromium superoxide for which a temperature-dependent magnetic characterization could be achieved, and the first structurally characterized representative with chromium in an exclusive O-donor environment.*



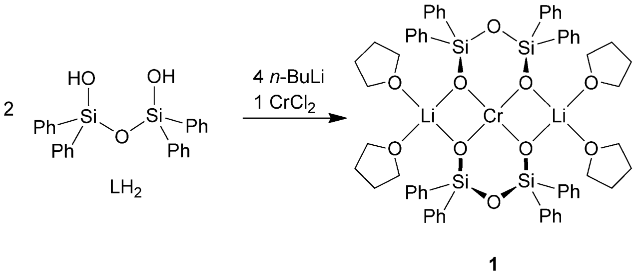
Scheme 1. Chromium(III) superoxide complexes characterized by X-ray diffraction analysis.[3b,4]

Owing to its triplet ground state, the utilization of O_2 for oxidation reactions typically requires a prior activation at a metal center, both in laboratories and in nature. Enzyme active sites containing just one metal center, such as those found in mononuclear iron or copper oxygenases,[1,2] often activate O_2 by reaction to metal superoxide species, which overall represent key intermediates in oxidation catalysis. Their high reactivity in general hampers the isolation and characterization of molecular metal superoxide species and the number of structurally characterized representatives is low. A few synthetic mononuclear chromium(III) superoxide compounds with the superoxido ligand in “end-on” or “side-on” coordination have been discussed as chemical models for O_2 activating metalloenzymes,[3] but to date only one complex with an end-on bound O_2^- ligand (**I**)[3b] and one complex with a side-on O_2^- coordination (**II**)[4] both being based on polydentate N-donor ligands have been structurally characterized (Scheme 1). Herein we describe a complex featuring a chromium(III) superoxide unit in an all O-donor environment binding to a Lewis acid, namely Li^+.

N-ligated Cr^{II} complexes have been shown to react with O_2 yielding superoxido,[3–5] peroxido,[6] and oxido[7–10] species. Recently we have demonstrated that siloxide ligand environments for Cr^{II} are worth being considered in this context, too.[11] A dinuclear chromium(II) complex based on a tripodal siloxide ligand, $PhSi(OSiPh_2O^-)_3$, cleaved O_2 forming a complex in which two $Cr^{IV}{=}O$ units form a unique asymmetric diamond core that is still reactive towards O_2: It mediates THF oxidation with labelled O_2 and during this process the O_2 exchanges its label, not only with the terminal oxido ligand but also with the O atoms of the siloxide ligand.[11]

We reckoned that by decreasing the ligand complexity further information on the formation of the initial O_2 activation steps might be gathered and therefore employed 1,1,3,3-tetraphenyl-1,3-disiloxandiol (LH_2) as a ligand precursor, providing $[\text{-OSi(Ph)}_2O^-]$ donor functions, too, but only two per ligand entity.

LH_2 dissolved in THF was deprotonated and subsequently 0.5 equivalent of $CrCl_2$ was added at room temperature (Scheme 2). After workup, recrystallization of the crude material from toluene/*n*-hexane provided orange block-



Scheme 2. Synthesis of complex **1**.

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shaped crystals suitable for X-ray diffraction analysis. The molecular structure determined revealed that indeed the envisaged mononuclear chromium(II) complex $[L_2Cr][Li(THF)_2]_2$ (**1**) had formed, co-crystallizing with one molecule of toluene (Figure 1).

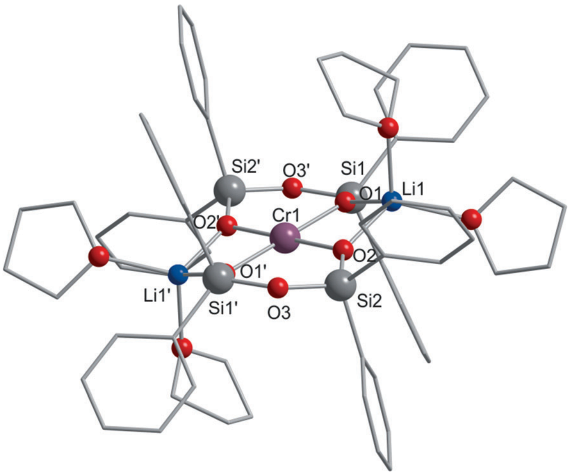


Figure 1. Molecular Structure of **1**·toluene. Hydrogen atoms and a co-crystallized toluene molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: O1–Cr1 1.9875(11), O2–Cr1 2.0099(10), O2–Li1 1.901(3), O1–Li1 1.903(3), Cr1–Li1 2.790(3); O1-Cr1-O1′ 180.0, O2-Cr1-O2′ 180.0, O1-Cr1-O2 84.68(4).

Within **1**, two disiloxide ligands form an almost perfectly square-planar coordination sphere for the chromium(II) center. Two six-membered chelate rings are thus formed, which are clamped by two Li^+ counterions. These ions compensate the charges of the central $[L_2Cr^{II}]^{2-}$ ion and additionally bind two THF molecules each. Over two decades ago, a similar chromium(II) complex was reported by Sullivan et al. but with sodium instead of lithium cations.[12] Even though **1**·toluene is not isotypic to this complex the structural parameters are comparable.

Compound **1** is paramagnetic with a constant effective magnetic moment of 4.78 μ_B above 50 K (Figure S6 in the Supporting Information), similar to other square-planar Cr^{II} compounds.[13,14] The data thus reveal the presence of a $3d^4$ high-spin configuration with $S=2$ (spin-only value 4.9 μ_B), as expected for four-coordination. The low-temperature data appeared to be somewhat obscured by weak intermolecular interactions in the solid powder sample, but multi-field measurements show typical nesting. This result confirms moderate zero-field splitting, as found for other d^4 ions with non-degenerate orbital ground states, such as the chromium(II) hexaqua complex ($D=-2.2\,cm^{-1}$)[15] and most manganese(III) compounds (-1.2 to $-4.5\,cm^{-1}$),[16] which have been investigated by high-field EPR measurements. Although the sign of D could not be unambiguously determined for **1** from the SQUID data, we adopt a negative value based on the "elongated", quasi-octahedral ligand field situation. Optimization yielded $D=-1.9(5)\,cm^{-1}$, $E/D=0.06(6)$.

To investigate its O_2 reactivity the chromium(II) complex **1** was dissolved in THF and exposed to dioxygen at −20 °C. The formation of a purple product could be observed; this product persisted at this temperature for hours but quickly decomposed at temperatures higher than 0 °C. Monitoring the reaction by UV/Vis spectroscopy (Figure 2) revealed the evolution of UV/Vis absorptions at 506, 691, and 882 nm that are characteristic of an "end-on" chromium(III) superoxide complex.[3] The same product can also be generated at −20 °C in acetonitrile or toluene, where, however, its lifetime is shorter. Resonance Raman measurements performed in acetonitrile at −20 °C with an excitation wavelength of 488 nm (Figure 2) corroborated the formation of a superoxide. After bubbling $^{16}O_2$ into an acetonitrile solution of **1** a new single band appeared at 1130 cm^{-1}, which was shifted to 1070 cm^{-1} when $^{18}O_2$ was employed. Both the positions of the absorption bands and the isotopic shift $\Delta(^{16}O-^{18}O)=60\,cm^{-1}$ are typical of chromium bound "end-on" superoxide ligands.[3,5] Crystals of the product grown from *n*-hexane-layered THF solutions at −80 °C proved to be exceptionally unstable and could not be stored as a solid material. Nevertheless we were able to isolate and analyze single crystals by X-ray diffraction, which confirmed the formation of a chromium(III) superoxide complex $[L_2CrO_2(THF)][Li_2(THF)_3]$ (**2**; Scheme 3).

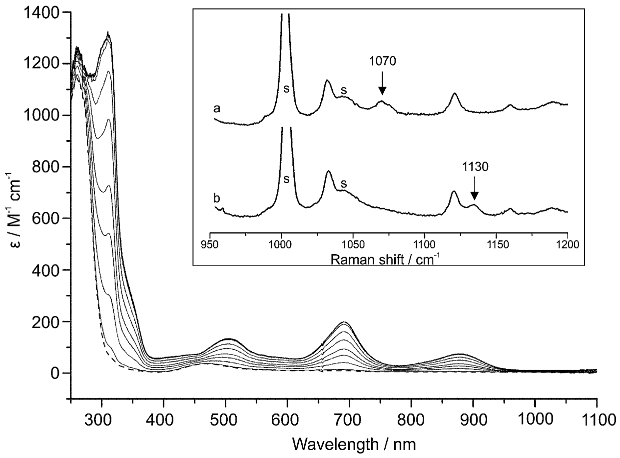
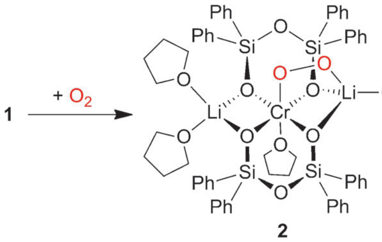


Figure 2. UV/Vis absorption spectrum of **1** (2 mmol in THF, dashed line) and the spectral changes in 5 s intervals upon addition of O_2 at −20 °C. Inset: The resonance Raman spectra of **2** prepared by treating **1** with $^{16}O_2$ (b) and with $^{18}O_2$ (a) in acetonitrile at −20 °C. Acetonitrile solvent bands (s) appear at 1005 cm^{-1} and 1040 cm^{-1}.

Remarkably, in the course of various crystallization procedures three different pseudo-polymorphs emerged (denoted as $\mathbf{2^a}$, $\mathbf{2^b}$, $\mathbf{2^c}$) differing in the amount of co-crystallized THF molecules that do not interact with the main molecule. Crystals of the solvent-free complex, $\mathbf{2^a}$ occurred only rarely. Typically the two solvates ($\mathbf{2^b}$, $\mathbf{2^c}$) crystallized, and they could be isolated from several batches of the same solvent mixture. Owing to the flexibility of the ligand, the three pseudo-polymorphs show conformational differences (see Figure S2 for details). The structural parameters of the superoxide



Scheme 3. Synthesis of complex **2**.

entity in the different polymorphs are almost identical (see Supporting Information), and therefore only the structure of **2**^{a} is discussed in detail. The chromium center is located in a slightly distorted octahedral coordination sphere; it is ligated by four siloxide donors as well as by the superoxido ligand and a THF solvent molecule *trans* to the superoxido ligand. The Cr1-O1-O2 angle is 117.5(3), the Cr1−O1 distance is 1.883(3) Å and the O1−O2 bond length 1.334(4) Å, which is at the high end for transition-metal complexes with terminal superoxido ligands. In fact among the structurally characterized "end-on" superoxide complexes found in a CSD search there is only one (cobalt-based) complex, for which a longer O−O bond is reported, however the data was collected at room temperature.[18]

The O2–Li1 distance is 2.028(9) Å which is well in the range of distances found for lithium ions coordinating to oxygen donor ligands. Hence, the compound might be best described as a heterobimetallic chromium(III) *cis*-μ-1,2-superoxido lithium complex. Li1 is significantly displaced out of the plane defined by the four oxygen atoms O3, O5, O6, O8 of the siloxide ligands coordinating to the chromium center, while the Li2 atom is in this plane (Figure 3). This result is further evidence of a significant electrostatic (coordinative) interaction between Li1 and the β-oxygen atom of the superoxido ligand. Notably, the wavenumber of the band assigned to the O−O stretching vibration in the resonance Raman spectrum is lower than the one reported for **I** (1170 cm^{-1}). In agreement with this result the O−O bond is at 1.334(4) Å significantly longer than the one in **I** (1.231(6) Å).[3] We hold the additional coordination of the superoxide to the lithium ion responsible for this elongation of the O−O bond and the accompanying decrease of the corresponding ν_{O-O} stretching vibration frequency.

Magnetic-moment measurements performed directly after complex formation with a frozen THF solution of **2**, in showed an effective magnetic moment of 2.57 μ_B at 160 K (Figure S8). Since the value is close to the spin-only value for $S = 1$ (2.8 μ_B) and similar to the value found for **I**, we infer an antiferromagnetic coupling of chromium(III), $S = 3/2$ with an $O_2^{\bullet-}$ radical, $S = 1/2$, yielding a well isolated ground state with total spin $S = 1$. The low-temperature data showed only weak zero-field splitting, $D = 1.2$ cm^{-1}, which is expected, because the 3d^{3} configuration of chromium(III) usually affords weak zero-field splitting and the radical does not contribute to D owing to its doublet nature. The measurement hence is consistent with a description of **2** as a Cr^{III} complex with an O_2^- ligand, and to our knowledge is the first temperature-dependent magnetic characterization of a chromium superoxide complex. The results are also in agreement with the reported magnetic ground state of $S = 1$ for **I**.[19]

While to date only two other chromium(III) superoxide compounds have been structurally characterized, from which **2** clearly differs through the oxo environment around the chromium center, another unique feature of **2** is its M-(*cis*-μ-1,2-OO$^{\bullet-}$)-M′ moiety. Since the first reports by Nam and co-workers,[20] the stabilization of reactive metal/oxygen species by redox-inert, Lewis acidic cations (M′) and the influence of these cations on reactivity has become a subject of intense research. Redox-inactive metal centers have been found to accelerate O_2 activation[21–27] by forming heterobimetallic O_2 adducts, which, however, have rarely been isolated and/or structurally characterized.[21,22,28] To our knowledge superoxide representatives have remained inaccessible. General procedures to construct M/O$_x$/M′ assemblies require either the initial synthesis of a (reactive) metal–oxygen species followed by the addition of redox-inactive metal ions, M', or the generation of metal–oxygen species in the presence of M'.[21–26,28–30] In our system, the Lewis acid has been an integral part of the precursor complex and already pre-arranged in close proximity to the low-valent metal center that activates dioxygen; these favorable circumstances may have allowed the structural characterization of such a moiety.

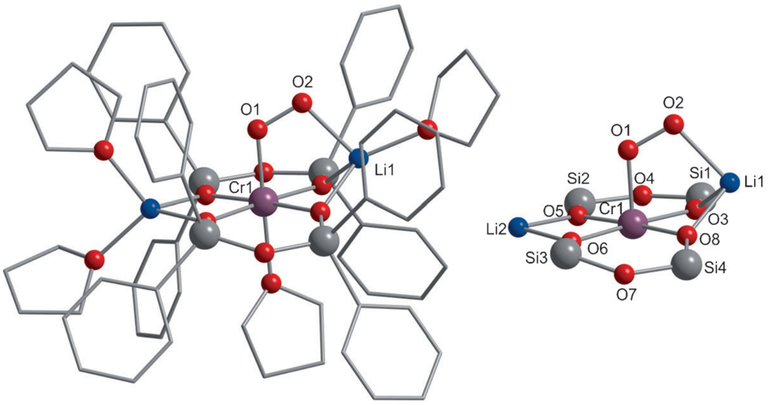


Figure 3. Molecular structure of **2**^{a} (left) and its core motif (right). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–O1 1.883(3), O1–O2 1.334(4), Li1–O2 2.028(9), Cr1–O3 1.972(3), Cr1–Li1 2.650(5), Cr1–Li2 2.841(5); Cr1-O1-O2 117.5(3), O1-Cr1-O8 91.33(14), O1-Cr1-O5 90.87(14), O8-Cr1-O5 177.41(14).

The bonding situation in **2** may also have relevance to biological systems: For example in the oxygen evolving complex (OEC) in photosystem II the binding of a dioxygen species between a redox inactive calcium ion and a manganese cation might play a crucial role, considering that the O−O bond formation is proposed to occur by a nucleophilic attack of a water molecule ligated to a calcium ion at either a Mn^{IV}–oxyl radical or a Mn^{V}–oxo species.[31] Recently Borovik and co-workers reported a Mn^{II}/Ca^{II} model system for the OEC and proposed the formation of a Mn^{III}-(OO$^{\bullet-}$)-Ca^{II} intermediate in the course of the dioxygen reduction at the manganese(II) complex, but spectroscopic evidence is lacking to date.[23]

With regard to its potential to oxidize external substrates, it was at first sight surprising that **2** neither showed significant H-atom abstraction reactivity, nor reacted with reagents that are typically oxidized by nucleophilic or electrophilic oxidants (see Supporting Information), while Nam et al. reported that complex **I** is capable of oxidizing C−H/O−H bonds[32] and transferring O atoms.[3a] However, the space filling representation of **2**^{a} (see Figure 4) reveals that the superoxide entity is well shielded by the ligands' phenyl residues, so that it is difficult to access, which may explain the low reactivity of the chromium superoxide towards external substrates.

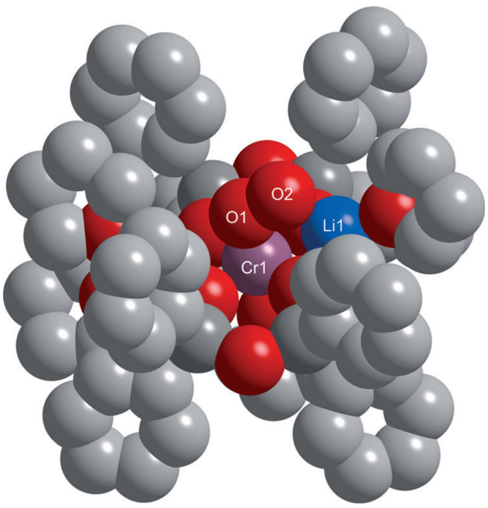
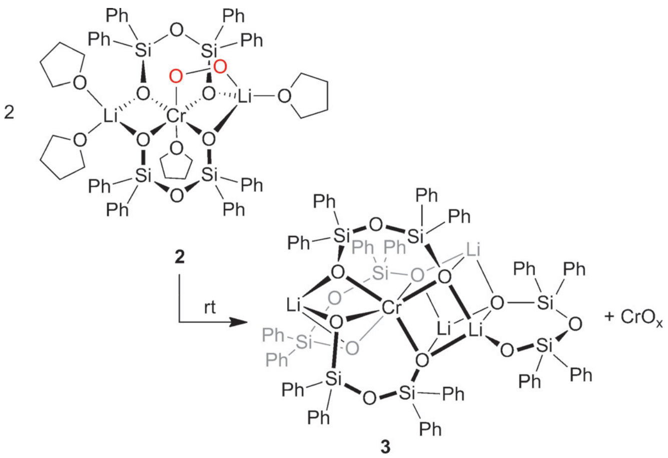


Figure 4. Space-filling representation of **2a**, as derived for the structure in Figure 3.

However, **2** is not intrinsically stable. If warmed to room temperature, the characteristic bands for the chromium(III) superoxide complex vanish from the UV/Vis spectrum with concomitant formation of a new band at 352 nm (see Supporting Information). The NMR spectrum of the crude material still showed broad, paramagnetically shifted resonances, and attempts to crystallize the/a product from *p*-xylene/*n*-hexane yielded green crystals. An X-ray diffraction analysis revealed the formation of a homoleptic chromium(IV) siloxide complex [L_4CrLi_4] (**3**) with the chromium center in an octahedral coordination sphere surrounded by six siloxide functions. The remaining charge is compensated by two lithium cations and additionally **3** contains one equivalent of LLi_2. Altogether these components assemble to a cube-like CrO_4Li_3 core (Scheme 4 and Supporting Information). To balance the stoichiometry of the thermal decomposition, we assume that in parallel to **3** CrO_x species are also formed. Complex **3** is a rare example of a complex with chromium(IV) in an exclusive siloxide environment for which there is only one precedent report by Marshak and Nocera.[33]

In summary, we showed that treating a chromium(II) siloxide precursor with O_2 resulted in the formation of a chromium(III) superoxide complex that could be characterized by a single-crystal structure analysis and various spectroscopic methods. For the first time temperature-dependent magnetic data of a chromium superoxide were reported and the determination of the molecular structure revealed a unique $Cr^{III}(\mu\text{-}1,2\text{-}OO^{\bullet-})Li^{+}$ core. Probably owing to steric shielding, the chromium superoxide unit is unreactive in contact with external substrates but it is thermally unstable: At room temperature it decomposes to yield a chromium(IV) siloxide complex.



Scheme 4. Thermal decomposition of complex **2** to **3** and CrO_x.

In future work we will explore the influence of the Lewis acid on the behavior of the chromium superoxide entity by replacing Li^{+} by other redox-inert cations (or even removing it) and the effect of reducing the steric bulk of the residues at the silicon atoms on reactivity.

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Keywords: chromium · dioxygen activation · Lewis acid · siloxides · superoxide

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