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Chromium(IV) Siloxide

Michael P. Marshak and Daniel G. Nocera*

Department of Chemistry, Room 6-335, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139-4307, United States

Supporting Information

ABSTRACT: The reaction of Na(OSi^{t}Bu$_2$Me) with $CrCl_3$ yields solid $[Cr(OSi^tBu_2Me)_3]_n$ (**1**), which can be crystallized in the presence of excess Na(OSi^{t}Bu$_2$Me) to yield $[Na(THF)][Cr(OSi^tBu_2Me)_4]$ (**2**). This complex is oxidized to yield $Cr(OSi^tBu_2Me)_4$ (**3**), a crystalline chromium(IV) siloxide complex that is air- and moisture-stable. Electronic spectroscopic analysis of the absorption spectrum of **3** indicates a particularly weak ligand field (Δ_T = 7940 cm^{-1}) and covalent Cr−O bonding. **3** provides the first structural and spectroscopic characterization of a homoleptic chromium(IV) siloxide complex and provides a benchmark for tetrahedral chromium(IV) ions residing in solid oxide lattices.

Chromium siloxide complexes have been explored for their coordination chemistry and magnetism and as precursors for heterogeneous catalysts.[1−11] Siloxide ligands are able to coordinate chromium in oxidation states ranging from II to VI, with the chromium(V) siloxide oxidation state being more elusive.[12] We have examined the alkoxide ligand ^{t}Bu$_2$MeCO (ditox) with the goal of enforcing a pseudotetrahedral ligand field about metal ions such as chromium(IV) and chromium(V).[13] The oxo complexes are particularly unusual because, in contrast to other chromium(V) oxo species, Cr(O)(ditox)$_3$ has significant radical character on the oxo moiety and participates in 1e$^-$ oxidation reactions. Because siloxides have been suggested to participate in more ionic bonding with transition metals than alkoxides,[14] we sought to develop a parallel chemistry with siloxide owing to the attribute that more weakly interacting siloxide ligands would confer greater electrophilicity and reactivity of oxo complexes derived from such platforms. We now report the coordination chemistry of the siloxide ligand ^{t}Bu$_2$MeSiO (DTBMS)[15] with chromium and provide the first crystallographically and spectroscopically characterized homoleptic chromium(IV) siloxide complex, Cr(DTBMS)$_4$.

The reaction of Na(DTBMS) (3 equiv) with $CrCl_3(THF)_3$ yields a blue solid with the formula $[Cr(DTBMS)_3]_n$ (**1**). Although **1** is insoluble in hydrocarbon solvents, the addition of 10 equiv of Na(DTBMS) permits isolation of [Na(THF)][Cr(DTBMS)$_4$] (**2**) as a royal-blue crystalline solid. Because dissolution of **2** in pentane led to the formation of **1** and Na(DTBMS), it is likely that **1** and **2** assume the following equilibrium:

$$[Na(THF)][Cr(DTBMS)_4] \rightleftarrows [Cr(DTBMS)_3]_n + Na(DTBMS) \quad (1)$$

The X-ray crystal structure of **2** (Figure 1) is similar to that of Li(THF)Cr(OCH^{t}Bu$_2$)$_4$,[16] except that the alkali ion in **2** coordinates three siloxide ligands as opposed to two alkoxides in the structure of the former. The geometry of **2** is a distorted tetrahedron with the three siloxide ligands coordinated to the Na ion assuming nearly octahedral angles of 90°. The Si−O(4) fragment displays a much shorter Cr−O(4) bond length, which reflects substantial π donation to the chromium. As a result, this distortion stabilizes three half-occupied d orbitals of the chromium(III) ion.

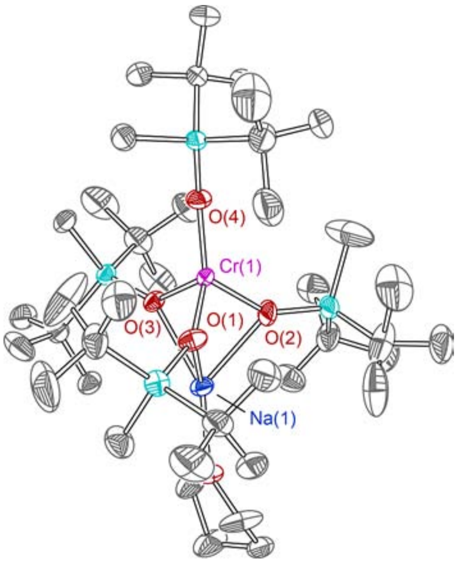

Figure 1. X-ray crystal structure of **2** with 50% probability ellipsoids. Selected bond distances (Å): Cr−O(1) 1.881(1), Cr−O(2) 1.889(1), Cr−O(3) 1.869(1), Cr−O(4) 1.843(1). Selected bond angles (deg): O(1)−Cr−O(2) 92.85(6), O(1)−Cr−O(3) 95.46(5), O(1)−Cr−O(4) 129.31(6), O(2)−Cr−O(3) 94.68(6), O(2)−Cr−O(4) 125.27(6), O(3)−Cr−O(4) 111.07(5).

Oxidation of a solution containing Na(DTBMS) (4 equiv) and $CrCl_3(THF)_3$ with AgOTf yields the neutral complex Cr(DTBMS)$_4$ (**3**) as a dark-brown crystalline solid. The X-ray crystal structure of **3** (Figure 2) reveals a nearly tetrahedral environment around the chromium with a slight distortion to give ∠O−Cr−O angles of 108° and 112°. The Cr−O bond lengths contract from an average of 1.87 Å in **2** to an average of 1.76 Å in **3**, while the Si−O bond lengths increase from 1.62 to

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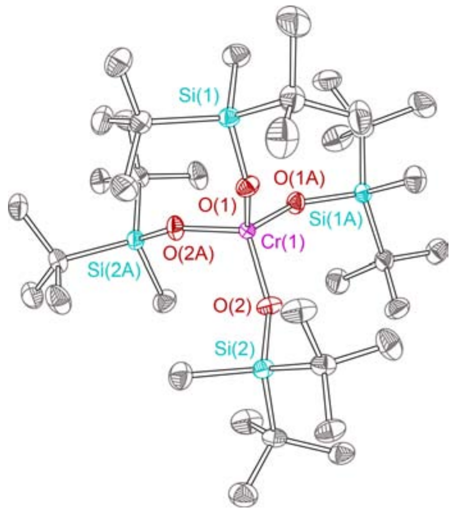
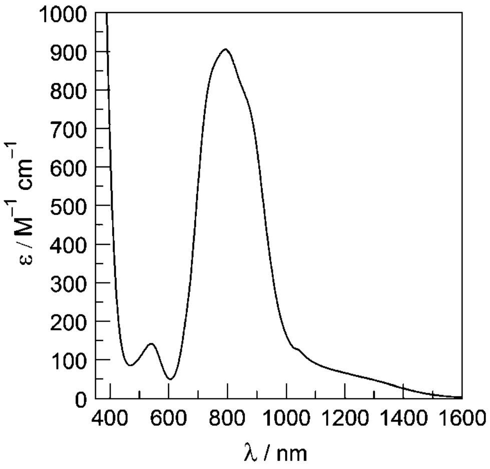


Figure 2. X-ray crystal structure of **3** with 50% probability ellipsoids. Hydrogen atoms were omitted for clarity. Selected bond distances (Å): Cr−O(1) 1.7640(8), Cr−O(2) 1.7647(8), Si(1)−O(1) 1.6659(8), Si(2)−O(2) 1.6658(8). Selected bond angles (deg): O(1)−Cr−O(1A) 112.61(5), O(1)−Cr−O(2) 108.02(4), O(1)−Cr−O(2A) 108.20(4), O(2)−Cr−O(2A) 111.83(6).



λ / nm	Energy / cm^{-1}	ε / M^{-1} cm^{-1}	Transition
278	36000	3731	CT
540	18520	140	$^1T_1(G) \leftarrow {}^3A_2(F)$
800	12500	900	$^3T_1(F) \leftarrow {}^3A_2(F)$
1042	9600	sh	$^1E(D) \leftarrow {}^3A_2(F)$
1240	8070	60	$^3T_2(F) \leftarrow {}^3A_2(F)$

Figure 3. Electronic absorption of **3** in a pentane solution and ligand-field parameters obtained from Tanabe−Sugano analysis of the spectrum in T_d symmetry.

1.67 Å. The stability of **3** to both air and moisture is likely due to the extremely bulky steric environment surrounding the chromium center.

Tetrahedral chromium(IV) siloxide complexes have been reported previously. Bradley et al. described the synthesis of $Cr(OSiEt_3)_4$ by silanolysis of $Cr(O^tBu)_4$,[11] and Fujdala and Tilley reported the mixed alkoxy−siloxy complexes $Cr(O^tBu)_3(OSi(O^tBu)_3)$ and $Cr(O^tBu)_2(OSi(O^tBu)_3)_2$.[6] Unlike the blue color of these compounds, **3** is brown. The absorption spectrum of **3** (Figure 3) shows four features assigned as metal d → d transitions, which were subjected to Tanabe−Sugano analysis in T_d symmetry. Fitting the Tanabe−Sugano diagram leads to the identification of four transitions relative to a $^3A_2(F)$ ground state; two spin-allowed transitions are observed as well as two spin-forbidden transitions. $^3T_1(F)$ has a standard intensity for a d → d transition in a tetrahedral complex. Splitting of $^3T_1(F)$ has been observed in other tetrahedral chromium(IV) species.[11,17−19] The lowest-energy transition $^3T_2(F)$ is weak because it is Laporte-forbidden. The ^1E transition is observed as a shoulder of $^3T_1(F)$. The highest-energy transition is either $^1T_1(G)$ or $^3T_1(P)$, which are energetically coincident. $^1T_1(G)$ is the preferred assignment because the $^3T_1(P)$ excited state corresponds to a two-photon transition corresponding to the $(t_2)^2$ configuration. Fitting these transitions to the appropriate Tanabe−Sugano diagram provides a ligand field, Δ_T, of 7940 cm^{-1}, which is significantly less than those observed for $Cr(O^tBu)_4$ (9430 cm^{-1})[11] and $Cr(CH_2{}^tBu)_4$ (14500 cm^{-1}).[17] This result suggests that **3** has a very weak ligand field for a molecular tetrahedral chromium(IV) complex, as might be expected owing to the typically poor donor ability of siloxide ligands.

Tanabe−Sugano analysis also yields the Racah parameter, which indicates the degree of covalency in metal−ligand bonding. The value found for **3** (530 cm^{-1}) matches well to that of $Cr(CH_2{}^tBu)_4$ (450 cm^{-1})[17] but not $Cr(O^tBu)_4$ (705 cm^{-1}).[11] These results taken together suggest that the Cr−O bond in the siloxide complex **3** is more covalent than that of the alkoxide complex.

In comparison with alkoxide ligands, siloxides have been suggested to participate in more ionic bonding with a transition metal because of the presence of the electropositive silicon center.[14] A recent review found an inverse relationship between the M−O and Si−O bond lengths among related siloxide complexes, whereas the M−Si bond remained remarkably constant.[20] This trend was explained by the electrostatic repulsion of metal and silicon nuclei. The d^2 Cr^{IV} ion in **3** has two valence electrons in the nine orbitals (3d, 4s, and 4p) available to bond the four oxygen atoms of the DTBMS ligand, which implies that the maximum Cr−O bond order in this complex is 2. The similarity in the Cr−O bond lengths of **3** to those of the discrete $CrO_4{}^{4-}$ tetrahedra observed in Ba_3CrO_5 [avg Cr−O = 1.769(3) Å[21]] suggests that the presence of the Si−O bond does not significantly affect the Cr−O bond length of **3** and that the Cr−O bond order is indeed 2. At the same time, the Si−O bond distances are the longest observed for a complex of this ligand. These bond lengths and the covalent bonding suggested by the Racah parameter can be rationalized by the existence of two different types of metal−siloxide bonding. In one case, the M−O bond is predominantly ionic and gives rise to the description of the siloxide ligands as "bulky pseudohalides".[14] In the other case, the metal forms a strong, covalent M−O bond, which concurrently lengthens the Si−O bond. These descriptions imply that the electropositive metal and silicon atoms compete in bonding the oxygen atom. In contrast, the C−O bond in an alkoxide is not as flexible, forcing alkoxides to coordinate in a more ionic fashion. This phenomenon is apparent in a comparison of the Si−O bonds in **2** and **3** (Δ = 0.05 Å) to those of the C−O bonds in $LiCr(OCH^tBu_2)_4(THF)$ and $Cr(OCH^tBu)_4$ (Δ = 0.02 Å).[16]

Solid-state materials doped with chromium(IV) have received attention as near-IR laser-diode materials.[22−27]

However, in the case of **3**, solutions of the complex at 20 and −78 °C and frozen toluene glasses at −196 °C show no emission between 400 and 1500 nm (λ_{exc} = 400 or 800 nm). This stands in contrast to the chromium(III) ion in an octahedral ligand field. Both chromium(III) (O_h) and chromium(IV) (T_d) possess similar ground- and excited-state topologies, except for the spin manifold, which is quartet/doublet for chromium(III) and triplet/singlet for chromium(IV). In chromium(III) (O_h), the lowest-energy manifold is $^4A_{2g}$−^2E_g−$^4T_{2g}$, whereas for chromium(IV) (T_d), the state parentage is $^3A_2$−^1E−$^3T_2$. The lasing action for chromium(III) (e.g., ruby lasers) is derived from pumping the ^2E_g state via the quartet manifold. Stimulated emission from this ^2E_g state is responsible for the lasing at 694 nm. A similar situation may exist for chromium(IV) (T_d), where the ^1E state is pumped via the triplet manifold. This situation will prevail at stronger ligand fields, but for extremely weak fields, as is the case for **3**, the $^3T_1(F)$ state lies at lower energy than ^1E. Hence, nonradiative decay from $^1E \rightarrow {}^3T_1$ will circumvent emission from the spin-forbidden ^1E state. For chromium(III) (O_h), such deactivation of the ^2E_g state is not possible because the ^2E_g state always lies at lower energy than $^4T_1(F)$ for all ligand-field strengths. Hence, the observed photophysical properties of **3** are entirely consistent with the extremely weak ligand field engendered by DTBMS.

The homoleptic chromium(IV) siloxide complex reported herein provides the first structural and spectroscopic characterization of chromium(IV) in an extremely weak ligand field. Accordingly, the complex provides a useful benchmark for tetrahedral chromium(IV) ions residing in solid oxide lattices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, material vendors and abbreviations used, details of synthesis and compound characterization, and crystallographic details and summary of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dnocera@fas.harvard.edu.

Notes

The authors declare no competing financial interest.

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