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An "End-On" Chromium(III)-Superoxo Complex: Crystallographic and Spectroscopic Characterization and Reactivity in C−H Bond Activation of Hydrocarbons

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Oxygen-coordinating metal intermediates, such as metal-superoxo, -peroxo, -hydroperoxo, and -oxo species, play central roles in many biological and catalytic processes.[1] Among the metal−oxygen adducts, metal-superoxo species attracted much attention recently, since the intermediates have been invoked as reactive species in C−H bond activation of substrates in nonheme iron and copper enzymes.[2,3] In biomimetic and synthetic chemistry, a number of metal-superoxo complexes have been synthesized and characterized with various spectroscopic methods and X-ray crystallography.[4] However, their reactivity has been rarely explored in C−H bond activation reactions,[5] although copper(II)-superoxo complexes have recently been shown reactivities in ligand oxidation and the oxidation of organic compounds with weak O−H and N−H bonds.[6]

Mononuclear chromium(III)-superoxo complexes with the superoxo ligand in an end-on (η^1) or side-on (η^2) fashion have been synthesized and characterized spectroscopically.[7,8] While the molecular structure of a side-on Cr(III)-superoxo complex, [Tp^{tBu,Me}Cr(pz'H)(O$_2$)]BARF (**A**), was determined by X-ray crystallography,[8] no crystal structure of end-on Cr(III)-superoxo complexes has been yet reported. Further, while the reactivities of Cr(III)-superoxo species have been reported in hydrogen atom (H-atom) transfer reactions using transition-metal hydrides and hydroperoxides as substrates,[9,10] the reactivities of chromium-superoxo species have yet to be reported in C−H bond activation reactions. Herein, we report the first crystal structure of an end-on Cr(III)-superoxo complex and the first kinetic studies of C−H bond activation of hydrocarbons by this intermediate.

The starting chromium complex, [Cr^{II}(14-TMC)(Cl)]$^+$ (**1**) (14-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), was synthesized and characterized with X-ray crystallography (Figure 1a), UV−vis spectroscopy (Figure 2a), and electrospray ionization mass spectrometry (ESI-MS) (Supporting Information (SI), Figure S1). The crystal structure of **1** shows a vacant site *trans* to the chloride ligand (Figure 1a). Bubbling O$_2$ through a blue solution of **1** in CH$_3$CN at −10 °C produced a violet intermediate, **2**, with distinct absorption features at 331 (ε = 3800 M^{-1} S^{-1}), 391 (ε = 290 M^{-1} S^{-1}), 469 (ε = 150 M^{-1} S^{-1}), 549 (ε = 240 M^{-1} S^{-1}), 643 (ε = 130 M^{-1} S^{-1}), and 675 nm (ε = 140 M^{-1} S^{-1}) (Figure 2a). The intermediate persists for several hours at −10 °C. The ESI-MS of **2** exhibits a prominent ion peak at a mass-to-charge (*m*/*z*) ratio of 375.0 (Figure 2b), whose mass and isotope distribution pattern correspond to [Cr(14-TMC)(O$_2$)(Cl)]$^+$ (**2**-^{16}O) (calculated *m*/*z* of 375.2). When the reaction was carried out with isotopically labeled ^{18}O$_2$, a mass peak corresponding to [Cr(14-TMC)(^{18}O$_2$)(Cl)]$^+$ (**2**-^{18}O) appeared at *m*/*z* of 379.0 (calculated *m*/*z* of 379.2) (Figure 2b, inset). The shift in four mass units on substitution of ^{16}O with ^{18}O indicates that **2** contains an O$_2$ unit.

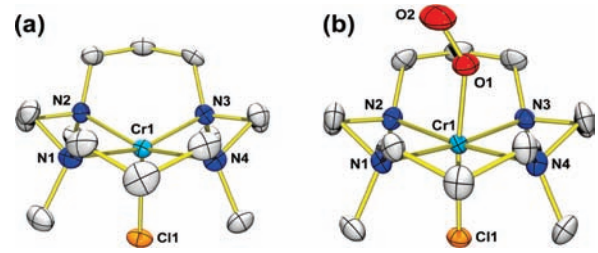

Figure 1. ORTEP plots of (a) [Cr(14-TMC)(Cl)]$^+$ (**1**) and (b) [Cr(14-TMC)(O$_2$)(Cl)]$^+$ (**2**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. All four *N*-methyl groups of the 14-TMC ligand in **1** and **2** point toward the chloride ligand. Selected bond lengths (Å) and angles (deg) for **2**: Cr1−O1 1.876(4), Cr1−Cl1 2.3166 (19), O1−O2 1.231(6), Cr1−O1−O2 146.3(4), O1−Cr1−Cl1 174.55(15). See SI Tables S1 and S2 for crystallographic and structural data and Figure S2 for space-filling representations of **1** and **2**.

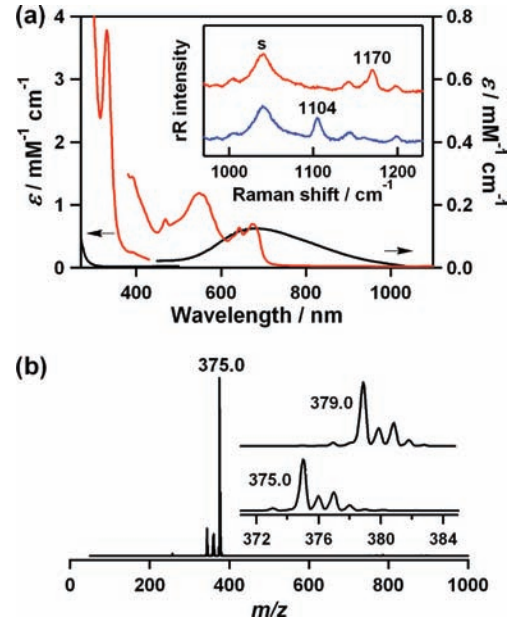

Figure 2. (a) UV−vis absorption spectra of **1** (black line) and **2** (red line) in CH$_3$CN at −10 °C, where ε values from 400 nm should be read in the right-hand axis. Inset shows resonance Raman spectra of **2** prepared with ^{16}O$_2$ (red line) and ^{18}O$_2$ (blue line). (b) ESI-MS of **2**. Inset shows isotope distribution patterns for **2**-^{16}O (lower) and **2**-^{18}O (upper).

The resonance Raman spectrum of **2** (32 mM) was collected using 442-nm excitation in CH$_3$CN at −20 °C. **2** prepared with ^{16}O$_2$ exhibits an isotopically sensitive band at 1170 cm^{-1}, which shifts to 1104 cm^{-1} when ^{18}O$_2$ is used, consistent with its assignment as an O−O stretching vibration on the basis of the $^{16}\Delta - {}^{18}\Delta$ value

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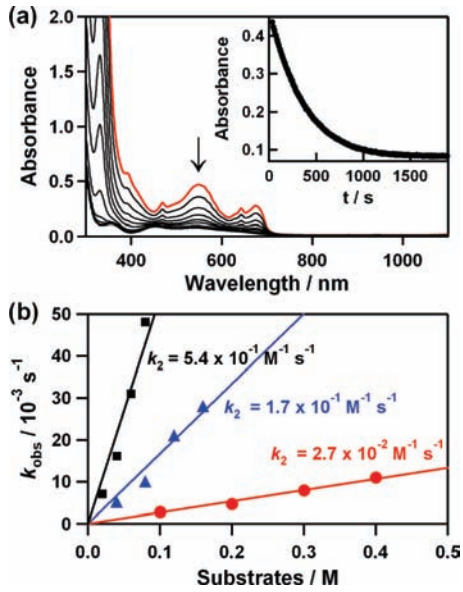

Figure 3. (a) UV−vis spectral changes of **2** (2 mM) upon addition of CHD (50 equiv to **2**, 100 mM) in CH_3CN at −10 °C. Inset shows the time course of the decay of **2** monitored at 550 nm. (b) Plots of k_{obs} against the concentration of xanthene (■), DHA (▲), and CHD (●) to determine second-order rate constants at −10 °C.

of 66 cm^{-1} ($^{16}\Delta - {}^{18}\Delta$ (calculated) = 67 cm^{-1}) (Figure 2a, inset).[11] This value is comparable to those recorded for spectroscopically characterized end-on Cr(III)-superoxo complexes, such as $[Cr(O_2)(H_2O)_5]^{2+}$ (1166 cm^{-1}) and $[Cr(cyclam)(O_2)(H_2O)]^{2+}$ (1134/1145 (doublet) cm^{-1}),[7] but is higher than that of the side-on Cr(III)-superoxo complex, **A** (1072 cm^{-1}).[8,11]

The X-ray crystal structure of **2**-Cl·$2CH_3CN$ revealed the mononuclear end-on chromium-superoxo complex in a distorted octahedral geometry (Figure 1b). Notably, the O−O bond length (1.231(6) Å) of **2** is shorter than that of the side-on Cr(III)-superoxo complex, **A** (1.327 Å);[8] the O−O bond length of **2** lies toward the low end of the range of metal-superoxo compounds (∼1.2−1.3 Å).[11] The relatively short O−O bond distance is consistent with the high frequency of the O−O stretching vibration obtained in resonance Raman measurement (vide supra). In addition, the Cr−O bond length (1.876 Å) of **2** is slightly shorter than the average Cr−O bond length (1.882 Å) of **A**.[8] Taken together, the spectroscopic and structural data indicate clearly that **2** is an end-on chromium(III)-superoxo complex.

The oxidative reactivity of **2** was explored in the C−H bond activation of substrates with weak C−H bond dissociation energies (BDEs), such as 1,4-cyclohexadiene (CHD, 78 kcal/mol), 9,10-dihydroanthracene (DHA, 77 kcal/mol), and xanthene (75.5 kcal/mol).[12] Upon reacting **2** with substrates in CH_3CN at −10 °C, the characteristic UV−vis absorption bands of **2** disappeared with a pseudo-first-order decay (Figure 3a), and product analysis of the reaction solutions revealed that benzene (90 ± 10%), anthracene (80 ± 10%), and xanthone (90 ± 10%) were produced in the oxidation of CHD, DHA, and xanthene, respectively. In addition, $[Cr^{III}(14\text{-TMC})(OH)(Cl)]^+$ was found in the reaction solutions as a decomposed product of **2** (see SI, Figure S3 for ESI-MS analysis).[13] The pseudo-first-order rate constants increased proportionally with substrate concentration (Figure 3b), from which second-order rate constants were determined (Figure 3b).[14] We also obtained a kinetic isotope effect (KIE) value of 50(5) in the oxidation of DHA by **2** (see SI, Experimental Section for experimental data). Such a high KIE value implies a hydrogen tunneling mechanism in H-atom abstraction by **2**.[15] Further, this KIE value is greater than those reported in nonheme iron- and copper-containing enzymes (e.g., KIE values of 8−16),[2b,c,16,17] where iron(III)- and copper(II)-superoxo species were proposed as reactive species for the C−H cleavage of substrates.[2,3] The large KIE value, with the dependence of the rate constants on the C−H BDE of substrates, implicates an H-atom abstraction as the rate-determining step for the C−H bond activation by **2**.[18]

In conclusion, we have reported the first structurally characterized end-on chromium(III)-superoxo complex, $[Cr^{III}(14\text{-TMC})(O_2)(Cl)]^+$, which was synthesized by reacting $[Cr^{II}(14\text{-TMC})(Cl)]^+$ with O_2. The Cr(III)-superoxo intermediate has shown reactivity with activated C−H bonds via a H-atom abstraction mechanism, perhaps supporting the findings that iron- and copper-superoxo intermediates are viable oxidants in nonheme iron- and copper-containing enzymes, respectively.[2,3]

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Supporting Information Available: Experimental Section, Tables S1−S2, and Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Nam, W. *Acc. Chem. Res.* **2007**, *40*, 465, and review articles in the special issue.
(2) (a) Bruijnincx, P. C. A.; van Koten, G.; Klein Gebbink, R. J. M. *Chem. Soc. Rev.* **2008**, *37*, 2716–2744. (b) Bollinger, J. M., Jr.; Krebs, C. *Curr. Opin. Chem. Biol.* **2007**, *11*, 151–158. (c) Xing, G.; Diao, Y.; Hoffart, L. M.; Barr, E. W.; Prabhu, K. S.; Arner, R. J.; Reddy, C. C.; Krebs, C.; Bollinger, J. M., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 6130–6135.
(3) (a) Prigge, S. T.; Eipper, B. A.; Mains, R. E.; Amzel, L. M. *Science* **2004**, *304*, 864–867. (b) Chen, P.; Solomon, E. I. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 13105–13110. (c) Klinman, J. P. *J. Biol. Chem.* **2006**, *281*, 3013–3016. (d) Rolff, M.; Tuczek, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 2344–2347.
(4) (a) Klotz, I. M.; Kurtz, D. M., Jr. *Chem. Rev.* **1994**, *94*, 567–568, and review articles in the special issue. (b) Cho, J.; Sarangi, R.; Annaraj, J.; Kim, S. Y.; Kubo, M.; Ogura, T.; Solomon, E. I.; Nam, W. *Nat. Chem.* **2009**, *1*, 568–572. (c) Cramer, C. J.; Tolman, W. B. *Acc. Chem. Res.* **2007**, *40*, 601–608. (d) Itoh, S. *Curr. Opin. Chem. Biol.* **2006**, *10*, 115–122. (e) Yao, S.; Bill, E.; Milsmann, C.; Wieghardt, K.; Driess, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7110–7113. (f) Würtele, C.; Gaoutchenova, E.; Harms, K.; Holthausen, M. C.; Sundermeyer, J.; Schindler, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3867–3869.
(5) (a) Kelm, H.; Krüger, H.-J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2344–2348. (b) Abel, E. W.; Pratt, J. M.; Whelan, R.; Wilkinson, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7119–7120.
(6) (a) Maiti, D.; Fry, H. C.; Woertink, J. S.; Vance, M. A.; Solomon, E. I.; Karlin, K. D. *J. Am. Chem. Soc.* **2007**, *129*, 264–265. (b) Fujii, T.; Yamaguchi, S.; Hirota, S.; Masuda, H. *Dalton Trans.* **2008**, 164–170. (c) Maiti, D.; Lee, D.-H.; Gaoutchenova, K.; Würtele, C.; Holthausen, M. C.; Narducci Sarjeant, A. A.; Sundermeyer, J.; Schindler, S.; Karlin, K. D. *Angew. Chem., Int. Ed* **2008**, *47*, 82–85. (d) Kunishita, A.; Kubo, M.; Sugimoto, H.; Ogura, T.; Sato, K.; Takui, T.; Itoh, S. *J. Am. Chem. Soc.* **2009**, *131*, 2788–2789.
(7) Bakac, A.; Scott, S. L.; Espenson, J. H.; Rodgers, K. R. *J. Am. Chem. Soc.* **1995**, *117*, 6483–6488.
(8) Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2333–2335.
(9) Bakac, A. *Coord. Chem. Rev.* **2006**, *250*, 2046–2058.
(10) (a) Bakac, A. *J. Am. Chem. Soc.* **1997**, *119*, 10726–10731. (b) Vasbinder, M. J.; Bakac, A. *Inorg. Chem.* **2007**, *46*, 2921–2928.
(11) Cramer, C. J.; Tolman, W. B.; Theopold, K. H.; Rheingold, A. L. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3635–3640.
(12) (a) Lam, W. W. Y.; Man, W.-L.; Lau, T.-C. *Coord. Chem. Rev.* **2007**, *251*, 2238–2252. (b) Roth, J. P.; Mayer, J. M. *Inorg. Chem.* **1999**, *38*, 2760–2761.
(13) We propose that $[Cr^{III}(14\text{-TMC})(OOH)(Cl)]^+$ is formed upon H-atom abstraction by **2**, followed by the formation of Cr(IV or V)-oxo species via O−O bond cleavage of the Cr(III)−OOH intermediate. The resulting Cr-oxo species might also be involved in the H-atom abstraction reaction, giving the $[Cr^{III}(14\text{-TMC})(OH)(Cl)]^+$ product.
(14) The reactivity of fluorene (BDE of 80 kcal/mol) is ∼8 times lower than that of CHD. See Experimental Section for data and reaction conditions.
(15) Costas, M.; Chen, K.; Que, L., Jr. *Coord. Chem. Rev.* **2000**, *200−202*, 517–544.
(16) Baldwin, J. E.; Abraham, E. *Nat. Prod. Rep.* **1988**, *5*, 129–145.
(17) Francisco, W. A.; Merkler, D. J.; Blackburn, N. J.; Klinman, J. P. *Biochemistry* **1998**, *37*, 8244–8252.
(18) (a) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441–450. (b) Borovik, A. S. *Acc. Chem. Res.* **2005**, *38*, 54–61.

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