7828 J. Am. Chem. Soc. **1995,** *117,* 7828−7829

$\{HB(3,5\text{-}Me_2pz)_3\}_2Sm(\eta^2\text{-}O_2)$: First Example of a Lanthanide Superoxo Complex

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Received April 6, 1995

The activation of molecular oxygen by transition metals and the chemistry of metal dioxygen complexes are intensely investigated areas of research.[1] The rewards are practical applications to synthesis and potential understanding of biological processes. Although the lanthanides and actinides have a great affinity for oxygen donor ligands, and f-element oxides occupy an important place in the chemistry of these elements,[2] this high oxophilicity also disfavors the formation of simple dioxygen complexes. Indeed, with the exception of the peroxyuranates[3] there are only a few actinide complexes containing the μ-η^2:η^2-peroxo bridge,[4] and to the best of our knowledge, there is only one example of a structurally characterized lanthanide complex, $(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)[La\{N(SiMe_3)_2\}_2(OPPh_3)]_2$.[5] It is well recognized that steric factors can play a crucial role in stabilizing reactive species and metal complexes with unusual coordination number or geometry. Thus the use of the highly hindered hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate and hydrotris(3-*tert*-butyl-5-isopropylpyrazolyl)borate ligands allowed the isolation of the first side-on-bonded superoxo−Co(II), $(Tp^{^tBu,Me})Co(\eta^2\text{-}O_2)$,[6a] and superoxo−Cu(II), $(Tp^{^tBu,^iPr})Cu(\eta^2\text{-}O_2)$,[6b] complexes, respectively. In lanthanide chemistry, the successful isolation of a unique series of dinuclear species, $(C_5Me_5)_2Sm(\mu\text{-}L)Sm(C_5Me_2)_2$ (L = styrene,[7a] HNNH,[7b] N_2,[7c] Bi_2,[7d] Te_2[7e]), was attributed to the stabilizing effect provided by the cage-like environment of the four C_5Me_5 ligands.

In a previous communication,[8] we reported that reaction of $Sm(Tp^{Me_2})_2$ (Tp^{Me_2} = $HB(3,5\text{-}Me_2pz)_3$) with azobenzene in a 1:1 or 2:1 ratio yielded the same mononuclear product, $(Tp^{Me_2})_2Sm(\eta^2\text{-}PhN{=}NPh)$. This contrasts the behavior of $Sm(C_5Me_5)_2$, which gives both mononuclear $(C_5Me_5)_2Sm(\eta^2\text{-}PhN{=}NPh)(THF)$ and dinuclear $(C_5Me_5)_2Sm(\mu\text{-}\eta^2\text{-}PhN{=}NPh)Sm(C_5Me_5)_2$.[9] We rationalized that the bulky nature of the Tp^{Me_2} ligands prevented formation of a bridged dinuclear complex. Consistent with this assumption we now report that $Sm(Tp^{Me_2})_2$ reacts with dioxygen at low temperature to give the first example of a lanthanide *superoxo* complex.

When a slurry of purple $Sm(Tp^{Me_2})_2$ (**1**) in toluene was stirred at −78 °C under an atmosphere of dioxygen, the solid slowly dissolved and after *ca.* 3 h an intensely colored red solution was obtained (eq 1), a vivid demonstration of ready reaction between **1** and O_2. As the solution was allowed to warm to room temperature, and excess dioxygen was removed, the color changed from red to pale green. Compound **2** was obtained as a pale green solid.[10] Characterization of **2** proved challenging, while the nature of the "red solution" remains unresolved.

$$\underset{\mathbf{1}\ (\text{purple})}{Sm(Tp^{Me_2})_2} \xrightarrow[\text{toluene, }-78\ ^\circ C]{O_2(g),\ 1\ atm} \text{red solution} \xrightarrow[-78\ ^\circ C\text{ to room temperature}]{} \underset{\mathbf{2}\ (\text{pale green})}{(Tp^{Me_2})_2Sm(\eta^2{-}O_2)} \quad (1)$$

Compound **2** is soluble in polar solvents such as THF, CH_3CN, and $CHCl_3$ and aromatic solvents like toluene, but only sparingly soluble in aliphatic hydrocarbons. The solid compound is thermally robust. It does not undergo any visible change up to 130 °C under a dynamic vacuum. The ^1H NMR spectrum is deceptively simple and exhibits only a single set of pyrazolyl resonances, three signals in a 3:3:1 ratio. The pattern of the signals remains temperature invariant down to −100 °C. The ^{11}B NMR spectrum displays one peak. Although uninformative as to the molecular structure, the NMR features established that the Tp^{Me_2} ligand remained intact in the molecule. The highest mass peak in the mass spectrum corresponded to the $(M^+ - O_2)$ fragment. The UV spectrum of the compound in CH_2Cl_2 solution exhibited an intense absorption at 240 nm ($\epsilon = 4.8 \times 10^3\ M^{-1}\ cm^{-1}$), slightly shifted from the characteristic band of KO_2 (250(1) nm, ϵ = 2686(29) $M^{-1}\ cm^{-1}$; ref 11), and first hinted at the possible presence of the superoxide ligand in compound **2**. However, the complex is ESR-silent down to −176 °C. Good evidence for O_2^- coordination came from the Raman spectrum of the complex. As shown in Figure 1, all bands, except the peak at 1124 cm^{-1}, remain unchanged in a sample prepared with $^{18}O_2$. This band is in the region associated with the stretching of the superoxo ligand,[12] and as expected, the band shifts to lower frequency (1059 cm^{-1}) upon isotopic substitution. The observed shift of 65 cm^{-1} is exactly as predicted for a pure O-O stretch from the change in reduced mass.

Final corroboration came from a single-crystal X-ray analysis. The study showed that the crystal contains well-separated, *monomeric* $(Tp^{Me_2})_2Sm(\eta^2\text{-}O_2)$ units,[13] Figure 2. The dioxygen ligand is bonded to samarium in a symmetrical, side-on fashion; the Sm−O distances, 2.329(3) and 2.321(3)Å, are nearly identical. The O−O bond distance is 1.319(5)Å and is consistent with the superoxo formulation of the O_2 ligand. The

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(10) Data for **2**: IR (KBr, cm^{-1}) 2545 (ν_{B-H}); MS (EI, 70 eV, 240 °C) 744 ($M^+ - O_2$); ^1H NMR (toluene-d_8, 25 °C, δ ppm) 9.58 (s, $\Delta_{1/2}$ = 13 Hz, 18H, pz-Me), 5.82 (s, $\Delta_{1/2}$ = 4Hz, 6H, pz-H), 5.3 (br s, $\Delta_{1/2}$ = 180Hz, 2H, B−H), 3.10 (s, $\Delta_{1/2}$ = 6 z, 18H, pz-Me); ^{11}B NMR (toluene-d_8, 25 °C, δ ppm) −6.3(s, $\Delta_{1/2}$ = 270Hz), UV−vis (CH_2Cl_2, 25 °C, 4.5×10^{-3} M) 240 nm ($\epsilon = 4.8 \times 10^3\ M^{-1}\ cm^{-1}$). Anal. Calcd for $C_{37}H_{52}N_{12}O_2B_2Sm$ (**2**·toluene): C, 51.15; H, 6.03; N, 19.34. Found: C, 51.22; H, 6.07; N, 19.52.

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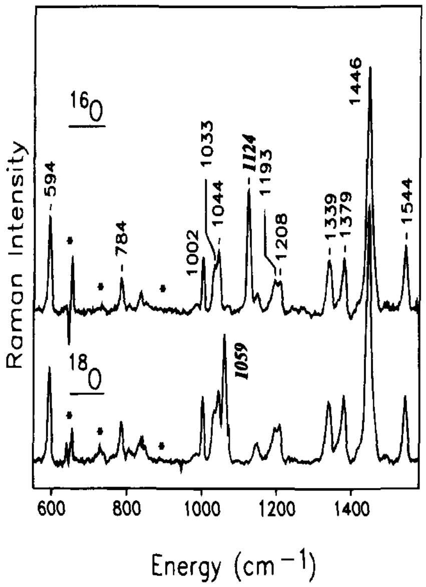

Figure 1. Raman spectra of (a) $(Tp^{Me_2})_2Sm(\eta^2\text{-}^{16}O_2)$ and (b) $(Tp^{Me_2})_2$-$Sm(\eta^2\text{-}^{18}O_2)$. Spectral features marked with an asterisk are artifacts arising from subtraction of the CD_2Cl_2 solvent spectrum. Spectra were excited with 25 mW of 457.9 nm light and detected with a CCD detector coupled to a single monochromator. Total accumulation time was 5 min for each sample. Frequencies are accurate to ± 1.5 cm^{-1}.

length of this bond is somewhat longer than the corresponding distances in $(Tp^{^tBu,Me})Co(\eta^2\text{-}O_2)$ (1.262(8) Å)[6a] and $(Tp^{^tBu,^iPr})$-$Cu(\eta^2\text{-}O_2)$ (1.22(3) Å)[6b] but in the range of the values found in NaO_2 (1.33(6) Å)[14a] and KO_2 (1.28(7) Å).[14b] Both Tp^{Me_2} ligands are coordinated to samarium in a η^3-fashion. The coordination geometry is best described as distorted pentagonal bipyramidal with N22 and N42 occupying the axial sites and N12, N32, N42, N52 and the midpoint of the O_2^- ligand spanning the equatorial positions. The distances to the axial pyrazolyl nitrogens (average 2.493(5) Å) are shorter than to the equatorial nitrogens (average 2.62(2) Å) and reflect the less congested nature of the former sites. The same is true in the related $(Tp^{Me_2})_2Sm(\eta^2\text{-azobenzene})$[8] and $(Tp^{Me_2})_2Sm(\eta^1\text{-}OC_6H_2\text{-}(CMe_3)_2O)$[15] complexes. Complex **2**, like the above compounds, has approximate C_2 symmetry in the solid state, but contrary to the azobenzene derivative, which maintains a rigid structure in solution, complex **2** is highly fluxional. The low activation energy for the fluxional process is obviously due to the lack of substituents on the O_2^- moiety. The isolation and stability of **2** are direct consequences of the unique environment provided by the two Tp^{Me_2} ligands. It can be seen in the figure that the two Tp^{Me_2} ligands provide a protective cradle which shields the O_2^- ligand, in particular by methyl groups C17 and C67.

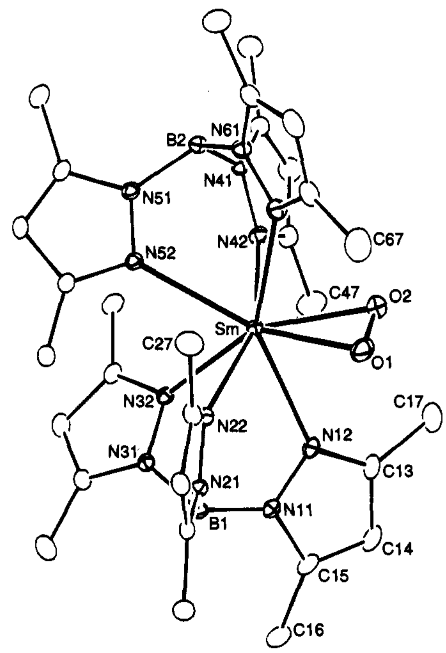

Figure 2. Structure of $(Tp^{Me_2})_2Sm(\eta^2\text{-}O_2)$ (**2**). Important bond lengths (Å, standard error on Sm–O/N 0.003Å) and bond angles (deg) are as follows: Sm–O1 2.329, Sm–O2 2.321, O1–O2 1.319(5), Sm–N12 2.642, Sm–N22 2.498, Sm–N32 2.591, Sm–N42 2.488, Sm–N52 2.619, Sm–N62 2.647; N22–Sm–N42 159.0(1), O1–Sm–O2 33.0(1).

Binding of O_2^- to samarium is strong. The ligand is not displaced by donor solvents such as THF or CH_3CN. However, preliminary reactivity studies show that it can participate in oxygen transfer reactions, delivering one oxygen atom to triphenylphosphine; the nature of the resultant samarium complex is under investigation.

In summary, we have shown that the unique protective, cradle-like, environment provided by the two Tp^{Me_2} ligands has allowed the isolation of the first superoxo lanthanide complex. It is tempting to postulate that this same coordination environment may allow the stabilization of other unusual diatomic moieties. The scope of this postulate is under intense scrutiny as are the reactivity of **2** and the nature of the "red solution".

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support.

Supporting Information Available: Summary of X-ray analysis, atomic coordinates, positional and anisotropic thermal parameters, bond distances and angles for **2** (24 pages); observed and calculated structure factors (40 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) After numerous unsuccessful attempts, X-ray quality single crystals were finally obtained from slow crystallization of **2** from a 1:1 mixture of hexane/dimethoxyethane at −40 °C. X-ray data for $(Tp^{Me_2})_2Sm(\eta^2\text{-}O_2)$ (**2**·DME) at −50 °C: triclinic, space group $P\bar{1}$ (No. 2) with $a = 10.531(2)$ Å, $b = 11.025(1)$ Å, $c = 18.129(2)$ Å, $\alpha = 100.297(7)°$, $\beta = 97.423(9)°$, $\gamma = 100.571(9)°$, $V = 2007.1(8)$ Å^3, and $Z = 2$ ($d_{calcd} = 1.434$ g·cm^{-3}); 7281 reflections measured (6987 unique; 5526 with $I > 3\sigma(I)$); $R = 0.034$, $R_w = 0.042$, GOF = 1.298.

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