



Geometric and electronic structure of a crystallographically characterized thiolate-ligated binuclear peroxo-bridged cobalt(III) complex

Maksym A. Dedushko¹ · Dirk Schweitzer¹ · Maike N. Blakely¹ · Rodney D. Swartz¹ · Werner Kaminsky¹ · Julie A. Kovacs¹

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Abstract

In order to shed light on metal-dependent mechanisms for O–O bond cleavage, and its microscopic reverse, we compare herein the electronic and geometric structures of O₂-derived binuclear Co(III)– and Mn(III)–peroxo compounds. Binuclear metal peroxo complexes are proposed to form as intermediates during Mn-promoted photosynthetic H₂O oxidation, and a Co-containing artificial leaf inspired by nature's photosynthetic H₂O oxidation catalyst. Crystallographic characterization of an extremely activated peroxo is made possible by working with substitution-inert, low-spin Co(III). Density functional theory (DFT) calculations show that the frontier orbitals of the Co(III)–peroxo compound differ noticeably from the analogous Mn(III)–peroxo compound. The highest occupied molecular orbital (HOMO) associated with the Co(III)–peroxo is more localized on the peroxo in an antibonding $\pi^*(\text{O}–\text{O})$ orbital, whereas the HOMO of the structurally analogous Mn(III)–peroxo is delocalized over both the metal *d*-orbitals and peroxo $\pi^*(\text{O}–\text{O})$ orbital. With low-spin *d*⁶ Co(III), filled t_{2g} orbitals prevent π -back-donation from the doubly occupied antibonding $\pi^*(\text{O}–\text{O})$ orbital onto the metal ion. This is not the case with high-spin *d*⁴ Mn(III), since these orbitals are half-filled. This weakens the peroxo O–O bond of the former relative to the latter.

Keywords Dioxygen activation · Transition-metal peroxo chemistry · Electronic structure · X-ray crystallography

Introduction

Photosynthesis is one of the most important biochemical processes for maintaining aerobic life on this planet [1, 2]. This process involves the capture of solar energy and storage in chemical bonds via the catalytic oxidation of H₂O, the extraction of electrons, and formation of O₂ as a by-product [3–6]. Nature had three billion years to refine this highly efficient Mn-containing catalyst, which is referred to as the oxygen evolving complex (OEC). The OEC consists of a CaMn₃O₄ cubane with an additional dangling Mn ion. Insights into the mechanism of water oxidation and O₂

evolution, as well as its microscopic reverse, would contribute to the development of solar fuel cells. The O–O bond-forming step is not well understood [7] since it follows the rate-determining step [8–12]. An unobserved Mn–peroxo intermediate is proposed to form [9–11], followed by the rapid release of O₂ [13]. Despite the fundamental importance of Mn–dioxygen chemistry, it remains relatively unexplored [14–16]. Small molecules provide an advantage in that lower temperatures can be accessed by using organic solvents, thereby providing an opportunity to observe metastable intermediates. Mononuclear Mn–peroxo complexes include side-on η^2 -bound peroxo [Mn^{III}(O₂)(13-TMC)]⁺ [17], and [Mn^{III}(O₂)κ⁴-N₄py]⁺ [18]. There are fewer examples of binuclear Mn–peroxo compounds, and no examples of Mn clusters containing a coordinated peroxo. Our group reported the first example of a spectroscopically and structurally characterized, metastable binuclear peroxo-bridged Mn(III) complex derived from dioxygen [14, 19]. In addition, we have examined the effect of coordination environment on peroxo O–O bond lengths [20].

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✉ Julie A. Kovacs
kovacs@uw.edu

¹ The Department of Chemistry, University of Washington,
Box 351700, Seattle, WA 98195-1700, USA

The inherent instability and reactive nature of dinuclear Mn(III)–peroxo complexes, both posited in nature and their synthetic analogues, renders the experimental investigation of their electronic and geometric structures difficult. Most of the reported Mn(III)–peroxo complexes are mononuclear with a peroxo moiety bound in a side-on (η^2) binding mode [15, 21–24]. There are very few examples of structurally characterized multi-nuclear Mn(III)–peroxo complexes [25]. We reported the first crystallographically characterized binuclear example, $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}(6\text{-Me-DPEN}))]_2(\mu\text{-O}_2)\}^{2+}$ (**1**) [19] derived from O_2 . Reduced $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}(6\text{-Me-DPEN}))]^+$ (**2**) binds dioxygen on the millisecond timescale to form a superoxo intermediate [19], which then converts to **1**, en route to a binuclear μ -oxo end-product, $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}(6\text{-Me-DPEN}))]_2(\mu\text{-O})\}^{2+}$ (**3**) [14, 19]. The isolation of peroxo complex **1** was possible because the rate-determining step was determined to be the O–O bond-cleaving step [19]. The N-heterocycles (N^{Ar}) of $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}(6\text{-Me-DPEN}))]^+$ (**2**) can be derivatized providing a convenient method for determining how steric and electronic properties affect the reactivity and relative stability of metastable dioxygen intermediates [19]. Manganese-dioxygen intermediates are not observed in the absence of steric bulk, for example with a H-substituent in the 6-position, $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}(6\text{-H-DPEN}))]^+$ (**4**), or with primary amines in the ligand scaffold, $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))]^+$ (**5**). Our group has shown that steric bulk increases metal ion Lewis acidity by lengthening metal–ligand bonds, resulting in a stronger peroxo O–O bond [26].

More recent work by our group has led to the observation of two new metastable peroxo intermediates formed in the reaction between O_2 and thiolate-ligated Mn(II) derivatives (Fig. 1) of **2**, $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}(6\text{-MeO-DPEN}))]^+$ (**6**) and $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}(\text{quinoEN}))]^+$ (**7**) [20]. Changing the steric bulk and electron donor character of the ligand was shown to affect the barriers to O_2 binding and release, as well as O–O bond cleavage [20]. The less sterically encumbered 6-MeO-pyridine complex **6** binds O_2 more readily than the

other derivatives, **2** and **7**, and O_2 release from the superoxo is more favored. In addition, the 6-MeO-pyridine complex forms a total of four metastable intermediates with dioxygen, two of which follow a peroxo [20]. Thiolate ligands (RS^-) were incorporated, because they have been shown to lower the activation barrier to O_2 binding [27, 28], as well as provide a convenient spectroscopic handle for observing reactive dioxygen intermediates [29].

The photosynthetic OEC's dioxygen-evolving properties can also be mimicked by cobalt complexes, the most notable example being Nocera's bioinspired artificial leaf [5, 30]. Discrete molecular Co_4O_4 cubane clusters, such as $[\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4]^+$, have also been shown to evolve O_2 upon the addition of OH^- [31]. A Co–peroxo is proposed to form as an intermediate, however, it was not observed. The mechanism is proposed to involve an oxidized trapped valence $\text{Co}^{\text{III}}_2\text{Co}^{\text{IV}}_2$ cubane cluster, and coupling between two oxygens on an adjacent Co^{IV}_2 pair ($\text{O}-\text{Co}^{\text{IV}}-\text{Co}^{\text{IV}}-\text{O} \rightarrow \bullet\text{O}-\text{Co}^{\text{III}}-\text{Co}^{\text{III}}-\text{O}\bullet$) to afford an unobserved $\text{Co}^{\text{III}}-\text{O}-\text{O}-\text{Co}^{\text{III}}$ peroxo [30].

The mechanism for the O–O bond-forming step is likely to be different for Co and Mn, given that the oxo wall separates them [32]: the former is almost certain to proceed via an oxyl coupling mechanism [12], whereas the latter could proceed via a nucleophilic attack mechanism involving $\text{Mn}(\text{V})=\text{O}$ and $\text{M}-\text{OH}$ ($\text{M}=\text{Ca}(\text{II})$ or $\text{Mn}(\text{III})$) intermediates [33]. Developing a better understanding of the geometric and electronic structural differences between Mn(III) and Co(III) peroxo complexes, and the properties critical to O_2 release [12], is likely to shed more light on these reactions, and provide insight into metal-dependent mechanisms. There are many examples of synthetic Co(II) complexes that readily react with molecular O_2 at room temperature to form isolable dinuclear μ -peroxo Co(III) complexes, including a crystallographically characterized pac-man Schiff-base calixpyrrole-ligated binuclear Co(III) peroxo [34], and a crystallographically characterized fused pincer-ligated binuclear Co(III)

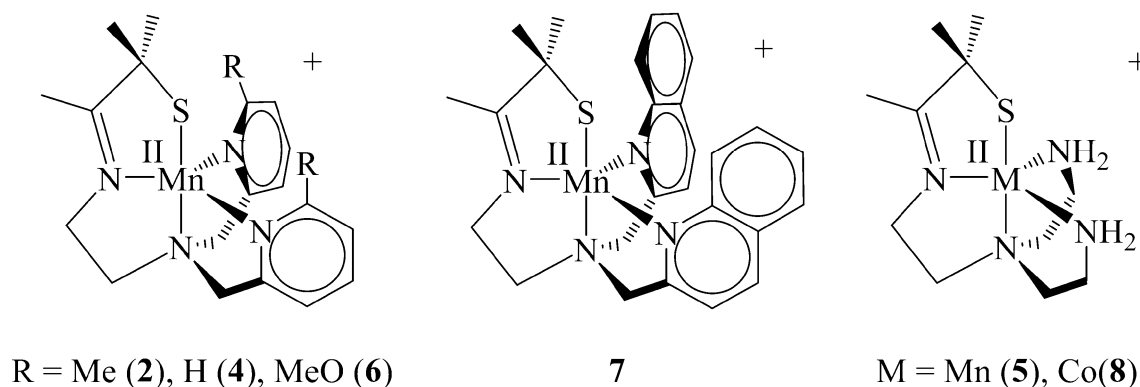


Fig. 1 Chemdraw depictions of $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}(6\text{-Me-DPEN}))]^+$ (**2**), $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}(6\text{-H-DPEN}))]^+$ (**4**), $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}(6\text{-MeO-DPEN}))]^+$ (**6**), and $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}(\text{quinoEN}))]^+$ (**7**), $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))](\text{PF}_6)$ (**5**) and $[\text{Co}^{\text{II}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))](\text{PF}_6)$ (**8**)

peroxo complex [35–40]. However, there are few (if any) structurally analogous pairs of binuclear μ -peroxo-bridged Co(III) and Mn(III) complexes. Whereas Mn(III) peroxo complexes are metastable, the added stability of low-spin d^6 transition-metal complexes is likely to stabilize a Co(III) peroxo, making it easier to obtain structural information. Described herein, is a crystallographically characterized, O_2 -derived thiolate-ligated Co(III)- μ -peroxo complex, which is structurally analogous to our previously reported series of O_2 -derived Mn-peroxo complexes [19].

Experimental

General methods

All manipulations were performed using Schlenk-line techniques or under a N_2 atmosphere in a glovebox. Reagents and solvents purchased from commercial vendors were of highest available purity and were used without further purification unless otherwise noted. MeOH ($Mg(OMe)_2$) was dried and distilled prior to use. Acetonitrile, Diethyl ether, and THF were rigorously degassed and purified using solvent purification columns housed in a custom stainless-steel cabinet and dispensed by a stainless-steel Schlenk-line (GlassContour). $[Co^{II}(S^{Me_2}N_4(tren))](PF_6)$ (**8**) was prepared according to literature procedures [41]. NMR spectra were recorded on a Bruker DPX 500 FTNMR spectrometer and referenced to the residual protio solvent. Electrospray-ionization mass spectra were obtained on a Bruker Esquire Liquid Chromatograph-Ion Trap mass spectrometer. Cyclic voltammograms were recorded in MeCN solutions with $Bu_4N(PF_6)$ (0.100 M) as the supporting electrolyte, using an EG&G Princeton Applied Research potentiostat with a glassy carbon working electrode, an SCE reference electrode, and a platinum auxiliary electrode. Electronic absorption spectra were recorded using a Hewlett-Packard 8453 diode array spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

Synthesis of $[Co^{III}(S^{Me_2}N_4(tren))]_2(trans-\mu-1,2-O_2)(PF_6)_2 \cdot MeCN$ (**9**)

Reduced $[Co^{II}(S^{Me_2}N_4(tren))](PF_6)$ (**8**) (317 mg, 0.71 mmol) was dissolved in 100 mL of acetonitrile. The solution was exposed to air at room temperature and left to stir overnight. The dark red solution was evaporated to dryness, and the resulting red powder was washed with diethyl ether over a frit. The remaining solid was dissolved in 10 mL acetonitrile and layered with 30 mL of diethyl ether. The two layers were allowed to diffuse overnight at $-40^\circ C$ to afford red crystals of **9**. ESI-MS: calculated m/z for $[C_{22}H_{50}Co_2N_8O_2S_2]^{2+}$ or $[C_{11}H_{25}CoN_4OS]^+ = 320.1$ found $m/z = 320.0$. Electronic

absorption spectrum (MeCN): λ_{max} (nm) (ϵ ($M^{-1}cm^{-1}$)): 270(6500). 1H NMR (500 MHz, CD_3CN) δ ppm 1.45 (s, 6H), 2.05 (s, 3H), 2.44 (s, 2H), 2.72 (dd, $J = 11.07, 4.37$ Hz, 2H), 2.78 (q, $J = 6.38$ Hz, 2H), 3.00 (s, 2H), 3.33 (dd, $J = 12.00, 5.44$ Hz, 2H), 3.40 (t, $J = 8.50, 8.50$ Hz, 2H), 3.66 (t, $J = 7.22, 7.22$ Hz, 2H). Reduction potential (MeCN, vs. SCE): +220 mV (reversible). Elemental analysis for $C_{22}H_{50}Co_2F_{12}N_8O_2P_2S_2$ Calcd: C, 28.39; H, 5.42; N, 12.04. Found: C, 28.86; H, 5.41; N, 12.92.

X-ray crystallographic structure determination

A $0.19 \times 0.17 \times 0.14$ mm³ black prism of $[Co(III)(S^{Me_2}N_4(tren))]_2(trans-\mu-1,2-O_2)(PF_6)_2 \cdot MeCN$ (**9**) was mounted on a glass capillary with oil. Data were collected at $-143^\circ C$ on a Nonius Kappa CCD single crystal X-ray diffractometer, Mo $K\alpha$ -radiation. Crystal-to-detector distance was 30 mm and exposure time was 15 s per degree for all sets. The scan width was 2° . Data collection was 94.5% complete to 29.61° in θ and 96.9% complete to 25° in θ . A total of 18,295 partial and complete reflections were collected covering the indices, $h = -9$ to 8, $k = -13$ to 14, $l = -15$ to 14. 6556 reflections were symmetry independent and the $R_{int} = 0.0408$ indicated that the data were above average quality (0.07). Indexing and unit cell refinement indicated a triclinic P lattice. The space group was found to be P-1 (no. 2). The data for **9** were integrated and scaled using *hkl*-SCALEPACK [42, 43]. Solution by direct methods (SHELXS, SIR97) produced a complete heavy atom phasing model consistent with the proposed structure [44, 45]. The structure was completed by difference Fourier synthesis with SHELXL [46, 47]. Scattering factors are from Waasmaier and Kirfel [11]. Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.95–1.00 Å. Isotropic thermal parameters U_{eq} were fixed such that they were 1.2 U_{eq} of their parent atom U_{eq} for CHs and 1.5 U_{eq} of their parent atom U_{eq} in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Final solution plotted using ORTEP and POV-Ray programs [48, 49].

Computational details

Calculations were performed using the ORCA v.4.0.0 quantum chemistry package developed by Neese and coworkers [50]. Geometry optimizations employed the B3LYP hybrid functional and 6-311G basis set for all complexes. Tight convergence criteria were required for self-consistent field (SCF) solutions. The Grid4 (GridX4) integration grid size, and the conductor-like polarizable continuum model (CPCM) were used for geometry optimizations [51].

Crystallographic coordinates were used as a starting point for geometry optimizations of peroxo $\{[\text{Co}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))]_2(\text{trans-}\mu\text{-1,2-O}_2)\}^{2+}$ (**9**) using the B3LYP/6-311G functional/basis set. Details regarding the theoretical calculations for peroxo-bridged $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{quinoEN}))]_2(\mu\text{-O}_2)(\text{BPh}_4)_2$ (**10**) and $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeO-DPEN}))]_2(\mu\text{-O}_2)\}^{2+}$ (**11**) are reported elsewhere [20]. Canonical molecular orbital isosurfaces were visualized at an isovalue of 0.03 a_0^3 using UCSF Chimera software [52].

Results and discussion

The reaction between $[\text{Co}^{\text{II}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))](\text{PF}_6)$ (**8**) and dioxygen (O_2) in MeCN at ambient temperature results in a color change from pale yellow to red, with the concomitant growth of peaks at $\lambda_{\text{max}}(\epsilon \text{ (M}^{-1} \text{ cm}^{-1})) = 280$ (11,350), 385 (3085), and 485 (1250) nm (Figure S2). The ^1H NMR of this dioxygen product, **9** (Figure S3), only contains peaks in the diamagnetic region of the spectrum, consistent with oxidation of the $S=3/2$ Co(II) precursor [41] to low-spin (L.S.) $S=0$ Co(III). The ESI-MS of **9** (Fig. 2) displays a peak at $m/z = 320.0$, consistent with either the addition of two oxygen atoms to a dicationic dimer ($M+32$, where $M=608.2$, $z=2$), or the addition a single oxygen atom to a monocationic monomer ($M+16$, where $M=304.1$, $z=1$). These two possibilities would be distinguishable based on their isotope distribution pattern. As shown in the simulated spectrum of Figure S1, peaks would be separated by 1/2 mass unit for a dicationic dimer, versus one mass unit for a monocationic monomer. The experimental data would therefore be

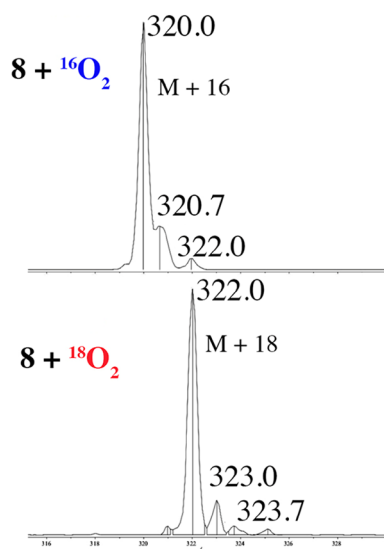


Fig. 2 ESI-MS of peroxo-bridged **9** derived from $^{16}\text{O}_2$ (top) and $^{18}\text{O}_2$ (bottom)

consistent with the former. This was consistently the case across a wide range of applied skim voltages (4–10 V to 30–70 V), implying that we are looking at either a Co-peroxo with a remarkably weak O–O bond, or a Co-oxo. The reaction of **8** with isotopically labeled $^{18}\text{O}_2$ results in a peak shift to $m/z = 322.0$ ($M+18$), consistent with incorporation of one oxygen atom, derived from dioxygen.

Crystallization from MeCN/ Et_2O afforded single crystals of **9** suitable for X-ray crystallography. As shown in the ORTEP diagram of Fig. 3, $\{[\text{Co}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))]_2(\text{trans-}\mu\text{-1,2-O}_2)\}^{2+}$ (**9**) is binuclear and contains an O_2 moiety bridging between two Co ions in a *trans-μ-1,2*-configuration. The Co–S bond length of **9** (2.2180 (9) Å) is 0.083 Å shorter than the reduced precursor **8** (Co–S = 2.3006(7) Å), and the average Co–N bond length distance is 0.173 Å shorter than the corresponding distance in **8**. More importantly, the Co–S, average Co–N, and Co–O bond lengths in **9** are comparable (Table 1) to the previously characterized hydroxo complex $[\text{Co}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))(\text{OH})]^+$ (**12**) [53], consistent with the oxidation of the high-spin Co(II) ($S=3/2$) ion in **8** to a low-spin Co(III) ($S=0$) ion in **9**. The Co–O bond length in **9** (1.899 (2) Å) is comparable to that of **12**, as well as other previously reported Co(III) peroxo compounds [35, 54, 55]. The O–O bond length of dicationic **9** (1.482(4) Å) is consistent with a peroxo, but is 0.054 Å longer than that of neutral $(\text{B}_2\text{pz}_4\text{Py})\text{Co}^{\text{III}}\text{--O--O--Co}^{\text{III}}(\text{B}_2\text{pz}_4\text{Py})$, which contains two dianionic ligands [50]. This indicates that the peroxo in **9** is highly activated. The two halves of the dimer are twisted relative to each other with a dihedral angle of 180° , and the plane containing the Co(III)–O–O–Co(III) core is approximately perpendicular to the plane containing two Co–S bonds. The Co–O–O bond angle (114°) is more obtuse than the corresponding Mn–O–O angle of **1** (Table 1), but is comparable to most Co^{III} –peroxo compounds [35, 54–61].

Structure **9** is analogous to our previously reported crystallographically characterized *trans-μ-1,2*-peroxo bridged Mn(III) complex, $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPEN}))]_2(\text{trans-}\mu\text{-1,2-O}_2)\}^{2+}$ (**1**) [19], as well as two additional

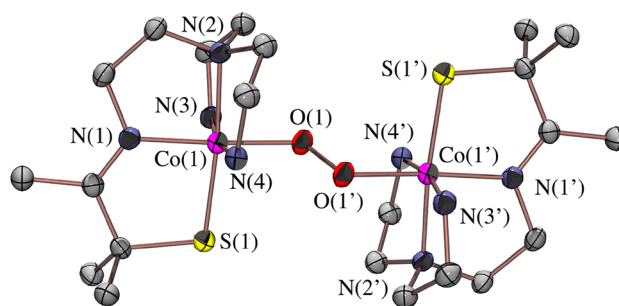


Fig. 3 ORTEP of peroxo-bridged $\{[\text{Co}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))]_2(\text{trans-}\mu\text{-1,2-O}_2)\}^{2+}$ (**9**) showing 50% probability ellipsoids and the atom labeling scheme. Hydrogens are omitted for clarity

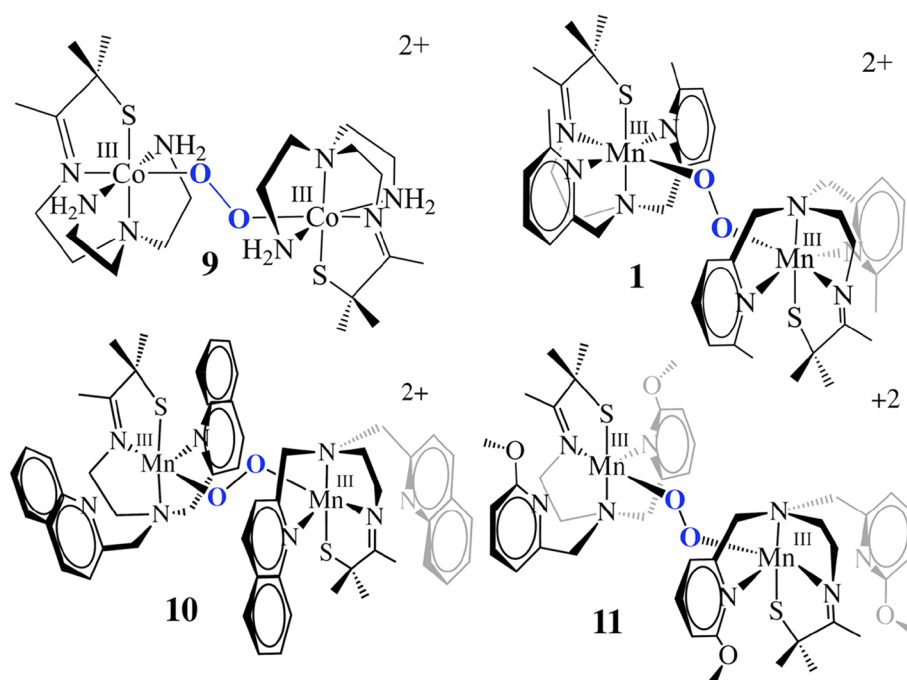
Table 1 Selected bond distances (Å) and bond angles (deg) for $[\text{Co}^{\text{II}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))](\text{PF}_6)$ (**8**), peroxo-bridged $[\text{Co}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))]_2(\text{trans-}\mu\text{-1,2-O}_2)(\text{PF}_6)_2\cdot\text{MeCN}$ (**9**), peroxo-bridged $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeO-DPEN}))]_2(\text{trans-}\mu\text{-1,2-O}_2)(\text{PF}_6)_2\cdot\text{MeCN}$ (**10**), peroxo-bridged $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{quinoEN}))]_2(\mu\text{-O}_2)$ (**11**), and hydroxo bound $[\text{Co}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))(\text{OH})](\text{PF}_6)$ (**12**)⁵⁴

	8 (d^7 , $S = 3/2$; H.S.)	9 (d^6 , $S = 0$; L.S.)	1 (d^4 , $S = 2$; H.S.)	12
M(1)–S(1)	2.3006 (7)	2.2180 (9)	2.275 (11)	2.217 (3)
M(1)–N(1)	2.050 (2)	1.900 (2)	2.040 (3)	1.892 (8)
M(1)–N(2)	2.223 (2)	1.978 (3)	2.203 (3)	1.971 (8)
M(1)–N(3)	2.107 (2)	1.935 (2)	2.410 (3)	1.935 (6)
M(1)–N(4)	2.086 (2)	1.963 (2)	2.492 (3)	1.935 (6) ^a
M(1)–O(1)	N/A	1.899 (2)	1.832 (3)	1.869 (6)
O(1)–O(1')	N/A	1.482 (4)	1.452 (5)	N/A
M(1)··O(1')	N/A	2.845	2.481	N/A
M(1)··M(1')	N/A	4.604	4.113	N/A
M(1)–O(1)–O(1')	N/A	114.0 (2)	97.5 (6)	N/A
O(1)–M(1)–S(1)	N/A	94.88 (7)	85.12 (9)	95.8 (2)
O(1)–M(1)–N(3)	N/A	90.9 (1)	92.4 (1)	87.7 (2)
O(1)–M(1)–N(1)	N/A	174.24 (9)	165.5 (1)	178.0 (3)
O(1)–M(1)–N(2)	N/A	90.61 (9)	111.1 (1)	90.0 (3)
S(1)–M–N(2)	163.96 (6)	174.24 (7)	163.3 (1)	174.3 (2)
S(1)–M–N(3)	112.25 (6)	94.10 (8)	109.0 (1)	94.23 (17)
S(1)–M–N(4)	106.90 (6)	94.05 (8)	105.6 (1)	94.23 (17) ^a
N(1)–M–N(4)	125.14 (8)	92.0 (1)	101.7 (1)	92.17 (17) ^a

^aN(4) = N(3') for this structure, since a crystallographic mirror plane relates the two atoms (N(3) and N(3'))

spectroscopically characterized Mn(III)–peroxo compounds, $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{quinoEN}))]_2(\mu\text{-O}_2)(\text{BPh}_4)_2$ (**10**) and $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeO-DPEN}))]_2(\mu\text{-O}_2)\}^{2+}$ (**11**), for which

spectroscopically calibrated DFT-calculated structures are available (Scheme 1) [20]. Relative to **1** (1.452 (5)), the peroxo O–O bond of bimetallic Co(III)–peroxo **9** is 0.03 Å



Scheme 1 ChemDraw sketches of $\{[\text{Co}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))]_2(\text{trans-}\mu\text{-1,2-O}_2)\}^{2+}$ (**9**), $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeO-DPEN}))]_2(\text{trans-}\mu\text{-1,2-O}_2)^{2+}$ (**1**),²⁶ $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{quinoEN}))]_2(\mu\text{-O}_2)\}^{2+}$ (**10**),¹⁹ and $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeO-DPEN}))]_2(\mu\text{-O}_2)\}^{2+}$ (**11**)¹⁹

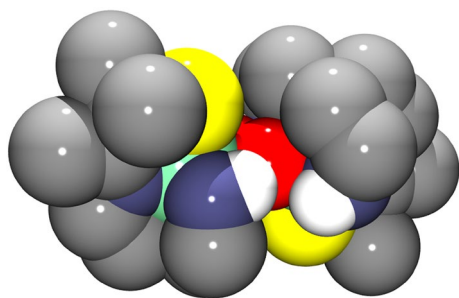


Fig. 4 Space-filling diagram of peroxo-bridged $\{[\text{Co}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))]_2(\text{trans-}\mu\text{-1,2-O}_2)\}^{2+}$ (**9**) showing N–H hydrogen bonding to the peroxo (red)

longer, and closer to that of O_2^{2-} (1.49 Å) [62], indicating that the peroxo is more activated in **9**. An activated O–O bond should be susceptible to cleavage, consistent with our inability to observe the intact dimer by mass spectrometry (*vide supra*). Only half of the dimer, consisting of a monocationic cobalt-oxo, is detected by ESI–MS, even at the lowest applied skim voltage (4–10 V) (Fig. 2). Peroxos are π -donors that can be stabilized via the removal of antibonding electron density from the peroxo π^* orbitals, via π -back-donation into a metal ion t_{2g} d -orbital. With low-spin d^6 Co(III), the π -symmetry t_{2g} orbitals are filled, whereas they are only half-filled with a high-spin d^4 Mn(III) ion. If the t_{2g} orbitals are filled, then the above described pathway for O–O bond stabilization is not available. In addition, with cobalt peroxo **9** there are two short H-bonds ($\text{N}(2)\text{--H}(2\text{E})\cdots\text{O}(1')=2.051$ Å) to the bridging peroxo oxygens (Fig. 4), which are absent in the Mn(III) compound. It is possible that these H-bonds also contribute to O–O bond activation in **9**. However, there are other examples of bridging Co peroxo compounds lacking H-bonds with similar distances [35, 63].

We recently showed that metal ion Lewis acidity can influence peroxo O–O bond lengths by facilitating π -back-donation of electron density from the peroxo π^* orbital [16, 26]. Metal ion Lewis acidity was found to depend on the steric properties of the ligand scaffold. Ligands with sterically demanding substituents on the aryl ring (e.g., **2**, **6**, and **7**, Fig. 1) were found to possess unusually long $\text{M}\cdots\text{N}^{\text{Ar}}$ distances in the corresponding M(III) derivatives [64]. Elongation of the $\text{Mn}\cdots\text{N}^{\text{Ar}}$ distances was shown to increase metal ion Lewis acidity and create a virtual coordinatively unsaturated metal ion [16, 26]. This facilitates π -back-donation from the filled peroxo $\pi^*(\text{O}=\text{O})$ orbital to the metal ion, resulting in a shorter peroxo O–O bond [16]. With less sterically demanding primary amines (e.g., **5** and **8**, Fig. 1), on the other hand, M–N (M = Mn or Co) distances in the corresponding M(III) derivatives were found to be significantly shorter.

To gain more insight into the electronic structure differences governing peroxo O–O bond activation, DFT

calculations were performed on Co-peroxo **9** and compared to the broken symmetry (BS) DFT-calculated structures for our previously reported Mn-peroxo compounds $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{quinoEN}))]_2(\mu\text{-O}_2)\}^{2+}$ (**10**) and $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeO-DPEN}))]_2(\mu\text{-O}_2)\}^{2+}$ (**11**) of Scheme 1 [20]. Complex **9** was geometry optimized using the B3LYP hybrid functional and the 6-311G basis set, yielding metal–ligand and peroxo O–O bond lengths that are in reasonable agreement with crystallographic parameters (maximum bond length deviation of 3.7%) (Figure S4). Notably, the calculated O–O bond length of 1.521 Å supports a more activated peroxo moiety in **9**.

The DFT-calculated Mulliken charges of the metal ions in **9** (+1.45), **11** (+1.59), and **10** (+1.60) indicate that metal ion Lewis acidity does not necessarily follow the expected periodic trends of $\text{Co} > \text{Mn}$. Steric constraints imposed by the ligand elongate two of the $\text{Mn}\cdots\text{N}^{\text{Ar}}$ distances [20] for the Mn-peroxo complexes $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{quinoEN}))]_2(\mu\text{-O}_2)\}^{2+}$ (**10**, Scheme 1) and $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeO-DPEN}))]_2(\mu\text{-O}_2)\}^{2+}$ (**11**, Scheme 1), and this is reproduced by the calculations. Conversely, the calculated electron density localized on the bridging peroxo oxygens is higher with Co-containing **9** (−0.56), relative to Mn-containing **11** (−0.48) and **10** (−0.49). This trend reflects the fact that the $\pi^*(\text{O}=\text{O})$ orbital cannot π -back-donate into the filled t_{2g} orbitals of a L.S. d^6 Co(III) ion, resulting in the localization of electron density on the peroxo oxygens and destabilization of the peroxo O–O bond. An analysis of the frontier orbital of both the Co and Mn-peroxo complexes, **9** and **11** (Fig. 5), corroborates the strong dependence of the extent of O–O bond activation on the electronic properties of the metal ion. The highest occupied molecular orbital (HOMO) contains significant $\pi^*(\text{O}=\text{O})$ character for both Co-peroxo **9** and Mn-peroxo **11**. However, the HOMO of Mn-peroxo $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeO-DPEN}))]_2(\mu\text{-O}_2)\}^{2+}$

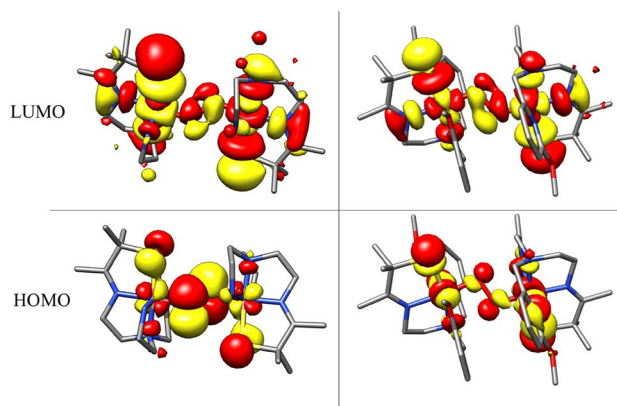


Fig. 5 Frontier orbitals of $\text{Co}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))]_2(\text{trans-}\mu\text{-1,2-O}_2)\}^{2+}$ (**9**) (left) and $\{[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeO-DPEN}))]_2(\text{trans-}\mu\text{-1,2-O}_2)\}^{2+}$ (**11**) (right)¹⁹ visualized at an isovalue of 0.03 a_0^3

(**11**, Scheme 1) is fairly delocalized, extending over both the O–O π^* and singly occupied t_{2g} Mn d -orbitals (Fig. 5, right). This would be consistent with higher calculated Lewis acidity of the Mn ions in **11** as well as the observed stabilization of the peroxo O–O bond. The HOMO of Co–peroxo **9** (Fig. 5, left), however, is dominated by the $\pi^*(\text{O}=\text{O})$ orbital and predominantly peroxo in character, consistent with lack of π -back-donation into the fully occupied Co t_{2g} d -orbitals (Fig. 5). The LUMO of both **9** and **11** is antibonding with respect to the M–O(peroxo) bond.

Conclusions

This work describes the structure and properties of a O_2 -derived thiolate-ligated, peroxo-bridged Co(III) dimer and provides a comparison with structurally analogous peroxo-bridged Mn(III) dimers. It also provides a rationale for the effects that both electronic structural differences and the ligand scaffold can have on peroxo O–O bond activation. The electronic structure of the metal ion, as well as the metal ion Lewis acidity, is shown to have a profound impact on peroxo O–O bond activation and stability. The lack of steric bulk in the Co–peroxo compound is shown to decrease metal ion Lewis acidity relative to the Mn–peroxo compounds, resulting in a more activated peroxo O–O bond. In addition, with its completely filled π -symmetry t_{2g} set of orbitals, the L.S. d^6 Co(III) ion is incapable of providing stability to the peroxo O–O bond through π -back-donation from the $\pi^*(\text{O}=\text{O})$. DFT calculations support this by showing that, with Co(III), the HOMO contains more electron density localized in the peroxo $\pi^*(\text{O}=\text{O})$ orbital, relative to the HOMO of the structurally analogous Mn(III) peroxo complex, resulting in a more activated peroxo O–O bond. The substitution-inert character of the Co(III) ion facilitates the isolation of a significantly more activated peroxo. Insight into some of the key factors governing O–O bond activation can serve as a benchmark for future small-molecule design.

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