J. Am. Chem. Soc. **1998,** *120,* 10567−10568 10567

First Synthesis and Structural Characterization of Dinuclear M(III) Bis(μ-oxo) Complexes of Nickel and Cobalt with Hydrotris(pyrazolyl)borate Ligand[†]

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Received May 27, 1998

C−H bond functionalization by metal-coordinated active oxygen species, such as O_2^-, O_2^{2-}, OOH^- and O^{2-}, is one of the attractive subjects from synthetic, catalytic, and bioinorganic viewpoints.[1] A recent advance in metal−dioxygen complex chemistry reveals that a high-valent metal−oxo (O^{2-}) species is formed via O−O bond cleavage of a metal-coordinated O_2^{2-} species and works as an active intermediate for C−H bond oxygenation. Especially, bimetallic $M_2(\mu\text{-}O)_2$ species of Cu(III/III), Fe(III/IV), and Fe(IV/IV) take part in biological and chemical activation processes of aliphatic C−H bond.[2−4] Herein we report the first isolation and structural characterization of a dinuclear Ni(III)−bis(μ-oxo) complex, $Tp^{Me_3}Ni(\mu\text{-}O)_2NiTp^{Me_3}$. Characterization of an analogous Co(III)−bis(μ-oxo) complex is also presented.

At first, we examined the reaction of a dinuclear Ni(II)−bis(μ-hydroxo) complex bearing the $Tp^{Pr^i_2}$ ligand, $Tp^{Pr^i_2}Ni(\mu\text{-}OH)_2NiTp^{Pr^i_2}$ (**1**),[5] with 1 equiv of H_2O_2 at −78 °C. This reaction resulted in the formation of a brown compound **2** which could not be characterized due to its thermal instability and gave a product oxygenated at the proximal Pr^i group as found for the Co(II) derivative.[6,7] To prevent the oxygenation initiated by H-abstraction from the Pr^i methine part, the Pr^i substituents were replaced by methyl groups much more resistant to H-abstraction. As a result, the use of hydrotris(3,4,5-trimethyl-1-pyrazolyl)borate, Tp^{Me_3},[8] led to the successful isolation of the brown species (eq 1).

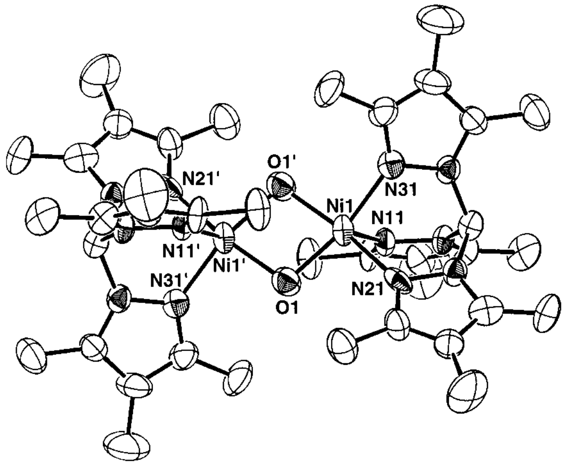
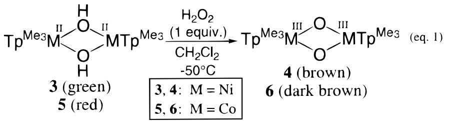


Figure 1. ORTEP drawing of $Tp^{Me_3}Ni^{III}(\mu\text{-}O)_2Ni^{III}Tp^{Me_3}\cdot 4CH_2Cl_2$ (**4**·$4CH_2Cl_2$) (drawn at the 50% probability level). All hydrogen atoms and the CH_2Cl_2 molecules are omitted for clarity. The molecular structure of the Co derivative **6** is very similar to the presented structure of **4**.



$$Tp^{Me_3}\overset{II}{M}(\mu\text{-}OH)_2\overset{II}{M}Tp^{Me_3} \xrightarrow[\substack{CH_2Cl_2\\ -50°C}]{\substack{H_2O_2\\ (1\ equiv.)}} Tp^{Me_3}\overset{III}{M}(\mu\text{-}O)_2\overset{III}{M}Tp^{Me_3} \quad \text{(eq. 1)}$$

3 (green)
5 (red)

3, **4**: M = Ni
5, **6**: M = Co

4 (brown)
6 (dark brown)

Reaction of a green Ni(II)−hydroxo complex, $Tp^{Me_3}Ni(\mu\text{-}OH)_2NiTp^{Me_3}$ (**3**),[9] and 1 equiv of H_2O_2 in CH_2Cl_2 at −50 °C gave a brown metastable complex (**4**) similar to the above-mentioned $Tp^{Pr^i_2}$ complex **2**. The isolated brown complex **4** exhibited two intense characteristic absorption bands at 318 (ϵ = 5600 $M^{-1}cm^{-1}$) and 410 (4200) nm in its UV−vis spectrum. Remarkable physicochemical characteristic of **4** was its apparent diamagnetism as indicated by ^1H NMR. This observation suggests that **4** has a magnetically coupled bimetallic core. Finally, single crystals suitable for X-ray analysis were successfully obtained from a CH_2Cl_2 solution cooled at −78 °C. As expected, **4** has a dinuclear structure that sits on a crystallographically imposed inversion center (Figure 1). Two slightly distorted square pyramidal Ni centers are bridged by two oxygen atoms, and the O- - -O separation (2.34 Å) clearly indicates nonbonding interaction between them. As summarized in Table 1, Ni−Ni, Ni−O, Ni−N_{ave} distances are shorter than those of the starting dinuclear Ni(II)−bis(μ-hydroxo) complex **3**. These structural features are quite similar to those of the Tolman's R_3-TACN−Cu complexes.[2d] The high electronegativity of the

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[†] Abbreviations used in this paper: Tp^R, hydrotris(3,5-substituted-1-pyrazolyl)borate; $Tp^{Pr^i_2}$, hydrotris(3,5-diisopropyl-1-pyrazolyl)borate; Tp^{Me_3}, hydrotris(3,4,5-trimethyl-1-pyrazolyl)borate.

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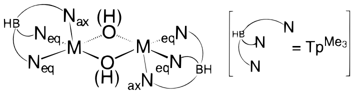
S0002-7863(98)01837-X CCC: $15.00

Table 1. Selected Interatomic Distances (Å) and Bond Angles (deg) for the Bis(μ-hydroxo) and Bis(μ-oxo) Complexes of Ni and Co with Tp^{Me_3}



	Ni		Co	
	3 (Ni(II)−hydroxo)	**4** (Ni(III)−oxo)	**5** (Co(II)−hydroxo)	**6** (Co(III)−oxo)
M−O (Å)	1.964(3); 1.977(3)	1.841(7); 1.870(8)	1.992(6); 2.019(4)	1.783(4); 1.796(5)
$M-N_{eq}$ (Å)	2.074(3); 2.076(3)	1.995(9); 2.001(10)	2.124(4); 2.141(6)	2.017(5); 2.018(4)
$M-N_{ax}$ (Å)	2.022(3)	2.039(9)	2.049(4)	2.111(4)
$M-N_{ave}$ (Å)	2.057	2.012	2.105	2.049
M- - -M (Å)	3.130(2)	2.882(3)	3.141(2)	2.728(2)
O- - -O (Å)	2.394(6)	2.34(1)	2.49(1)	2.318(9)
M−O−M (deg)	105.2(1)	101.9(3)	103.1(2)	99.3(2)
O−M−O (deg)	74.8(1)	78.1(3)	76.9(2)	80.7(2)

oxygen atom donors results in inversion of the $M-N_{ax}$ and $M-N_{eq}$ distances between **3** ($N_{eq} > N_{ax}$) and **4** ($N_{eq} < N_{ax}$); i.e., the energy level of $d_{x^2-y^2}$ orbital becomes higher than that of d_{z^2} in **4**. Similar inversion due to the Jahn−Teller effect has been also observed for the dinuclear Mn(II)−bis(μ-hydroxo) and Mn(III)−bis(μ-oxo) complexes with $Tp^{Pr^i_2}$.[10] We thus conclude that the metastable brown complex **4** is the first structurally characterized Ni(III)−bis(μ-oxo) complex.[11,12] It is worth noting that **4** and **2** are not obtained by reaction of the hydroxo complexes with other oxidizing reagents such as *t*-BuOOH, mCPBA, and $KMnO_4$.[10,13] Therefore, the dinuclear Ni(III)−bis(μ-oxo) core should not be formed via simple oxidation of the starting $Ni^{II}(\mu\text{-}OH)_2Ni^{II}$ core but by homolysis of the O−O bond in a corresponding dinuclear Ni(II) μ-peroxo intermediate (probably μ-η^2:η^2-peroxo) which results from dehydrative condensation of $Ni^{II}(\mu\text{-}OH)_2Ni^{II}$ and H_2O_2 as found for the $Tp^{Pr^i_2}$−Cu(II) complex.[14,15]

Analogous stoichiometric reaction of a red Tp^{Me_3}Co(II)−bis(μ-hydroxo) complex **5** with H_2O_2 at −50 °C also afforded the corresponding dark brown dinuclear Co(III)−bis(μ-oxo) complex **6**, whose THF solution exhibited charactristic UV−vis spectrum (360 ($\epsilon = 7600$), 490 (1500), and 614 (800) nm), as characterized crystallographically (eq 1 and Table 1). Crystallographic cell parameters and atomic coordinates of **6** were almost identical with those of the Ni analogue **4**. The O- - -O separation (2.33 Å) and the shorter Co−Co, Co−O, and $Co-N_{ave}$ distances of **6** compared to those of the starting hydroxo complex **5** clearly indicate that **6** is assignable as a 5-coordinated dinuclear Co(III)−bis(μ-oxo) complex. Although cubane type tetranuclear $[(Co^{III}-oxo)_4]^{4+}$ and trinuclear Co(III)−μ_3-oxo complexes with low-spin, 6-coordinated octahedral Co(III) centers have been reported,[16] the present dinuclear Co(III)−bis(μ-oxo) complex **6** contains two 5-coordinated Co(III) centers having a slightly distorted square pyramidal geometry. Due to this unusual coordination environment of the metal centers, **6** is not diamagnetic as found for the usual Co(III) complexes; in a ^1H NMR spectrum at room temperature, paramagnetically shifted Me signals of the Tp^{Me_3} ligand were located at δ −35.2, 2.0, and 26.0. Co(III) ions (d^6) strongly favor an octahedral geometry with low-spin ($S = 0$) state, and only a limited number of structurally characterized 5-coordinated paramagnetic Co(III) species is known.[17] Detailed analysis of the paramagnetic property of **6** will be performed.

In general, peroxides such as H_2O_2 and *t*-BuOOH are used to oxidize Co(II) precursors to give Co(III) compounds; in fact, the previously reported Co(III)−oxo clusters are prepared by oxidation of Co(II) precursors by H_2O_2, but no Co(II)−peroxo species are detected.[16] In contrast, a Co(II)−alkylperoxo complex was formed via dehydrative condensation of the Co(II)−hydroxo complexes **5** with 2 equiv of *t*-BuOOH as found for the analogous $Tp^{Pr^i_2}$ complex,[6b] and treatment of **5** with $KMnO_4$ did not afford **6**. Therefore, in a manner similar to the Ni system (vide supra), O−O cleavage of a dinuclear Co(II)−μ-peroxo intermediate rather than an outerspheric oxidation of the $Co^{II}(\mu\text{-}OH)_2Co^{II}$ core may be a feasible formation mechanism of the dinuclear Co(III)−bis(μ-oxo) complex **6**.[15,18]

Although the dinuclear Ni(III)− and Co(III)−bis(μ-oxo) complexes with Tp^{Me_3} were stable at low temperature, the Ni complex **4** decomposed within 1 h at room temperature, and the Co complex **6** were decomposed very slowly. Preliminary spectral analysis of the decomposition products indicated that the methyl groups in the Tp^{Me_3} ligands proximal to the metal centers were oxygenated as found for the $Tp^{Pr^i_2}$Co system.[6]

In summary, we succeeded in the first synthesis and structural characterization of thermally unstable high-valent dinuclear metal bis(μ-oxo) complexes of Ni(III) and Co(III), which exhibit unusual physicochemical properties and are closely related to the recently developed high-valent $M(\mu\text{-}O)_2M$ complexes of Cu and Fe.[2−4] Detailed investigations of their physicochemical properties and reactivities are now under way, and the results will be report in due course.

Acknowledgment. This research was supported in part by a Grant-in-Aid for Specially Promoted Scientific Research (No. 08102006) from the Ministry of Education, Science, Sports and Culture of the Japanese government.

Supporting Information Available: Summary of X-ray analysis, atomic coordinates, thermal parameters, and bond lengths and angles for **3**, **4**, **5**, and **6** (28 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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