High oxidation-state molecular compounds or polymeric oxides of Mn or Ce have a wide range of applications in diverse areas involving inorganic, organic, environmental, and industrial chemistry owing to their ability to oxidize both inorganic and organic substrates.[1–8] The high oxidation-state tetranuclear Mn cluster that is present near photosystem II of
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green plants is responsible for the oxidation of H2O to dioxygen[1,2] As a result, a number of Mn4 complexes have been made to model its structural and functional properties[3] CeIV has also been used in the homogeneous and heterogeneous catalysis by Ru complexes of water oxidation to molecular dioxygen[4] Similarly, MnO4– and CeIV are commonly employed as oxidants in inorganic synthesis, such as in the formation of MnIV and/or MnIV clusters, or mixed-valent CoIIIIV complexes[5,6] In addition, compounds such as MnO4–, MnO2, and (NH4)2[Ce(NO3)6] have a long history as oxidizing agents for a vast variety of organic substrates[5,6] Further, MnIII, MnIV and CeIV oxides have been widely used, either alone or as mixed Mn/Ce oxides, in a number of heterogeneous catalytic oxidation processes[7,8] For example, CeIV/MnIV composite oxides are being widely used in sub- and supercritical catalytic wet oxidations for the treatment of wastewater containing toxic organic pollutants such as ammonia, acetic acid, phenol, polyethylene glycol, and others[8] Mixed CeIV/MnIV molecular analogues of these Ce/Mn oxide catalysts have not been available for study, but would likely prove to have interesting oxidative and other properties We herein report the synthesis, crystallographic characterization and magnetic properties of a novel family of mixed CeIV/MnIV complexes with various Ce:Mn ratios These are also the first crystallographically characterized molecular Mn/Ce complexes in general.

The new compounds described below were all obtained as part of a larger investigation of the oxidation of Mn3+ reagents by CeIV under a variety of conditions The reaction of Mn(NO3)2·xH2O and 2,2’-bipyridine (bpy) with (NH4)2[Ce(NO3)6] in a 1:2 molar ratio in 25% aqueous acetic acid gave [CeIVMnIV(NO3)2(O2CMe)(NO3)(H2O)]·(bpy)2·H2O·2H2O (1-2H2O) in 40% yield Similarly, the reaction of [Mn(O2CMe)2]·4H2O and 6-methyl-2-hydroxy-pyridine (mhpH) with (NH4)2Ce(NO3)6 in a 4:9:6 molar ratio in 30% aqueous acetic acid gave [Ce3Mn2O6(NO3)2(mhpH)4]·2H2O (2-2H2O) in 24% yield Finally, the reaction of a solution of [Mn(O2CMe)2]·4H2O in 50% aqueous acetic acid with Ce(ClO4)3 (0.5M solution in HClO4) in a 2:3 molar ratio gave [CeIV3MnIV5O2(O2CMe)5(MeOH)3(H2O)](ClO4)3·3H2O·2MeCO2H (3-3H2O·2MeCO2H) in ~50% yield Charge consideration, inspection of metric parameters and bond valence sum calculations establish that all the Ce and Mn ions of 1-3 are in oxidation state IV[10] The structure of the cation of 1 (Figure 1)[11] comprises a [MnIII(NO3)2(O2CMe)]+ rhomb linked to a CeIV ion through a linear oxide bridge The Mn-Mn-Ce angle is 139.6(2)° The ten-coordinate CeIV ion is additionally ligated by four bidentate nitrate groups and a water molecule Octahedral coordination at each Mn is completed by a chelating bpy group and a terminal water molecule at Mn2 The Mn–O and Mn–N bond lengths, and the Mn–Mn separation (2.659 Å) are typical of those in discrete dinuclear complexes containing the [MnIII(NO3)2(O2CMe)]+ core[12] The Ce–O bond lengths (2.44–2.60 Å) are slightly longer than is typical for ten-coordinate CeIV (Ce–O bond lengths ~2.3–2.5 Å)[14] probably as a consequence of the very short CeIV–O2– bond (Ce–O5 ~1.945 Å), one of the shortest Ce–O

Figure 1 The cation of complex 1, labeled ORTEP plot (at the 50% probability level) in PovRay format.

Figure 2 Top: Complex 2, the methylpyridine groups are omitted, labeled ORTEP plot (at the 50% probability level) in PovRay format. Bottom: The [CeIV3MnIV5O2]3+ core of 2 emphasizing its trigonal bipyramidal topology.

protonated at their N atoms and binding only through their O atoms (O4 and O14). The molecule has crystallographically imposed C2v symmetry, the C2 axis passing through Ce2 and bisecting the O1···O1' vector. The Ce–O bond lengths are within the expected range for octa- and ennea-coordinate CeIV.\[10c\] The Ce3Mn2 trigonal bipyramidal topology has been observed in mixed 4f/3d chemistry only once before, in a NdIII•CeIII complex that contains hydroxide bridges, rather than oxide ones as in 2.\[12]\] The structure of 3 (Figure 3, top)\[11\] contains an unprecedented MnIV wheel. Its edges are bridged alternately by (μ2-O)(μ3-O)(μ2-O2CMe) and (μ4-O)(μ3-O2CMe)2 ligand sets, with Mn–Mn separations of 2.714 and 3.297 Å, respectively. The MnIV ions are those holding in place the central CeIV ion,\[12\] which lies slightly out of the almost planar Mn6 ring and is also coordinated to one MeOH and two water groups. The Ce–O bond lengths (2.271–2.483 Å) are within the expected range for ennea-coordinate CeIV.\[10c\] The MnIV–O2(\(=\)CMe) bonds of 1.931–1.975 Å are typical of MnIV values. Apart from being the first MnIV wheel, complex 3 is also the first MnIV complex with only oxide and carboxylate ligands, and its [Mn6O15] core (Figure 2, bottom) is of a structural type never seen before for any metal. In addition it is one of the few known examples of a cyclic Tr6Ln complex, that is, a wheel of transition-metal ions with a central lanthanide ion.\[11\]

Solid-state, magnetic susceptibility measurements were carried out on complexes 1–3 in the temperature range 5.0–300 K in a 10 kG dc magnetic field. The obtained data are shown as \(\chi_m T\) versus T plots (Figure 4; \(\chi_m\) is the magnetic susceptibility). All paramagnetism is associated with the MnIV ions, since CeIV is diamagnetic (\(f'\)). The data for 1 and 2 were fit to the theoretical \(\chi_m T\) vs. T expression for a d\(^3\)–d\(^3\) dimer.\[14\] The fits (solid lines in Figure 4) gave \(J = -45.7\) cm\(^{-1}\), \(\rho = 0.019\), and \(g = 1.95\) for 1, and \(J = -0.40\) cm\(^{-1}\), \(\rho = 0.010\), and \(g = 2.01\) for 2. \(J\) is the exchange interaction constant, and \(\rho\) is the fraction of paramagnetic impurity (assumed to be high-spin MnIII). A temperature independent paramagnetism (TIP) term was held constant at \(300 \times 10^{-6}\) cm\(^3\) mol\(^{-1}\) K\(^{-1}\) for 1, and \(500 \times 10^{-6}\) cm\(^3\) mol\(^{-1}\) K\(^{-1}\) for 2.\[15\] The data for 3 were fit by a matrix diagonalization method described elsewhere.\[16\] Three exchange constants were used as parameters, \(J_1\) and \(J_2\) for the [MnIV(O2CMe)\(^2\)] and [MnIV(O2CMe)\(^3\)] units, respectively, and \(J_3\) for a uniform next-nearest-neighbor interaction. The preliminary fit (solid line in Figure 4) using data above 25 K to avoid intermolecular interactions gave \(J_1 = -5.8\) cm\(^{-1}\), \(J_2 = -0.63\) cm\(^{-1}\), \(J_3 = 0\), \(\rho = 0.0299\), and \(g = 2.07\), with TIP held constant at \(700 \times 10^{-6}\) cm\(^3\) mol\(^{-1}\) K\(^{-1}\).\[15\]

Complexes 1–3 are thus all antiferromagnetically coupled with S = 0 ground states. The J value for 1 is in agreement with previously reported values (−24.6 to −67 cm\(^{-1}\)) for dinuclear complexes with a [MnIV\((\mu_2-O)(\mu_2-O_2CMe)\)] core.\[16\] The J value for 2 is very weak, as expected for two well separated MnIV ions interacting through four-bond superexchange pathways. The \(J_1\) value gauging the interaction within the [MnIV\((\mu_3-O_2CMe)\)] units of 3 is significantly smaller than the lower limit of the above range for dinuclear complexes. This is consistent with the attachment of the strongly Lewis acidic CeIV ion, which weakens the Mn–O\(^{2-}\) bonds that mediate the MnIV\(^2\) superexchange interaction. This is reflected in the significantly longer Mn–(μ2-O\(^3-\)) bond lengths (avg 1.859 Å) and Mn–Mn separations [avg 2.714 Å] in this unit in 3, compared with the Mn–(μ3-O\(^2-\)) bonds of 3 (avg 1.813 Å), and the Mn–Mn distances [range 2.58–2.67 Å] of dinuclear

![Figure 3. Top: Complex 3, labeled ORTEP plot (at the 50% probability level) in PovRay format. Bottom: The [Mn\(^{IV}\),Ce\(^{IV}\)O\(^{3-}\)]\(^{2+}\) core of 3.](image-url)
compounds containing the [MnIV,(μ-O)((μ-O)2C6Me3)] core.[10],[11]

The very small J value can also be rationalized on the basis of the long Mn–(μ−O2−) bond lengths [1.83 Å] and Mn–Mn separations [3.297 Å], although discrete dinuclear complexes containing the [MnIV,(μ-O)((μ-O)2C6Me3)] core are currently unknown and thus unavailable for comparison.

The described results establish synthetic access to a new class of mixed CeIV/MnIV/O2− molecular clusters. Although there are a few other reported examples of high oxidation state, mixed transition-metal/lanthanide complexes containing early transition-metal ions such as TiIV or NbV,[12f] compounds 1–3 are unique in that both component ions are strong oxidizing agents. The species obtained to date already (formation of CeIV/MnIV products, which perhaps involves the participation of atmospheric oxygen. Complexes generating MnIV. We believe that this is more than happening early transition-metal ions such as TiIV or NbV,[12f]

Experimental Section

1H2O: An orange solution of (NH3)2[Ce(NO3)6] (5.50 g, 10.03 mmol) in H2O/MeCO2H (19 mL/7 mL) was slowly added to a pale yellow-brown solution of Mn(NO3)2·H2O (0.90 g, 5.03 mmol) and bpy (0.78 g, 5.00 mmol) in H2O/MeCO2H (50 mL/16 mL) resulting in a dark greenish-brown solution. The solution was reduced in volume by 1.06 g (40% based on Mn). Elemental analysis calcd (%) for C17.20, H 3.10; found: C 16.90, H 3.00.

Analysis was carried out on a Jeol JPS-ALX 400 spectrometer.

Keywords: cerium · cluster compounds · lanthanides · magnetic properties · manganese · transition metals


[10] a) Bond valence sum (BVS) calculations for the Mn$^{10+}$ and Ce$^{1+}$ ions of complexes 1–3 gave values of: 4.16, 4.08, and 3.98 for Mn1, Mn2 and Ce, respectively, of 1; 4.06, 3.82 and 3.86 for Mn1, Ce1 and Ce2, respectively, of 2; 4.07–4.28 for Mn1–Mn6, and 3.84 for Ce of 3; b) W. Liu, H. H. Thorp, Inorg. Chem. 1993, 32, 4102; c) P. L. Roulhae, G. J. Palenik, Inorg. Chem. 2003, 42, 118.

[11] Crystal structure data for 1:2H$_2$O: C$_{60}$H$_{49}$N$_3$O$_{35}$CeMn$_3$, $M_r = 1051.53$, triclinic, space group $P1$, $a = 9.3132(6)$, $b = 12.3866(8)$, $c = 17.4899(12)$ Å, $\alpha = 87.810(2)$, $\beta = 83.871(2)$, $\gamma = 75.134(2)^\circ$, $V = 1938.8(2)$ Å$^3$, $T = 173$ K, $Z = 2$, $\rho_{\text{calc}} = 1.801$ g cm$^{-3}$, 17243 reflections collected, 8624 unique ($R_{int} = 0.0806$), $R1 = 0.0806$, $wR2 = 0.1743$, by using 5470 reflections with $I > 2\sigma(I)$. Crystal structure data for 2:2H$_2$O: C$_{59}$H$_{48}$N$_3$O$_{34}$CeCeMn$_2$, $M_r = 1577.04$, orthorhombic, space group Aba$_2$, $a = 22.6707(12)$, $b = 14.8735(8)$, $c = 5303.6(5)$ Å, $T = 173$ K, $Z = 4$, $\rho_{\text{calc}} = 1.970$ g cm$^{-3}$, 22828 reflections collected, 6051 unique ($R_{int} = 0.0638$), $R1 = 0.0250$, $wR2 = 0.0661$, using 5938 reflections with $I > 2\sigma(I)$. Crystal structure data for 3:3H$_2$O$^+$/H$_2$O$^-$: C$_{64}$H$_{50}$N$_5$O$_{30}$Ce$^3$Mn$^2$, $M_r = 1396.73$, triclinic, space group $P1$, $a = 12.2133(7)$, $b = 13.0106(8)$, $c = 16.6337(10)$ Å, $\alpha = 99.056(2)$, $\beta = 101.581(2)$, $\gamma = 111.188(2)^\circ$, $V = 2336.5(2)$ Å$^3$, $T = 193$ K, $Z = 2$, $\rho_{\text{calc}} = 1.982$ g cm$^{-3}$, 17436 reflections collected. 8194 unique ($R_{int} = 0.0477$), $R1 = 0.0728$, $wR2 = 0.1594$, using 6724 reflections with $I > 2\sigma(I)$. CCDC 219157–219159 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).


[15] A value of $100\times10^{-6}$ cm$^3$ mol$^{-1}$ K per Mn and per Ce was employed, which is a typical value for these ions$^{[6b,14b]}$.
