Cerium(IV)-containing oxomolybdenum cluster with a unique $Ce_6Mo_9O_{38}$ core structure†

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Interaction of $[Ce(L_{OEt})_2(NO_3)_2]$ (L_{OEt}^- = $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$) with $(NH_4)_6[Mo_7O_{24}]$ in water affords the cerium(IV)-containing oxomolybdenum cluster $[H_4(CeL_{OEt})_6Mo_9O_{38}]$, which exhibits a unique $Ce_6Mo_9O_{38}$ core structure.

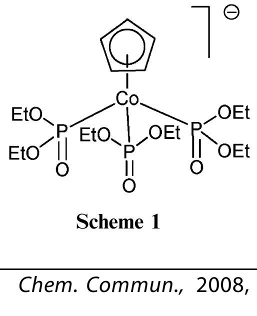
Ceria-containing materials have attracted much attention due to their applications in heterogeneous and environmental catalysis. Precious metals supported on ceria are found to exhibit high catalytic activity in various reactions including water–gas shift reaction and CO and hydrocarbon oxidation.[1–4] Although the mechanisms of ceria-supported catalysts are still the subjects of debate, it is believed that the success of these catalysts relies on (a) the Ce^{4+}–Ce^{3+} redox couple that facilitates the oxygen storage and release from the fluorite lattice and (b) metal–ceria interactions.[1] In order to gain insights into the nature of metal–support interactions of ceria-based catalysts, we sought to synthesise models based on heterometallic Ce^{IV} complexes in oxygen-rich ligand environments. Relatively few molecular heterometallic Ce^{IV} oxo compounds/clusters have been isolated to date.[5,6] Previously, we have demonstrated that in acidic aqueous solutions, titanyl and zirconyl complexes can be stabilised by Kläui's oxygen tripodal ligand[7] $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$ (Scheme 1) (denoted as L_{OEt}^- hereafter), and the resulting M^{IV}–L_{OEt} (M = Ti, Zr) species undergo self-assembly with oxo-anions to give oxo/hydroxo clusters whose core structures closely resemble those of solid materials.[8,9] This prompted us to explore the chemistry of analogous Ce^{IV} compounds and their use as building blocks for heterometallic oxo clusters. Herein, we describe the interactions of Ce^{IV}–L_{OEt} compounds with dichromate and molybdate and the isolation of a Ce^{IV}-containing oxomolybdenum cluster, which exhibits a unique $Ce_6Mo_9O_{38}$ core structure.

Treatment of $(NH_4)_2[Ce(NO_3)_6]$ with NaL_{OEt} in water led to formation of the bis(tripod) compound $[Ce(L_{OEt})_2(NO_3)_2]$ **1**. The mono-tripod compound could not be isolated even when excess $(NH_4)_2[Ce(NO_3)_6]$ was used, indicating the high affinity of Ce^{IV} for the oxygen tripod ligand. An X-ray diffraction study revealed that the Ce atom in compound **1** is 10-coordinated with two κ_2-nitrate ligands.[10] Compound **1**, which is soluble in both CH_2Cl_2 and water, proved to be a useful starting material for heterometallic Ce^{IV} complexes. The interactions of compound **1** with group 6 oxoanions have been studied.

Treatment of compound **1** with K_2CrO_4 in water resulted in an orange precipitate. Recrystallisation from CH_2Cl_2-hexane yielded a mixture of species according to NMR spectroscopy, which have not been separated. On the other hand, treatment of compound **1** with $K_2Cr_2O_7$ in water gave an orange precipitate, which was recrystallised from CH_2Cl_2-hexane to afford the dichromate compound $[Ce(L_{OEt})_2(Cr_2O_7)]$ **2**. It may be noted that a similar reaction with $[Ti_2(L_{OEt})_2(\mu\text{-}O)_2(\mu\text{-}SO_4)]$ afforded the tris(chromate)-bridged dimer $[Ti_2(L_{OEt})_2(\mu\text{-}CrO_4)_3]$.[9b] The solid-state structure of compound **2** containing a bidentate dichromate ligand is shown in Fig. 1.‡ The Ce(1) atom is found to lie on a two-fold axis. Compound **2** can oxidise benzyl alcohol under nitrogen to give approximately 3.5 equivalents of benzaldehyde indicating that it can function as a 7e oxidant.

Addition of compound **1** to Na_2MoO_4 in water gave a yellow precipitate, presumably a Ce^{IV} molybdate complex, in low yield. Recrystallisation from CH_2Cl_2–thf–hexane (thf = tetrahydrofuran) afforded orange crystals characterised as the oxomolybdenum cluster $[H_4(CeL_{OEt})_6Mo_9O_{38}]$ **3**. Cluster **3** could be isolated in higher yield (57%) along with $[MoL_{OEt}(O)_2]_2(\mu\text{-}O)$ **4** from reaction of **1** with $(NH_4)_6Mo_7O_{24}$ in water followed by recrystallisation from CH_2Cl_2–thf–hexane (Scheme 2).§ Interaction of **1** with Na_2WO_4 afforded a yellow precipitate, which exhibited a complex $^{31}P\{^1H\}$ NMR spectrum. We have not been able to crystallise any Ce^{IV} tungstate species for structure determination. The IR spectrum of **3** displays an intense band at 845 cm^{-1} assignable to $\nu(Mo{=}O)$ along with intense P=O bands at 1030–1100 cm^{-1}.

Although the exact mechanism for the formation of cluster **3** is not clear, it seems that (a) dissociation of $[MoO_4]^{2-}$ from $[Mo_7O_{24}]^{6-}$, (b) transfer of one L_{OEt}^- ligand from **1** to molybdate, and (c) self-assembly of $[CeL_{OEt}]^{3+}$ with $[MoO_4]^{2-}$ were involved. It should be noted that compound **4** could be prepared in good yield by treatment of NaL_{OEt} with $(NH_4)_6[Mo_7O_{24}]$ in acidic solutions. While organometallic derivatives of polyoxomolybdates derived from self-assembly



Scheme 1

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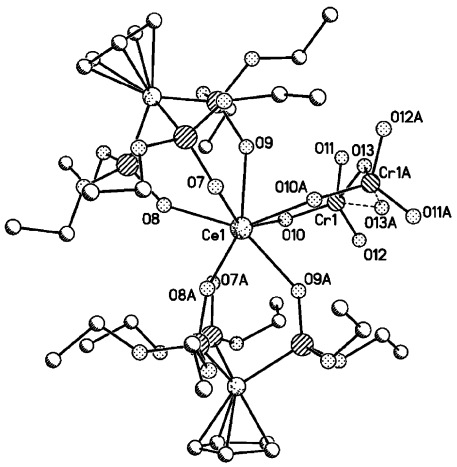
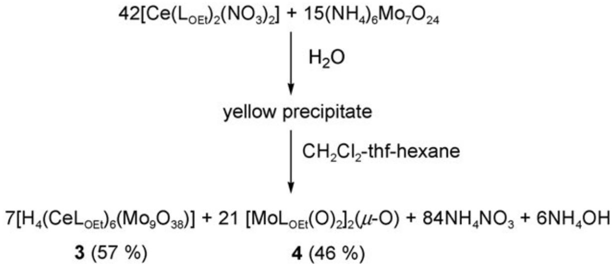


Fig. 1 Molecular structure of **2**. All hydrogen atoms are omitted for clarity. Symmetry operator: A = $y - x$, y, $3/2 - z$.



Scheme 2

of organometallic cations, notably $[Rh^{III}(\eta^5\text{-}C_5Me_5)]^{2+}$ and $[Ru^{II}(\eta^6\text{-arene})]^{2+}$,[11] with molybdate are well documented, the framework geometry of cluster **3** (see below) is completely different from that for reported organometallic polyoxomolybdates, which mostly contain central Mo_4O_4 cubic core(s).

The solid-state structure of **3** is shown in Fig. 2.‡ The core structure can be viewed as consisting of a cube with eight $\{MoO_4\}$ tetrahedra occupying the corners and one $\{MoO_6\}$ octahedron at the center. The Mo atom in the $\{MoO_6\}$ core, Mo(5), is found to lie on an inversion centre of the cluster. Each face of the cube is capped by a $\{CeL_{OEt}\}$ fragment *via* four Ce–O–Mo_{tet} and one Ce–O–Mo_{oct} linkages. No interactions were found between the $\{MoO_4\}$ tetrahedra and the $\{MoO_6\}$ octahedron. To the best of our knowledge, such a hetero polyoxomolybdate core structure has not been observed before. Although Ce^{IV}-containing polyoxometalates, notably $[CeMo_{12}O_{42}]^{8-}$ and $[CeW_{10}O_{36}]^{8-}$,[5] are well known, these compounds are mostly based on Ce^{4+} cation(s) encapsulated by mono- or di-vacant polyoxometalate anions. Polymeric Ce^{III} heteropolyoxometalates derived from self-assembly of Ce^{3+} with polyoxometalate anions have also been synthesised.[12] As far as we are aware, cluster **3** represents the first example of Ce^{IV}-rich oxomolybdate, in which the Ce atoms are located at the cluster framework. The ^1H and ^{31}P NMR spectra of **3** (Fig. S1 and S2, ESI†) display sharp signals typical for diamagnetic metal–L_{OEt} complexes, suggesting that the oxidation states for Ce and Mo are +4 and +6, respectively. Therefore, four protons are required for charge balance. No reactions were found between **3** and bases such as pyridine and Et_3N. The four non-exchangeable protons could not be identified by NMR spectroscopy or X-ray-diffraction, but are most likely attached to the oxygen atoms in the central $\{MoO_6\}$ octahedron on the basis of the following evidence. First, the $\{MoO_6\}$ core contains two shorter (1.839(10) Å) and four longer (1.956(7) and 2.005(9) Å) Mo–O bonds, which are longer than the $Mo–O_b$ bonds in $\{MoO_4\}$ tetrahedra (1.686–1.799 Å). Second, the rather small Mo–O–Ce bond angles for the Mo–O(short) bonds [150.3(4) and 152.1(4)° *cf.* 162.7(6)° for that of the Mo–O(long) bonds] are consistent with Ce–OH–Mo bridges.[13] Thus, **3** may be described as a dicationic cage $[Ce_6(L_{OEt})_6(MoO_4)_8]^{2+}$ with a dioxomolybdate(VI), $[Mo(O)_2(OH)_4]^{2-}$, at the center. It should be noted that six-coordinated dioxo-Mo^{VI} compounds of the type $[Mo(O)_2X_4]^{2-}$ are well known. The Ce–O(Mo_{tet}) distances

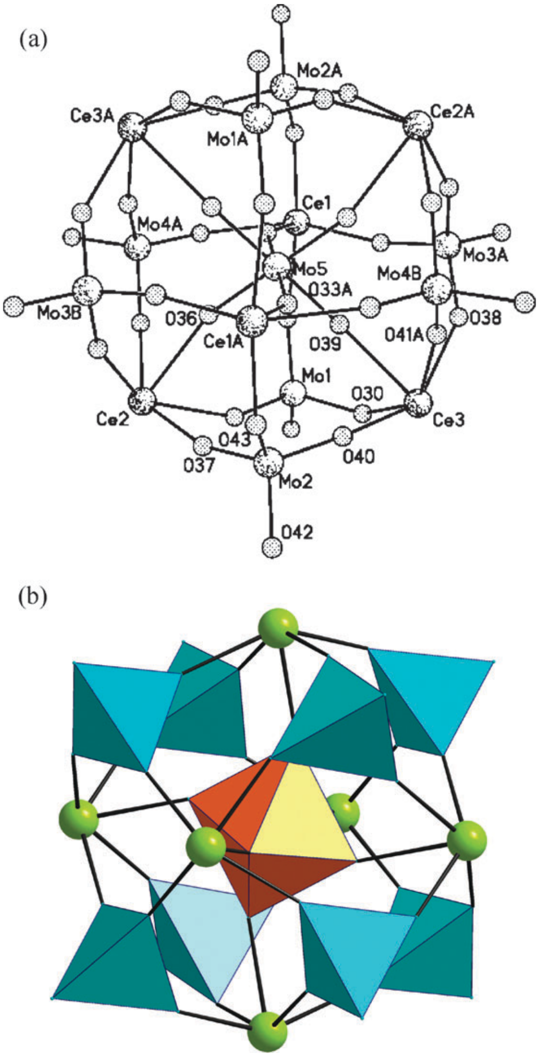


Fig. 2 (a) Structure of the oxometallic core (symmetry operator: A = $1 - x$, $1 - y$, $1 - z$) and (b) coordination polyhedral representation of **3**. All carbon and hydrogen atoms are omitted for clarity. Color code: green, Ce; blue, $\{MoO_4\}$ tetrahedra; brown, $\{MoO_6\}$ octahedron. Selected bond lengths (Å): Ce–O(L_{OEt}) 2.297(7)–2.378(7), Ce–O(Mo_{tet}) 2.217(7)–2.407(8), Ce–O(Mo_{oct}) 2.393(9), 2.451(9) and 2.405(7), Mo_{oct}–O 1.839(10), 1.956(7), 2.005(9), Mo_{tet}–O_t 1.630(9)–1.716(8), Mo_{tet}–O_b 1.686(14)–1.799(8).

(av. 2.289 Å) are significantly shorter than the Ce–O(Mo_{oct}) distances (av. 2.416 Å), which are comparable to those of $[CeMo_{12}O_{42}]^{8-}$ (*ca.* 2.51 Å).[5]

Attempts have been made to synthesise analogues of **3** derived from tetravalent metal ions such as Zr^{IV}. Treatment of $[Zr(L_{OEt})(CH_3CO_2)_3]$[14] with $(NH_4)_6Mo_7O_{24}$ in water yielded a yellow precipitate. Recrystallisation from $CHCl_3$–hexane afforded the heterometallic oxo cluster $[H_4(ZrL_{OEt})_6Mo_9O_{38}]$ **5**. A preliminary X-ray diffraction study allowed us to determine the unit-cell data for cluster **5** but unfortunately, the structure could not be solved and refined satisfactorily due to the poor crystal quality.[15]

In summary, we have developed a synthetic route to oxygen-rich heterometallic Ce^{IV} compounds using water-soluble **1** as a starting material. Preliminary studies showed that other heterometallic Ce–O–M compounds (*e.g.* M = Re or Os) could be synthesised similarly.[10] Interaction of **1** with molybdate afforded a Ce^{IV}–Mo^{VI} cluster, **3**, containing a unique $Ce_8Mo_9O_{38}$ oxometallic core that has not been found for organometallic polyoxometalates. Unlike previously reported heterobimetallic Ce^{IV} complexes, **3** is a rare example of Ce^{IV}-rich oxo cluster with Ce atoms located at the cluster framework. The study of reaction chemistry of this new class of heterometallic Ce^{IV} compounds is underway.

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Notes and references

‡ *Crystal data* for **2**·CH_2Cl_2: $C_{35}H_{72}CeCl_2Co_2Cr_2O_{25}P_6$, M_r = 1511.63, T = 100(2) K, hexagonal, space group $P6_122$, a = 11.9773(8), b = 11.9773(8), c = 71.426(9) Å, V = 8873.7(14) Å^3, μ(Mo-Kα) = 1.985 mm^{-1}, Z = 6, 27 500 reflections measured, 4732 unique (R_{int} = 0.1367), final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0643, $wR2$ = 0.1203. The Cr–O distances in **2** have not been analysed due to the disorder found for the dichromate ligand. *Crystal data* for **3**: $C_{104}H_{218}Ce_6Cl_4Co_6Mo_9O_{92}P_{18}$, M_r = 5697.80, T = 100(2) K, monoclinic, space group $P2_1/n$, a = 18.9736(13), b = 18.4007(13), c = 26.5030(18) Å, V = 9252.8(11) Å^3, μ(Mo-Kα) = 2.855 mm^{-1}, Z = 2, 51 182 reflections measured, 15 892 unique (R_{int} = 0.0568), final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0618, $wR2$ = 0.1388.

§ *Preparation* of **3**: To a solution of **1** (120 mg, 0.090 mmol) in water (30 mL) was added $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (37 mg, 0.30 mmol) in water (3 mL), and the mixture was stirred for 10 min. The yellow precipitate was collected, re-dissolved in CH_2Cl_2–thf–hexane (5 : 1 : 1 v/v/v), and dried over anhydrous Na_2SO_4. Slow evaporation of the solvent gave orange crystals of **3** (45 mg, 57%) and yellow crystals of **4** (28 mg, 46%). ^1H NMR ($CDCl_3$) for **3**: δ 1.26 (t, 108H, CH_3), 4.20 (m, 72H, OCH_2), 5.03 (s, 30H, C_5H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 117.8 (s). IR (KBr, cm^{-1}): 845 [νMo=O)]. MS (ESI): m/z 5510.12 [M^+ − OH]. Anal. Calc. for $C_{102}H_{214}Ce_6Co_6Mo_9O_{92}P_{18}$: C, 22.16; H, 3.90; P, 10.52. Found: C, 22.78; H, 3.86; P, 10.54%.

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14. $[Zr(L_{OEt})(CH_3CO_2)_3]$ was prepared by reaction of $[Zr(L_{OEt})F_3]$ (ref. 9*a*) with trimethylsilylacetate in refluxing dichloromethane.
15. *Crystal data* for **5**: T = 100(2) K, monoclinic, space group $P2_1$/n, a = 23.496(7), b = 29.036(9), c = 28.852(8) Å, β = 91.589(11)°, V = 19676(10) Å^3, Z = 4, 98 305 reflections measured, 45 971 unique (R_{int} = 0.2769).