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Homo- and Heterovalent Polynuclear Cerium and Cerium/Manganese Aggregates

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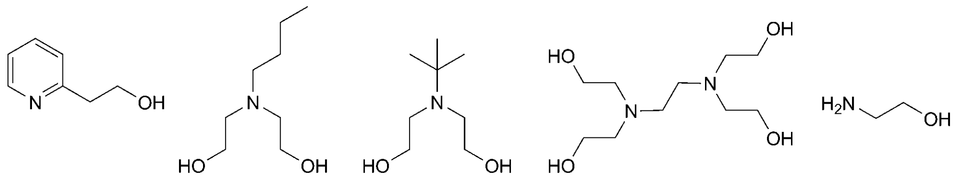
Dedicated to Professor *Jean-Claude Bünzli* on the occasion of his 65th birthday

Reactions of $Ce^{III}(NO_3)_3 \cdot 6\,H_2O$ or $(NH_4)_2[Ce^{IV}(NO_3)_6]$ with Mn-containing starting materials result in seven novel polynuclear Ce or Ce/Mn complexes with pivalato ($^tBuCO_2^-$) and, in most cases, auxiliary N,O- or N,O,O-donor ligands. With nuclearities ranging from 6–14, the compounds present aesthetically pleasing structures. Complexes $[Ce^{IV}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2C^tBu)_{12}]$ (**1**), $[Ce^{IV}_6Mn^{III}_4(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(O_2C^tBu)_{12}(ea)_4(OAc)_4] \cdot 4\,H_2O \cdot 4\,MeCN$ (ea^- = 2-aminoethanolato; **2**), $[Ce^{IV}_6Mn^{III}_8(\mu_4\text{-}O)_4(\mu_3\text{-}O)_8(pye)_4(O_2C^tBu)_{18}]_2[Ce^{IV}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2C^tBu)_{10}(NO_3)_4][Ce^{III}(NO_3)_5(H_2O)] \cdot 21\,MeCN$ (pye^- = pyridine-2-ethanolato; **3**), and $[Ce^{IV}_6Ce^{III}_2Mn^{III}_2(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(^tbdea)_2(O_2C^tBu)_{12}(NO_3)_2(OAc)_2] \cdot 4\,CH_2Cl_2$ ($^tbdea^{2-}$ = 2,2′-(*tert*-butylimino]bis[ethanolato]; **4**) all contain structures based on an octahedral $\{Ce^{IV}_6(\mu_3\text{-}O)_8\}$ core, in which many of the O-atoms are either protonated to give $(\mu_3\text{-}OH)^-$ hydroxo ligands or coordinate to further metal centers (Mn^{III} or Ce^{III}) to give interstitial $(\mu_4\text{-}O)^{2-}$ oxo bridges. The decanuclear complex $[Ce^{IV}_8Ce^{III}Mn^{III}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_3(\mu_3\text{-}OH)_2(\mu\text{-}OH)(bdea)_4(O_2C^tBu)_{9.5}(NO_3)_{3.5}(OAc)_2] \cdot 1.5\,MeCN$ ($bdea^{2-}$ = 2,2′-(butylimino]bis[ethanolato]; **5**) contains a rather compact Ce^{IV}_7 core with the Ce^{III} and Mn^{III} centers well-separated from each other on the periphery. The aggregate in $[Ce^{IV}_4Mn^{IV}_2(\mu_3\text{-}O)_4(bdea)_2(O_2C^tBu)_{10}(NO_3)_2] \cdot 4\,MeCN$ (**6**) is based on a quasi-planar $\{Mn^{IV}_2Ce^{IV}_4(\mu_3\text{-}O)_4\}$ core made up of four edge-sharing $\{Mn^{IV}Ce^{IV}_2(\mu_3\text{-}O)\}$ or $\{Ce^{IV}_3(\mu_3\text{-}O)\}$ triangles. The structure of $[Ce^{IV}_3Mn^{IV}_4Mn^{III}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_7(O_2C^tBu)_{12}(NO_3)(furan)] \cdot 6\,H_2O$ (**7** $\cdot 6\,H_2O$) can be considered as $\{Mn^{IV}_2Ce^{IV}_2O_4\}$ and distorted $\{Mn^{IV}_2Mn^{III}Ce^{IV}O_4\}$ cubane units linked through a central $(\mu_4\text{-}O)$ bridge. The Ce_6Mn_8 equals the highest nuclearity yet reported for a heterometallic Ce/Mn aggregate. In contrast to most of the previously reported heterometallic Ce/Mn systems, which contain only Ce^{IV} and either Mn^{IV} or Mn^{III}, some of the aggregates presented here show mixed valency, either Mn^{IV}/Mn^{III} (see **7**) or Ce^{IV}/Ce^{III} (see **4** and **5**). Interestingly, some of the compounds, including the heterovalent Ce^{IV}/Ce^{III} **4**, could be obtained from either $Ce^{III}(NO_3)_3 \cdot 6\,H_2O$ or $(NH_4)_2[Ce^{IV}(NO_3)_6]$ as starting material.

Introduction. – Since the discovery of the phenomenon of single-molecule magnet (SMM) behavior in Mn_{12}, a variety of SMMs are now known containing other metals, the majority of which are Mn^{III} complexes [1–4]. While there have been many reports of 3d-4f SMMs [5–8], there are still only limited examples of 3d-Ce complexes reported in the literature [9].

Ce-Containing compounds have attracted a lot of attention because of their application in catalysis. Ce Complexes are good oxidizing agents, and their combination with 3d-metal ions having multiple oxidation states, such as Mn, should generate redox processes that may lead to the isolation of Mn/Ce complexes presenting high oxidation states [10]. High-valent Mn or Ce oxo species are of relevance to a large number of areas such as chemistry, biology, industry, and the environment because of their ability to oxidize both inorganic and organic substrates [11–18]. For example, the highest oxidation state of the tetranuclear Mn complex $[Mn^{IV}_4Ca]$ in the water-oxidizing center (WOC) within Photosystem II is responsible for the oxidation of H_2O to O_2 [11][12]. This has stimulated extensive research efforts to model this site and as a result, a number of $[Mn_4]$ complexes have been synthesized in an effort to model its structural and functional properties [11]. Ce^{IV} has been used in homogeneous and heterogeneous catalysis by Ru complexes of H_2O oxidation to molecular dioxygen [12]. In biomimetic studies, the formation of high-oxidation-state Ru oxo complexes has been well established for H_2O oxidation in the presence of a strong oxidant such as Ce^{IV} or $[Ru(bpy)_3]^{3+}$ [19]. Recently, *Fukuzumi*, *Nam*, and co-workers employed Ce^{IV} as a one-electron oxidant in the generation of mononuclear non-heme Fe^{IV} oxo complexes and in the catalytic oxidation of organic substrates with H_2O as an O-atom source [20]. Despite these properties of Mn^{IV} and Ce^{IV} compounds, it is rather surprising that there are still rather few reports of Ce^{IV}-containing heterometallic complexes [9].

Aminoethanol (=ethanolamine) ligands are an attractive class of ligands in view of their extensively documented ability to bridge metal ions to afford a variety of complexes [21]. Our continued interest in this class of ligands has been focussed on the construction of novel metal-organic architectures and recently, we [22] and others [23] have reported a range of 3d-4f-polynuclear complexes presenting various topologies and interesting magnetic properties. Employing tripodal chelating and/or ancillary carboxylates, we were able to assemble lanthanide [24] and heterometallic 3d-4f aggregates [22][25]. In some of these studies, we observed that, particularly with higher-nuclear 3d-4f systems, we could not obtain the same core topology for all lanthanides [25b][26], presumably resulting from the decrease in Ln^{III} ionic radius along the lanthanide series – the lanthanide contraction – with its concomitant change in preferred coordination number. This problem appears particularly severe when attempting to synthesise La^{III} or Ce^{III} analogues of other 3d-4f aggregates, when the large size of the La^{III} ion and the ability of Ce^{III} to be oxidized to Ce^{IV} can lead to very different structures from those expected. Most of the few Ce-containing heterometallic compounds known have been reported by the *Christou* group. These include high-oxidation-state $Ce^{IV}Mn^{IV}$ aggregates [27], a family of Mn^{III}/Ce^{IV} complexes [28], and the high-nuclear $[Mn^{III}_{10}Ce^{IV}_2Ce^{III}_2O_{10}(OMe)_6(O_2CPh)_{16}(NO_3)_2(MeOH)_2(H_2O)] \cdot 4\,H_2O$, the latter being the only 3d-4f cluster with mixed valency in its lanthanide component [29]. Recently, a Ce^{IV}-containing oxomolybdenum cluster exhibiting a $[Ce_6Mo_9]$ core [30], as well as the heterobimetallic Ce^{IV} disiloxanediolates $[\{(Ph_2SiO)_2O\}\{K(thf)_2\}]_2Ce(O^tBu)_2$ and $[\{(Ph_2SiO)_2O\}_2\{(MeOCH_2CH_2OMe)KO^tBu\}\text{-}\{(Ph_2SiO_2)K\}Ce]_2$, obtained from the Ce^{IV} precursor $[(^tBuO)_3Ce^{IV}(NO_3)(thf)_2]$, have also been reported [31]. These compounds were all synthesized from Ce^{IV} starting materials, and to the best of our knowledge, there have been no reports of such heterometallic complexes resulting from the use of a Ce^{III} source. Hence, we were interested in investigating the structural evolution of Mn/Ce complexes obtained from the combination of structurally related chelating ligands with carboxylates in the presence of Mn and/or Ce sources. As part of our investigations into the structural diversity of 3d-4f-metal-organic frameworks [22][25][26], we report here the syntheses of polynuclear Ce and mixed-metal Mn/Ce complexes from reactions involving the free pivalic acid (=2,2-dimethylpropanoic acid) ligand, the free organic N,O or N,O,O ligands pyridine-2-ethanol (Hpye), *N*-butyldiethanolamine; H_2bdea), 2,2′-[(*tert*-butyl)imino]bis[ethanol] (=*N*-(*tert*-butyl)diethanolamine ($H_2{}^t$bdea), or 2,2′,2″,2‴-(ethane-1,2-diyldinitrilo)tetrakis[ethanol] (=ethylenediamine-*N*,*N*,*N*′,*N*′-tetraethanol (H_4edte) and either Ce^{III} or Ce^{IV} complexes. Many of these present aesthetically pleasing core topologies, and some show mixed valency: either the rare $Mn^{III}/Ce^{III/IV}$ or the novel $Mn^{III/IV}/Ce^{IV}$ combination.



Hpye H_2bdea $H_2{}^t$Bdea H_4edte Hea

Syntheses. – The reaction of $Ce(NO_3)_3 \cdot 6\,H_2O$ with the dinuclear pivalatocopper(II) complex $[Cu_2(\mu\text{-}OH_2)(O_2C^tBu)_4(^tBuCO_2H)_4] \cdot 2\,H_2O$ and 2,2′-iminobis[ethanol] under reflux in MeCN gave the complex $[Ce^{IV}{}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2C^tBu)_{12}]$ (**1**) as the only product. Compound **1** could also be obtained from the reaction of $Ce(NO_3)_3 \cdot 6\,H_2O$, $[Mn(OAc)_2] \cdot 4\,H_2O$, pivalic acid, and propane-1,3-diol in MeCN. So far, it was not possible to obtain **1** by a direct synthesis not involving a transition-metal complex.

The synthesis of the decanuclear complex $[Ce^{IV}{}_6Mn^{III}{}_4(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(O_2C^tBu)_{12}(ea)_4(OAc)_4] \cdot 4\,H_2O \cdot 4\,MeCN$ (**2**), involved reaction of H_4edte with $[Mn(OAc)_2] \cdot 4\,H_2O$, $Ce(NO_3)_2 \cdot 6\,H_2O$, and pivalic acid in MeCN. The deprotonated 2-aminoethanol ligand ea^- present in the structure presumably resulted from the decomposition of the H_4edte ligand.

Reaction pyridine-2-ethanol (Hpye) with $[Mn_6(O)_2(O_2C^tBu)_{10}(HO_2C^tBu)_{1.5}(4\text{-Me-py})_{2.5}]$ [22b] and $Ce(NO_3)_3 \cdot 6\,H_2O$ in MeCN resulted in the complex aggregate $[Ce^{IV}{}_6Mn^{III}{}_8(\mu_4\text{-}O)_4(\mu_3\text{-}O)_8(pye)_4(O_2C^tBu)_{18}]_2{}^{4+}[Ce^{IV}{}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2C^tBu)_{10}(NO_3)_4]^{2-}$ $[Ce^{III}(NO_3)_5(OH_2)]^{2-} \cdot 21\,MeCN$ (**3**). This procedure was similar to the one that we had used previously in the synthesis of a series of $[Mn_2Ln_2]$ complexes [22e]; the only difference was the use of $Ce(NO_3)_3 \cdot 6\,H_2O$ in place of the other lanthanide nitrates. For two aggregates of high nuclearity and opposite charge to crystallize as a salt is unusual although such co-crystallization of the cyano-bridged $[Mn_4{}^{III}Cr^{III}]$ and $[Mn_2{}^{III}Cr^{III}]$ heterometallic complexes has been previously observed [32]. Variation of the reaction conditions to favor the formation of just one or the other of the discrete $[Ce^{IV}{}_6Mn^{III}{}_8]$ or $[Ce^{IV}{}_6]$ complexes, by changing the molar ratio of the starting materials or use of other solvents or solvent mixtures, were not successful.

Reaction of the free 2,2′-[(*tert*-butyl)imino]bis[ethanol] ligand $H_2{}^t$bdea with $[Mn(OAc)_2] \cdot 4\,H_2O$, $^tBuCO_2H$, and either $Ce^{III}(NO_3)_3 \cdot 6\,H_2O$ or $(NH_4)_2[Ce^{IV}(NO_3)_6]$ in MeCN gave complex $[Ce^{IV}{}_6Ce^{III}{}_2Mn^{III}{}_2(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(^tbdea)_2(O_2C^tBu)_{12}(NO_3)_2(OAc)_2] \cdot 4\,CH_2Cl_2$ (**4**) or the corresponding MeCN solvate, depending on the crystallization conditions. This procedure was identical to that which we had previously used in the synthesis of a series of $[Mn^{III}_5Ln^{III}_8]$ (Ln = Pr, Nd, Sm, Gd, and Tb) complexes [26], but merely replacing the other lanthanide nitrates with $Ce(NO_3)_3 \cdot 6\,H_2O$ now gave a totally different structure.

The reaction of the isomeric ligand H_2bdea with a mixture of $[Mn(OAc)_2] \cdot 4\,H_2O$, $[Fe_3(O)(O_2C^tBu)_6(H_2O)_3]O_2C^tBu$, and $Ce^{III}(NO_3)_3 \cdot 6\,H_2O$ in MeCN gave a brown solution from which brown crystals of the decanuclear cluster compound $[Ce^{IV}_8Ce^{III}$-$Mn^{III}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_3(\mu_3\text{-}OH)_2(\mu\text{-}OH)(bdea)_4(O_2C^tBu)_{9.5}(NO_3)_{3.5}(OAc)_2] \cdot 1.5$ MeCN (**5**) were obtained in 30% yield. This procedure was similar to that previously used by us in the synthesis of $\{Mn_4\}$ complexes, in which we observed that no Fe^{III} was present in the product, with the reagent $[Fe_3(O)(O_2C^tBu)_6(H_2O)_3]O_2C^tBu$ only serving as a source of pivalato ligands [33]. The difference here is the stoichiometric ratio of the manganese and pivalato sources and the addition of $Ce(NO_3)_3 \cdot 6\,H_2O$ to the synthetic recipe. Therefore, we decided to apply a direct synthesis from the constituent reactants. When H_2bdea was treated with $[Mn(OAc)_2] \cdot 4\,H_2O$, pivalic acid, and $Ce^{III}(NO_3) \cdot 6\,H_2O$ in MeCN, the same product **5** was obtained in 25% yield. By contrast, reaction of H_2bdea with $[Mn(OAc)_2] \cdot 4\,H_2O$, pivalic acid, and $(NH_4)_2[Ce^{IV}(NO_3)_6]$ in MeCN afforded the bimetallic hexanuclear complex $[Ce^{IV}_4Mn^{IV}_2(\mu_3\text{-}O)_4(bdea)_2(O_2C^tBu)_{10}(NO_3)_2] \cdot 4$ MeCN (**6**). With H_2bdea, therefore, the oxidation state of the Ce salt determined the product obtained, while with $H_2{}^t$bdea the same product **4** was obtained whether Ce^{III} or Ce^{IV} was used.

Heating a mixture of $[Mn_6(O)_2(O_2C^tBu)_{10}(O_2C^tBu)_{1.5}(4\text{-Me-py})_{2.5}]$, $(NH_4)_2[Ce^{IV}$-$(NO_3)_6]$, and furoic acid (= furan-2-carboxylic acid; C_4H_3OCOOH) gave $[Ce^{IV}_3Mn^{IV}$-$_4Mn^{III}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_7(O_2C^tBu)_{12}(NO_3)(C_4H_4O)] \cdot 6\,H_2O$ (**7** $\cdot 6\,H_2O$), the furan ligand resulting from the oxidative decarboxylation of the furoic acid.

Description of Structures. – The complexes were structurally characterized by single-crystal X-ray crystallography. Crystallographic data and structure-refinement parameters are summarized in *Table 1*. Where this was in any doubt, the oxidation states of Mn- and Ce-atoms, and the degree of protonation of bridging oxo and hydroxo ligands, were determined by bond-valence-sum calculations (*Table 2*) [34].

$[Ce^{IV}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2C^tBu)_{12}]$ (**1**). Compound **1** crystallizes in the rhombohedral space group *R*-3 with *Z* = 3. The hexanuclear aggregate thus has -3 site symmetry; its structure is shown in *Fig. 1*. Each edge of the Ce_6 octahedron is bridged by a *syn,syn*-pivalato ligand. In the crystal structure, the O-atoms capping the two independent Ce_3 triangular faces are two-fold disordered: O(1A) or O(1B) bridging the two faces with threefold symmetry, O(2A) or O(2B) over the remaining six faces. In each case, the A component corresponds to an oxo ligand (Ce–O 2.178(5)–2.209(6) Å) and the B component to a hydroxo ligand (Ce–O 2.389(4)–2.418(6) Å). Charge neutrality requires that there be four oxo and four hydroxo ligands in total, and for both the disordered pairs, O(1A) and O(1B) or O(2A) and O(2B), the two half O-atoms could be refined anisotropically and unrestrained with 50% occupancy each. It can be assumed that the four oxo and four hydroxo ligands are evenly distributed over the faces, *i.e.*, any face with an oxo ligand is surrounded by three faces with hydroxo ligands, and *vice versa*. The oxo and hydroxo ligands are shielded by the pivalato *t*-Bu groups and are unable to be involved in H-bonds resulting in the observed disorder. The coordination environment of Ce(1) is completed by four O-atoms from different

Table 1. *Summary of Crystal Data and Refinement Details for Compounds* **1**–**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{60}H_{112}Ce_6O_{32}$	$C_{84}H_{156}Ce_6Mn_4N_8O_{48}$	$C_{328}H_{547}Ce_{19}Mn_{16}N_{38}O_{160}$	$C_{84}H_{156}Ce_8Cl_8Mn_2N_4O_{46}$	$C_{86.5}H_{165}Ce_9MnN_9O_{50.5}$	$C_{74}H_{136}Ce_4Mn_2N_8O_{34}$	$C_{64}H_{112}Ce_3Mn_5NO_{37}$
M_r	2186.22	3106.65	11124.36	3472.57	3455.29	2352.27	2182.61
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	100	100	100	100	100	100	150
Crystal system	trigonal	tetragonal	triclinic	triclinic	triclinic	monoclinic	triclinic
Space group	*R*-3	*I*-4	*P*-1	*P*-1	*P*-1	$P2_1/c$	*P*-1
Unit cell parameters:							
a [Å]	21.8220(4)	19.8581(4)	16.9169(10)	15.1649(5)	16.7662(12)	14.8219(6)	13.7922(14)
b [Å]	21.8220(4)	19.8581(4)	17.1062(10)	15.6035(5)	18.3737(13)	14.2845(6)	14.8754(14)
c [Å]	15.2295(6)	16.5071(7)	39.044(2)	16.5767(5)	22.6451(17)	24.6287(10)	25.391(2)
α [°]	90	90	99.759(1)	99.130(1)	113.897(1)	90	84.817(8)
β [°]	90	90	95.250(1)	106.524(1)	90.194(1)	100.188(1)	77.692(8)
γ [°]	120	90	102.000(1)	118.065(1)	91.869(1)	90	63.764(7)
V [Å^3]	6280.7(3)	6509.5(3)	10797.4(11)	3113.66(17)	6373.5(8)	5132.3(4)	4565.3(8)
Z	3	2	1	1	2	2	2
$F(000)$	3228	3096	5563	1706	3396	2380	2196
$\rho_{calc.}$ [Mg m^{-3}]	1.734	1.585	1.711	1.852	1.800	1.522	1.588
μ (MoK_α) [mm^{-1}]	3.267	2.503	2.494	3.305	3.321	2.051	2.209
Reflections measured	10286	20365	48115	21618	29191	32045	30142
R_{int}	0.0205	0.0327	0.0457	0.0198	0.0303	0.0211	0.0437
Unique data	3174	7437	40063	13444	24449	11661	18055
Data with $I > 2\sigma(I)$	2913	7063	19982	12151	15967	10245	13177
Refined parameters	169	328	2199	731	1385	645	982
wR_2 (all data)	0.0814	0.0622	0.0778	0.0989	0.1437	0.0706	0.1606
S (all data)	1.045	1.018	0.915	1.023	1.023	1.047	0.999
R_1 ($I > 2\sigma(I)$)	0.0318	0.0282	0.0487	0.0350	0.0515	0.0260	0.0600
Largest residuals [e Å^{-3}]	+1.38, −0.62	+0.97, −0.53	+1.15, −1.00	+2.17, −2.18	+1.86, −0.88	+1.15, −0.53	+0.94, −1.93

Table 2. *Bond-Valence Sums for the Ce and Mn Atoms in* **4**, **5**, *and* **7**

	Mn^{III}	Mn^{IV}	Ce^{III}	Ce^{IV}
		4		
Mn(1)	2.88			
Ce(1)				3.73
Ce(2)				3.87
Ce(3)				3.92
Ce(4)			2.95	
		5		
Mn(1)	2.90			
Ce(1)				4.02
Ce(2)				3.89
Ce(3)				3.92
Ce(4)				3.72
Ce(5)				3.76
Ce(6)				3.94
Ce(7)				3.92
Ce(8)				3.93
Ce(9)			3.05	
		7		
Mn(1)		4.03		
Mn(2)		4.05		
Mn(3)		3.99		
Mn(4)		4.01		
Mn(5)	2.87			
Ce(1)				4.00
Ce(2)				3.95
Ce(3)				3.96

pivalato ligands (Ce–O 2.362(2)–2.386(2) Å) giving an overall slightly distorted square antiprismatic coordination geometry.

Unusually, the Ce_6 octahedron in **1** does not contain an interstitial μ_6-oxo ligand. Such a hollow octahedron is rather rare in lanthanide chemistry. Except for the Ln_6 unit in the previously reported [Gd_6Cu_{12}] [35] and [Ln_{14}] clusters [36] and the hexanuclear Ce^{IV} complex [$Ce^{IV}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(acac)_{12}$] ($acac^-$ = pentane-2,4-dionato) [37], which is structurally closely related to **1**, all previously known octahedral Ln_6 clusters in molecular compounds have a μ_6-oxo ligand in the center of the octahedron, which was believed to play a key role in stabilizing the Ln_6 unit [38].

[$Ce^{IV}_6Mn^{III}_4(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(O_2C^tBu)_{12}(ea)_4(OAc)_4$] · 4 H_2O · 4 MeCN (**2**). Compound **2** crystallizes in the tetragonal space group *I*-4 with $Z = 2$; the Ce_6Mn_4 moiety has -4 site symmetry. The structure of **2** is shown in *Fig. 2*. The {$Ce^{IV}_6Mn^{III}_4(\mu_4\text{-O})_4(\mu_3\text{-O})_4$} core of **2** is related to that of **1**, but with the bridging hydroxo ligands in **1** now deprotonated and coordinating to Mn^{III} centers, forming (μ_4-O) bridges. As can be seen in *Fig. 2,b*, the four Mn^{III} centers are not, as might have been expected, symmetrically disposed with respect to the Ce_6 octahedron. The oxo bridge O(1) links Mn(1) to the apical Ce(1) and to Ce(2) and Ce(2′). Single *syn*,*syn*-pivalato bridges also link Mn(1) to

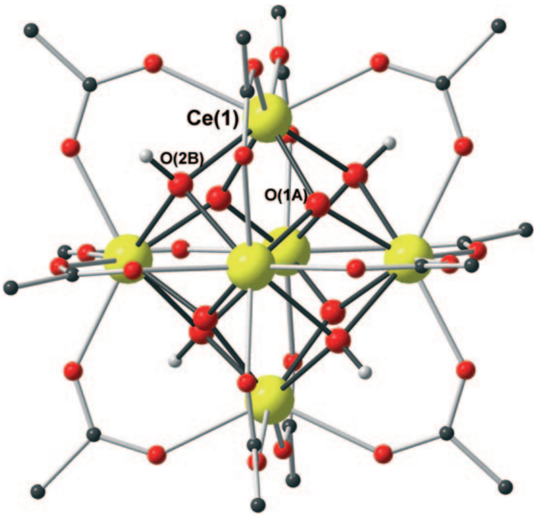


Fig. 1. *Molecular structure of the compound [$Ce^{IV}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2C^tBu)_{12}$]* (**1**). Only one of the possible arrangements of oxo and hydroxo ligands is shown, and Me groups of the pivalato ligands are omitted for clarity. Color code: Ce^{IV} yellow, O red, C black, and H white.

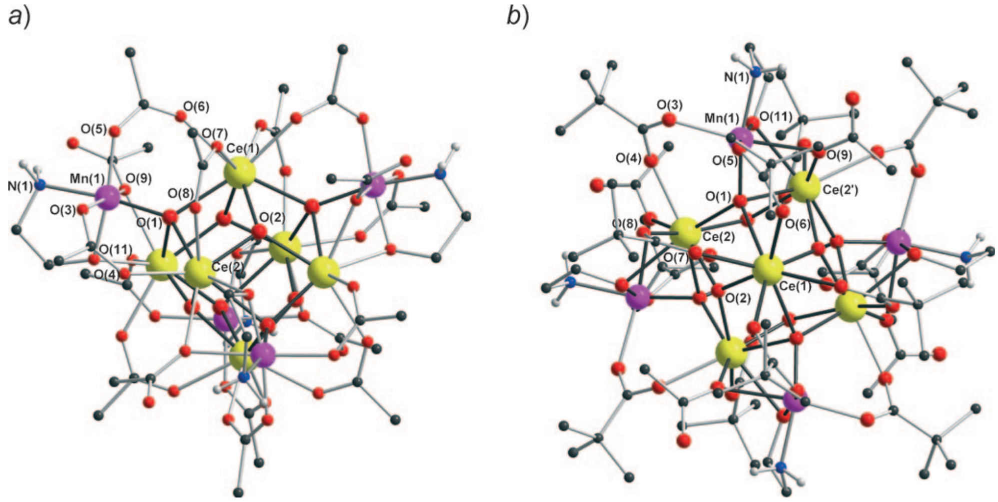


Fig. 2. a*) Molecular structure of* **2** (pivalato Me groups are omitted for clarity). b*) Structure viewed down the molecular* (and crystal) *-4 axis.* Color code: Mn^{III} purple, Ce^{IV} yellow, N blue, O red, and C black.

Ce(1) and Ce(2), but two single-atom O-bridges (the acetato O-atom O(9) and the deprotonated 2-aminoethanol O-atom O(11)) join Mn(1) to Ce(2′). It is this asymmetry in the Mn ⋯ Ce bridging that results in the rotation of the Mn_4 tetrahedron relative to the Ce_6 octahedron. As in **1**, there are 12 *syn*,*syn*-pivalato ligands in total. Four of these still bridge apical and equatorial Ce centers, as they do in **1**, but the introduction of the four Mn centers has forced the remaining eight pivalato ligands to open out, and these now bridge Mn ⋯ Ce edges of the core.

$[Ce^{IV}_6Mn^{III}_8(\mu_4\text{-}O)_4(\mu_3\text{-}O)_8(pye)_4(O_2C^tBu)_{18}]_2[Ce^{IV}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2C^tBu)_{10}\text{-}(NO_3)_4]\cdot[Ce^{III}(NO_3)_5(H_2O)]\cdot 21\ MeCN$ (**3**). Compound **3** crystallizes in the triclinic space group *P*-1 with $Z = 1$. It can be regarded, rather unusually in the chemistry of polynuclear complexes, as a double salt. The formula unit is composed of two tetradecanuclear dications $[Ce^{IV}_6Mn^{III}_8(\mu_4\text{-}O)_4(\mu_3\text{-}O)_8(pye)_4(O_2C^tBu)_{18}]^{2+}$, one hexanuclear dianion $[Ce^{IV}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2C^tBu)_{10}(NO_3)_4]^{2-}$, a dianionic mononuclear Ce^{III} complex $[Ce^{III}(NO_3)_5(OH_2)]^{2-}$, and lattice MeCN. The Ce_6Mn_8 dication occupies a general position in the asymmetric unit, while the Ce_6 and mononuclear dianions lie on different inversion centers. The anionic Ce_6 aggregate (*Fig. 3,a*) has a very similar core structure to that found in **1**, except that four Ce centers, which form a square within the Ce_6 octahedron, are now chelated by nitrato ligands, and two opposite edges of the square are no longer bridged by pivalato ligands.

The Ce_6Mn_8 dication (*Fig. 3,b*) is based on a central $\{Ce^{IV}_6Mn^{III}_4(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4\}$ core, which is closely related to that in **2**. However, the Mn and Ce centers along two opposite edges of the supertetrahedron are now further linked by (μ_3-O) bridges to four more Mn^{III} centers, with these linkages reinforced by bridges involving O-atoms from the pyridine-2-ethanolato and pivalato ligands. These additional Mn^{III} are also linked by *syn,syn*-pivalato bridges, so that the aggregate could be considered as consisting of two Mn_4 chains supported on either side of the Ce_6 octahedron. Together with the $Mn_{10}Ce_4$ species reported by *Christou* and co-workers [29], the Ce_6Mn_8 cation in **3** has the highest nuclearity yet found for a Ce/Mn aggregate.

The structure of the dianionic $[Ce^{III}(NO_3)_5(OH_2)]^{2-}$ complex is shown in *Fig. 3,c*. Although the complex unit lies on an inversion center, the molecule itself is acentric, so that the central Ce(10) is displaced off the center, and the complex thus shows 50 : 50 disorder against the inversion-derived molecule (shown pale in *Fig. 3,c*). The oxidation state of Ce(10), and thus the charge on the complex, could be established by bond-valence-sum methods, with the calculated value of 3.07 confirming the overall dianionic charge.

The packing of the cations and anions in **3** is shown schematically in *Fig. 3,d*. The mononuclear nitrato complexes (shown as blue spheres) and the Ce_6 dianions form alternating layers within the structure. The Ce_6Mn_8 dications form intervening layers with each Ce_6Mn_8 unit occupying a cavity formed between four mononuclear complexes and four Ce_6 units.

$[Ce^{IV}_6Ce^{III}_2Mn^{III}_2(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(^tbdea)_2(O_2C^tBu)_{12}(NO_3)_2(OAc)_2]\cdot 4\ CH_2Cl_2$ (**4**). Compound **4** crystallizes in the triclinic space group *P*-1 with $Z = 1$; the molecule thus has centrosymmetric site symmetry. The isostructural compound can also be obtained as an isomorphous MeCN solvate, but only the CH_2Cl_2 solvate will be discussed here. The structure of the aggregate in **4** is given in *Fig. 4*.

The mixed-valent $\{Ce^{IV}_6Ce^{III}_2Mn^{III}_2(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4\}$ core of complex **4** is again related to that in **2**. However, the four peripheral trivalent metal centers are now not all the same, but comprise two Mn^{III} and two Ce^{III}, and these are now arranged mutually coplanar to form a parallelogram, rather than the tetrahedron in **2**. This parallelogram (distorted from a square because of the differing ionic radii of Mn^{III} and Ce^{III}) is closely coplanar to a mirror plane of the Ce_6 octahedron. Additional bridging is provided by

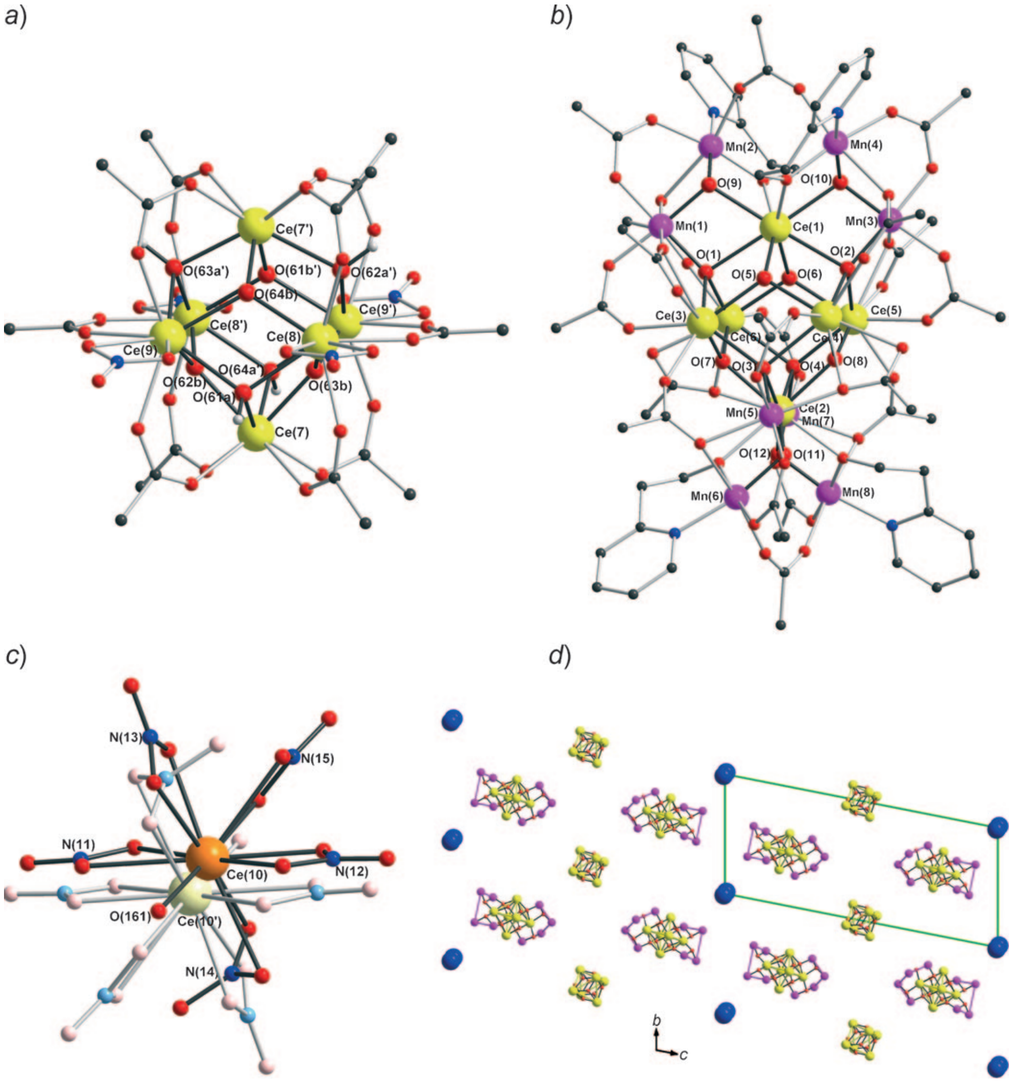


Fig. 3. *Structure of* a) *the anion* $[Ce^{IV}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2C^tBu)_{10}(NO_3)_4]^{2-}$ *of* **3** (only one of the arrangements of the oxo and hydroxo ligands is shown), b) *the tetradecanuclear cation* $[Ce^{IV}_6Mn^{III}_8(\mu_4\text{-}O)_4(\mu_3\text{-}O)_8(pye)_4(O_2C^tBu)_{18}]^{2+}$ *of* **3**, and c) *The anion* $[Ce^{III}(NO_3)_5(OH_2)]^{2-}$ *of* **3** *with the inversion-related disorder component drawn with pale atoms* (pivalato Me groups are omitted for clarity; color code: Mn^{III} purple, Ce^{IV} yellow, Ce^{III} orange, N blue, O red, and C black. d) *Packing of the cations and anions in the crystal structure of* **3**, *viewed down the* a-*axis, with the mononuclear nitrato complexes shown as blue spheres.*

two ^{t}bdea^{2-} ligands which chelate to Mn(1) and Mn(1′) with their O-atoms forming bridges to Ce^{IV} centers in the octahedron, eight *syn,syn*-bridging pivalato ligands, four $\eta^1:\eta^2:\mu$-pivalato ligands, and two $\eta^1:\eta^2:\mu_3$-acetato ligands which mediate the only

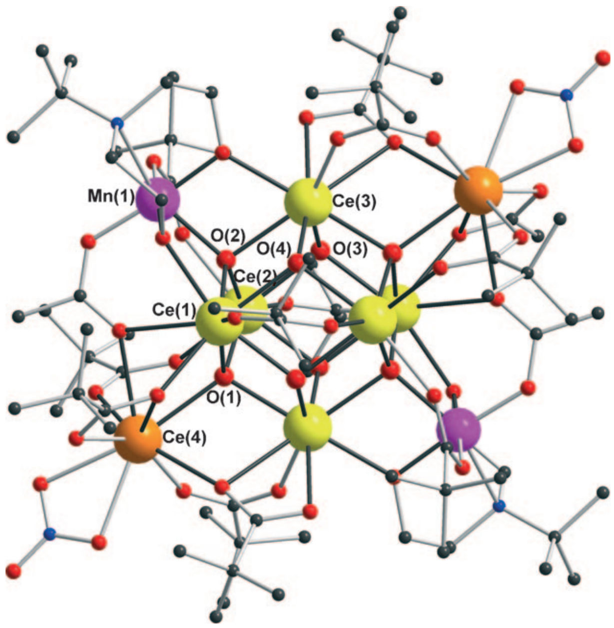


Fig. 4. *Molecular structure of* **4**. Color code: Mn^{III} pink, Ce^{III} orange, Ce^{IV} yellow, N blue, O red, and C black.

direct linkages between Mn^{III} and Ce^{III} centers. The Ce^{III} atoms are nine-coordinate, while the Ce^{IV} atoms are eight-coordinate. Such a core arrangement of metal atoms has been observed before in homometallic $[Mn^{II}_4Mn^{III}_6(N_3)_4(hmp)_{12}](X_2)_2$ (X = ClO_4, N_3) (Hhmp = 2-(hydroxymethyl)pyridine = pyridine-2-methanol) [39], heterometallic Gd/Zn complexes [40], or in niobium alcoholate clusters [41].

$[Ce^{IV}_8Ce^{III}Mn^{III}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_3(\mu_3\text{-}OH)_2(\mu\text{-}OH)(bdea)_4(O_2C^tBu)_{9.5}(NO_3)_{3.5}(OAc)_2]\cdot$ 1.5 MeCN (**5**). Compound **5** crystallizes in the monoclinic space group *P*-1 with *Z* = 2. The structure of the aggregate **5** and its inorganic $\{Ce^{IV}_8Ce^{III}Mn^{III}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_3(\mu_3\text{-}OH)_3(\mu\text{-}OH)\}$ core is shown in *Fig. 5*.

The overall structure of aggregate **5**, which has idealized mirror symmetry, is very unusual. The inorganic core of **5** (*Fig. 5*,*b*) contains a central $\{Ce^{IV}_4O_3(OH)\}$ cubane unit. Each of the three oxo ligands in this cubane, O(1), O(2), and O(3), then forms a μ_4-O bridge to a further Ce ion: O(1) and O(2) to Ce^{IV} and O(3) to a Ce^{III}, Ce(9). Ce(1), in the cubane, and Ce(4) and Ce(5) are then linked *via* three μ_3-O oxo bridges to the last two Ce^{IV} centers, Ce(2) and Ce(3). Finally, these two are linked through a μ_3-OH to the sole Mn^{III} center, Mn(1). Further significant bridging is provided by the four $bdea^{2-}$ ligands, the O-atoms of which form eight bridges, and by two *anti*,*syn*,*syn* acetato ligands. The coordination sphere is completed by nine *syn*,*syn*-bridging pivalato ligands and four chelating ligands, three nitrato and one disordered nitrato/pivalato ligand.

$[Ce^{IV}_4Mn^{IV}_2(\mu_3\text{-}O)_4(bdea)_2(O_2C^tBu)_{10}(NO_3)_2]\cdot 4$ MeCN (**6**). Compound **6** crystallizes in the monoclinic space group $P2_1/n$ with *Z* = 2. The centrosymmetric structure of

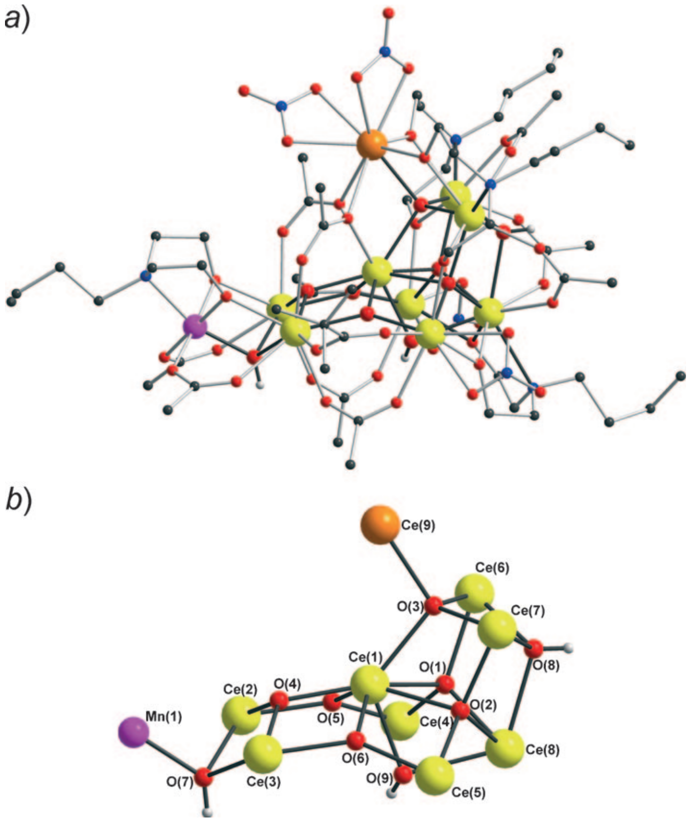


Fig. 5. a) *Molecular structure of* $[Ce^{IV}_8Ce^{III}Mn^{III}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_3(\mu_3\text{-}OH)_2(\mu\text{-}OH)(bdea)_4(O_2C^tBu)_{9.5}\text{-}(NO_3)_{3.5}(OAc)_2]\cdot 1.5\ MeCN$ (**5**). b) *Inorganic core of* **5**. Pivalato Me groups are omitted for clarity. Color code: Mn^{III} pink, Ce^{III} orange, Ce^{IV} yellow, N blue, O red, and C black.

6 is shown in *Fig. 6*. The inorganic core of complex **6** consists of a $\{Ce^{IV}_4Mn^{IV}_2(\mu_3\text{-}O)_4\}$ unit, in which the four exactly coplanar Ce^{IV} centers are linked by two (μ_3-O) bridges, O(1) and O(1′), to form a parallelogram. O(1) is only slightly displaced by 0.169 Å out of its Ce_3 triangle. Ce(1) and Ce(2) are then further linked by a (μ_3-O) bridge, O(2), to the Mn^{IV} center, Mn(1). The triangle defined by Mn(1), Ce(1), and Ce(2) makes a dihedral angle of 35.0° to the Ce_4 plane such that, although O(2) is displaced by 0.816 Å out of the $MnCe_2$ triangle, it is very close to coplanar with (out of plane by 0.014 Å) the Ce_4 parallelogram. The two $bdea^{2-}$ ligands each chelate a Mn^{IV}, with their O-atoms forming bridges to the adjacent Ce centers. Each Mn ⋯ Ce or Ce ⋯ Ce edge of the core is bridged by a *syn*,*syn*-pivalato ligand, with a chelating nitrato ligand completing the coordination environments of Ce(2) and Ce(2′). The Mn^{IV} ions are six-coordinate with the expected octahedral geometry. Ce(1) is eight-coordinate and Ce(2) is nine-coordinate, with coordination polyhedra that may best be described as distorted bi- and tri-capped trigonal prisms, respectively.

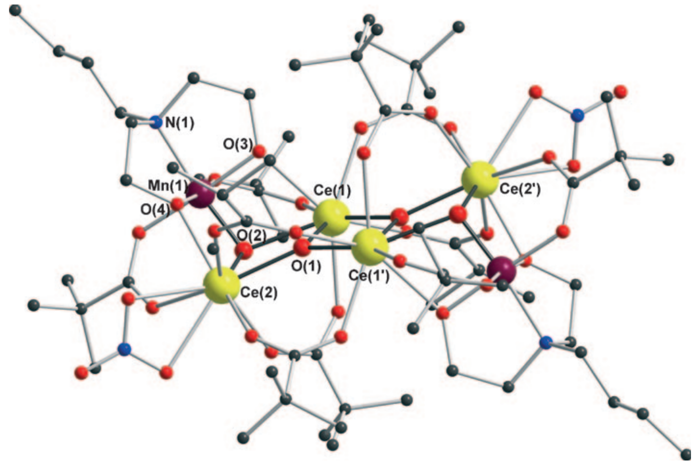


Fig. 6. *Molecular structure of the [$Ce^{IV}_4Mn^{IV}_2(\mu_3$-$O)_4(bdea)_2(O_2C^tBu)_{10}(NO_3)_2$] aggregate in* **6**. H-Atoms are omitted for clarity. Color code: Mn^{IV} plum, Ce^{IV} yellow, N blue, O red, and C black.

[$Ce^{IV}_3Mn^{IV}_4Mn^{III}(\mu_4$-$O)_2(\mu_3$-$O)_7(O_2C^tBu)_{12}(NO_3)(C_4H_4O)$] (**7**). Compound **7** crystallizes in the triclinic space group *P*-1 with $Z=2$. The molecular structure and inorganic core are shown in *Fig. 7.* The core of the compound can be considered as constructed from two heterometallic $\{Mn_2Ce_2O_4\}$ and $\{Mn_3CeO_4\}$ cubanes, although the latter must be considered distorted, as O(6) does not coordinate to Mn(5) (O(6)$\cdots$Mn(5) = 3.550 Å). The two cubanes are linked *via* the (μ_4-O) bridge O(2), with additional linkage involving O(1) and O(6). Peripheral ligation is provided by eleven *syn,syn-μ*-pivalato ligands, one η^1:η^2:μ-pivalato ligand, a nitrato anion chelating Ce(3), and a furan molecule at Mn(3). The latter presumably derives from oxidative decarboxylation of the furoic acid in the synthetic mixture.

Conclusions. – We described one Ce and a variety of Ce/Mn complexes presenting some interesting topologies. While the Ce/Mn ratios within the products do not reflect the stoichiometric ratios of the Ce and Mn sources in the synthetic reactions, it should be pointed out that the compounds reported herein were obtained from similar reactions performed with other lanthanides that yielded completely different compounds which we have previously reported [22a][22b][25b][26]. We also note that employing either Ce^{III} or Ce^{IV}, we were for a greater part of this work able to isolate mixed-valent Ce/Mn compounds. The nuclearity of the Ce_6Mn_8 cation in **3** equals that of the $Mn_{10}Ce_4$ species reported by *Christou* and co-workers [29], as the highest yet found for a Ce/Mn aggregate. To the best of our knowledge, compound **5** is only the second example of a 3d-4f complex presenting mixed-valency in the lanthanide component, while **7** is the first heterovalent Mn^{IV}/Mn^{III}/Ce aggregate.

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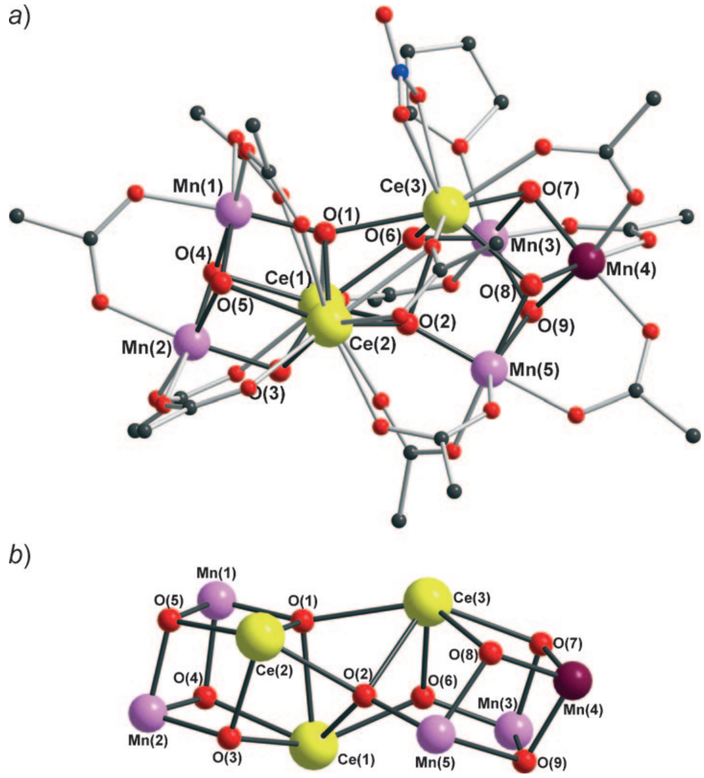

Fig. 7. a*) Molecular structure and* b*) inorganic core of compound* **7**. Pivalato Me groups are omitted for clarity. Color code: Mn^{IV} plum, Mn^{III} pink, Ce^{IV} yellow, N blue, O red, and C black.

Experimental Part

General. Unless otherwise stated, all reagents were obtained from commercial sources and were used as received without further purification. $[Mn_6(O)_2(O_2C^tBu)_{10}(4\text{-Me-py})_{2.5}(^tBuCO_2H)_{1.5}]$ was prepared as previously reported [22a][22b]. All reactions were carried out under aerobic conditions. FT-IR Spectra: *Perkin-Elmer-Spectrum-One* spectrometer with samples prepared as KBr discs; $\tilde{\nu}$ in cm^{-1}. Elemental analyses for C, H, and N: *Elementar-Vario-EL* analyzer; performed at the Institute of Inorganic Chemistry, University of Karlsruhe.

$[Ce^{IV}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2C^tBu)_{12}]$ (**1**). *Method A:* To a stirred soln. of $[Cu_2(\mu\text{-}H_2O)(O_2C^tBu)_4(^tBuCO_2H)_4]\cdot 2\,H_2O$ (0.21 g, 0.21 mmol) and $Ce(NO_3)_2\cdot 6\,H_2O$ (0.08 g, 0.21 mmol) in MeCN (10 ml) was gradually added a soln. of 2,2′-iminobis[ethanol] (H_2dea) (0.13 g, 1.26 mmol) in MeCN (5 ml). The resulting soln. was heated under reflux for 40 min, cooled, then filtered and allowed to stand undisturbed in slow evaporation. After two weeks, light green crystals were collected by filtration, washed with MeCN, and dried in air: **1** (13%, based on Ce).

Method B: Propane-1,3-diol (4 mmol, 0.30 g) in MeCN (5 ml) and $Ce(NO_3)_3\cdot 6\,H_2O$ (0.6 mmol, 0.26 g) were added to a stirred soln. of $[Mn(OAc)_2]\cdot 4\,H_2O$ (0.15 g, 0.6 mmol) and pivalic acid (0.20 g, 2.0 mmol) in MeCN (10 ml). The resulting soln. was further stirred for 1 h, then allowed to cool, filtered, and left to evaporate slowly at r.t. Very light brown crystals were obtained after 2 d, which were washed with MeCN and dried in air: **1** (22%, based on Ce). IR: 3378*w* (br.), 2964*s*, 2931*m*, 2873*m*, 1530v*s*, 1481v*s*, 1459*m*, 1411v*s*, 1374v*s*, 1225v*s*, 1075*m*, 1032*w*, 902*w*, 785*w*, 619*s*, 584*s*, 499*m*, 451*m*. Anal. calc. for $C_{60}H_{112}Ce_6O_{32}$ (2186.21): C 32.96, H 5.16; found: C 33.05, H 4.98.

$[Ce^{IV}_6Mn^{III}_4(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(O_2C^tBu)_{12}(ea)_4(OAc)_4] \cdot 4\,H_2O \cdot 4\,MeCN$ (**2**). To a stirred soln. of $[Mn(OAc)_2] \cdot 4\,H_2O$ (0.24 g, 1.00 mmol), $Ce(NO_3)_2 \cdot 6\,H_2O$ (0.40 g, 1.00 mmol), and pivalic acid (0.50 g, 5.00 mmol) in MeCN (20 ml) was gradually added a soln. of H_4edte (0.24 g, 1.00 mmol) in MeCN (5 ml). The resulting soln. was heated under reflux for 20 min, cooled, then filtered, and allowed to stand undisturbed in slow evaporation. After 1 d, light brown crystals were collected by filtration, washed with MeCN, and dried in air: **2** (31.7%, based on Mn). IR: 3402*w*, 2961*s*, 2926*m*, 2865*m*, 1562v*s*, 1530*m*, 1484v*s*, 1459*m*, 1425v*s*, 1377*m*, 1363*m*, 1311*m*, 1228*m*, 1078*m*, 1032*w*, 928*w*, 898*m*, 814*w*, 792*w*, 744*w*, 722*w*, 651*m*, 603*m*, 579*m*, 515*s*, 418*w*. Anal. calc. for $C_{76}H_{136}Ce_6Mn_4N_4O_{44} \cdot 3\,H_2O$ (2924.39): C 31.21, H 4.89, N 1.91; found: C 31.05, H 4.65, N 1.82.

$[Ce^{IV}_6Mn^{III}_8(\mu_4\text{-}O)_4(\mu_3\text{-}O)_8(pye)_4(O_2C^tBu)_{18}]_2[Ce^{IV}_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2C^tBu)_{10}(NO_3)_4][Ce^{III}(NO_3)_5\text{-}(H_2O)] \cdot 21\,MeCN$ (**3**). To a stirred slurry of $[Mn_6(O)_2(O_2C^tBu)_{10}(4\text{-Me-py})_{2.5}(^tBuCO_2H)_{1.5}]$ (0.20 g, 0.11 mmol) and pyridine-2-ethanol (Hpye; 0.22 g, 1.80 mmol) in MeCN (15 ml) was added under stirring $Ce(NO_3)_3 \cdot 6\,H_2O$ (0.34 g, 0.88 mmol). The resulting mixture was stirred for 30 min at r.t. and then heated at 65° for 20 min. The brown soln. was filtered and left undisturbed. After 2 d, the fully grown crystals were collected by filtration, washed with cold MeCN (5 ml) and dried in air: **3** (33%). IR: 2964*w*, 2926*m*, 1606*w*, 1573*m*, 1556*m*, 1482v*s*, 1442*m*, 1422*m*, 1381*m*, 1323*s*, 1312*s*, 1223*w*, 1167*w*, 1110*w*, 1074*s*, 1034*s*, 976*w*, 866*w*, 817*w*, 789*m*, 764*w*, 741*w*, 658*m*, 596*m*, 581*m*, 545*w*, 505*w*, 434*w*. Anal. calc. for $C_{286}H_{484}Ce_{19}Mn_{16}N_{17}O_{160} \cdot 4\,MeCN$ (10426.34): C 33.86, H 4.79, N 2.82; found: C 34.09, H 5.05, N 2.67.

$[Ce^{IV}_6Ce^{III}_2Mn^{III}_2(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(^tbdea)_2(O_2C^tBu)_{12}(NO_3)_2(OAc)_2] \cdot 4\,CH_2Cl_2$ (**4**). *Method A.* To a stirred slurry of $[Mn(OAc)_2] \cdot 4\,H_2O$ (0.025 g, 0.1 mmol), pivalic acid (0.071 g, 0.7 mmol), and $Ce(NO_3)_2 \cdot 6\,H_2O$ (0.35 g, 0.8 mmol) in MeCN was added dropwise a soln. of $H_2{}^t$bdea 0.32 g, 2 mmol) in MeCN (5 ml). The resulting dark brown soln. was stirred at r.t. for an additional 2 h and filtered. The precipitate was dissolved in CH_2Cl_2 (5 ml) and combined with the filtrate. This was allowed to evaporate slowly at r.t. Brown plates formed after 48 h, which were collected by filtration, washed with MeCN, and dried in air: **4** (28%, based on Mn). IR: 3608*w*, 3407*w* (br.), 2959*m*, 2928*w*, 2869*w*, 1588v*s*, 1569v*s*, 1557v*s*, 1483*s*, 1412*m*, 1402*m*, 1371*s*, 1355*s*, 1224*w*, 1094*m*, 1031*w*, 941*m*, 619*m*, 584*m*, 544*w*, 494*w*, 470*m*. Anal. calc. for $C_{80}H_{148}Ce_8Mn_2N_4O_{40}$ (corresponds to loss of all CH_2Cl_2) (3036.84): C 31.64, H 4.91, N 1.84; found: C 31.51, H 5.06, N 1.63.

Method B: As *Method A*, but with $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (0.44 g, 0.8 mmol) as source of Ce. The resulting mixture was filtered and the filtrate allowed to evaporate slowly at r.t. Brown plates of the MeCN solvate, isomorphous to **4**, were obtained directly after 24 h.

$[Ce^{IV}_8Ce^{III}Mn^{III}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_3(\mu_3\text{-}OH)_2(\mu\text{-}OH)(bdea)_4(O_2C^tBu)_{9.5}(NO_3)_{3.5}(OAc)_2] \cdot 1.5\,MeCN$ (**5**). *Method A:* To a stirred slurry of $[Mn(OAc)_2] \cdot 4\,H_2O$ (0.025 g, 0.1 mmol), $[Fe_3(O)(^tBuCO_2H)_6]O_2C^tBu$ (0.7 g, 0.7 mmol), and $Ce(NO_3)_2 \cdot 6\,H_2O$ (0.35 g, 0.8 mmol) in MeCN was added dropwise a soln. of H_2bdea (0.32 g, 2 mmol) in MeCN (5 ml). The resulting dark brown soln. was stirred at r.t. for an additional 2 h, filtered, and allowed to evaporate slowly. Orange triangular blocks were obtained after one week: **5** (32%, based on Mn).

Method B: To a stirred slurry of $[Mn(OAc)_2] \cdot 4\,H_2O$ (0.025 g, 0.1 mmol), pivalic acid (0.071 g, 0.7 mmol), and $Ce(NO_3)_2 \cdot 6\,H_2O$ (0.35 g, 0.8 mmol) in MeCN was added dropwise a soln. of H_2bdea (0.32 g, 2 mmol) in MeCN (5 ml). The resulting dark brown soln. was stirred at r.t. for an additional 2 h, filtered, and allowed to evaporate slowly. Orange triangular blocks were obtained after 48 h: **5** (25%, based on Mn). IR: 3612*w*, 3111*w*, 2957*s*, 2931*s*, 1588v*s*, 1568v*s*, 1480v*s*, 1457*w*, 1400v*s*, 1367*s*, 1355*s*, 1305*w*, 1261*w*, 1223*s*, 1091*s*, 1034*w*, 992*w*, 812*w*, 771*w*, 617*m*, 577*m*, 539*w*, 512*w*, 474*m*, 454*w*. Anal. calc. for $C_{83.5}H_{160.5}Ce_9MnN_{7.5}O_{50.5} \cdot 0.5\,MeCN$ (3414.20): C 29.72, H 4.78, N 3.28; found: C 29.81, H 5.05, N 3.43.

$[Ce^{IV}_4Mn^{IV}_2(\mu_3\text{-}O)_4(bdea)_2(O_2C^tBu)_{10}(NO_3)_2] \cdot 4\,MeCN$ (**6**). To a stirred slurry of $[Mn(OAc)_2] \cdot 4\,H_2O$ (0.025 g, 0.1 mmol), pivalic acid (0.071 g, 0.7 mmol), and $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (0.44 g, 0.8 mmol) in MeCN was added dropwise a soln. of H_2bdea (0.32 g, 2 mmol) in MeCN (5 ml). The resulting dark brown soln. was stirred at r.t. for an additional 2 h, filtered, and allowed to evaporate slowly. Orange triangular blocks were obtained after 48 h: **6** (30%, based on Mn). IR: 3602*w*, 3117*w*, 2942*s*, 2931*s*, 1593v*s*, 1567v*s*, 1478v*s*, 1456*w*, 1406v*s*, 1365*s*, 1351*s*, 1308*w*, 1263*w*, 1224*s*, 1089*s*, 1034*w*, 994*w*, 810*w*, 773*w*, 615*m*, 577*m*, 540*w*, 513*w*, 475*m*, 452*w*. Anal. calc. for $C_{66}H_{124}Ce_4Mn_2N_4O_{34} \cdot 2\,MeCN$ (2270.14): C 37.03, H 5.77, N 3.70; found: C 36.81, H 6.05, N 3.53.

[$Ce^{IV}{}_3Mn^{IV}{}_4Mn^{III}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_7(O_2C^tBu)_{12}(NO_3)(C_4H_4O)]\cdot 6\ H_2O$ (**7** · 6 H_2O). A stirred slurry of $[Mn_6(O)_2(O_2C^tBu)_{10}(4\text{-Me-py})_{2.5}(^tBuCO_2H)_{1.5}]$ (0.20 g, 0.11 mmol) in MeCN (10 ml) was heated to 70°, then $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (0.27 g, 0.50 mmol) and furoic acid (C_4H_3OCOOH; 0.11 g, 1.00 mmol) were added in small portions, resulting in a dark-brown soln. after 20 min. After stirring under reflux for additional 30 min, the soln. was filtered, and concentrated by slow evaporation to give dark-brown crystals after 4 d. These crystals were collected by filtration, washed with MeCN, and dried in air: **7** · 6 H_2O (24%). IR: 3154*w*, 2965*s*, 2930*m*, 2905*m*, 1570*s*, 1531v*s*, 1482v*s*, 1458*s*, 1410v*s*, 1373v*s*, 1355v*s*, 1224v*s*, 1176*w*, 1115*w*, 1086*w*, 1031*w*, 1013*w*, 902*m*, 785*m*, 739*w*, 619v*s*, 583*s*, 561*m*, 543*m*, 499*m*, 450*w*. Anal. calc. for $C_{64}H_{124}Ce_3Mn_5NO_{43}$ (2290.69): C 33.59, H 5.37, N 0.61; found: C 33.39, H 5.10, N 1.03.

X-Ray Crystallography[1]). Data were collected at 100 K with a *Bruker-SMART-Apex-CCD* diffractometer (for **1**–**6**) or a *Stoe-IPDS-II* area-detector diffractometer (for **7**), and were corrected semi-empirically [42][43] for absorption. Structure solution by direct methods and full-matrix least-squares refinement against F^2 (all data) were carried out with SHELXTL [42]. All ordered non-H-atoms were refined anisotropically. Many ligand *tert*-Bu groups showed rotational disorder and were refined with partial-occupancy Me groups. Geometrical and similarity (for thermal parameters) restraints were used as necessary within such disordered groups. O–H Bond lengths were restrained. In the structures of **2** and **3**, some or all the disordered MeCN molecules in the lattice could not be refined, and were handled with the SQUEEZE option in PLATON [44].

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1) CCDC 732222–732228 contain the supplementary crystallographic data for **1**–**7**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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