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Assembling Process of Charged Nonanuclear Cationic Lanthanide(III) Clusters Assisted by Dichromium Decacarbonyl Hydride

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The reaction of $Ln(acac)_3 \cdot 3H_2O$ (Ln = Sm, Eu, Gd, Dy, Yb) with $K[Cr_2(CO)_{10}(\mu\text{-}H)]$ at different molar ratios and solvents leads to the formation of nonanuclear lanthanide hydroxo acetylacetonate complexes of general formula $[Ln_9(OH)_{10}(acac)_{16}][HCr_2(CO)_{10}]$. The compounds are isomorphous, and the common cationic cluster core consists of a novel square antiprismatic arrangement of nine Ln atoms connected by μ_3, μ_4 hydroxo bridges and/or by acetylacetonate ligands as it results from the single-crystal X-ray analysis of the Sm derivative for which the most suitable crystals were obtained.

Interest in the synthesis and characterization of new materials with molecular dimensions in the nanometer scale has arisen for their potential applications in the electronic, catalytic, magnetic, and optical domains, characteristic of their dimensions.[1−5] Lanthanide clusters are subjected to deep investigation because they exhibit promising magnetic properties as a consequence of the unique spectroscopic and electronic characteristics associated with their $4f^n$ electronic configuration.[6] Manipulation of the cluster metal composition may give rise to a tunable behavior arising from their intra- and intercluster metal−metal interactions with consequent variation of their physicochemical properties as, for example, luminescence lifetimes for time-resolved luminescence spectroscopy for terbium(III) and europium(III) nanoclusters[7] and electron relaxation devices for the gadolinium nanoclusters based on water proton relaxation effects for magnetic resonance imaging applications.[8,9] Up to now very few examples of systematic synthesis of lanthanide−oxygen clusters can be found in the literature,[10,11] while most of these compounds are obtained by unexpected routes.[12] Polynuclear lanthanide complexes have been prepared by lanthanide hydrolysis controlled by different amino acids. These processes gave, in the case of glycine, alanine, or valine, the $[Ln_4(\mu_3OH)_4]^{8+}$ complexes of cubane-like structure, while with tyrosine pentadecanuclear lanthanide hydroxo complexes $[Ln_{15}(\mu_3OH)_{20}(\mu_5Cl)]^{24+}$ have been obtained.[10] The cubane-like structure is maintained in the “five vertex-sharing” $[Ln_4(\mu_3OH)_4]^{8+}$ unit glued by one μ_5Cl ion. This indicated that the anionic species in the cationic mixture can influence the nature of the resulting complex. Transmetalation of potassium *o*-nitrophenolate with anhydrous erbium or ytterbium trichloride in THF leads to tetradecanuclear clusters of general formula $[Ln_{14}(o\text{-}O_2NC_6H_4O)_{24}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}]$.[11] On the other hand particular attention has been paid, in these last years, also to the isolation of heteronuclear compounds produced by reaction of lanthanide complexes with transition metal carbonyls for applications of such systems in selective catalytic processes.[13] With the aim to provide new heteronuclear chromium carbonyl lanthanide

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[||] M.D.G. passed away on April 29, 2003. This paper is dedicated to her memory.

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complexes we have studied the reaction of the lanthanide tris-2,4-pentadionates, $Ln(acac)_3 \cdot 3H_2O$ (Ln = Sm, Eu, Gd, Dy and Yb), with the dichromium decacarbonyl hydride, $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$, where dichromium decacarbonyl hydride should act as reducing agent by oxidation of the hydridic hydrogen.[14] This system evidenced the formation, under mild conditions, of a series of polynuclear compounds as prevalent reaction products of general formula $[Ln_9(acac)_{16}(OH)_{10}]^+$ $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ (Ln = Sm **(1a)**, Eu **(1b)**, Gd **(1c)**, Dy **(1d)**, Yb **(1e)**) as deduced by X-ray analysis and chemical data (see below).

1a−**e** were shown to be the main products of the $K[Cr_2(CO)_{10}(\mu\text{-}H)]{:}Ln(acac)_3 \cdot 3H_2O$ reaction carried out under different conditions involving reactant molar ratios from 0.5:1 to 3:1, reaction solvents such as EtOH, THF, or Me_2CO, temperatures from 25 to 55 °C, and reaction times from 3 to 12 h. By reaction in EtOH, **1a**−**e** separated as crystalline yellow solids in variable but good yields, mainly depending on temperature and reaction times. The products are very soluble in CH_2Cl_2 or $CHCl_3$, soluble in THF and Me_2CO, slightly soluble in MeOH or EtOH, and insoluble in Et_2O and water. Well-dried solid samples of **1a**−**e** are moderately air stable, and can be stored under N_2 for several days without appreciable decomposition, whereas their solutions are instead very air sensitive.

FTIR spectra in Nujol mull of **1a**−**e** show three sharp bands in the ν(CO) region at 2030 (m), 1940 (vs), 1868 (s) cm^{-1} characteristic of the square pyramidal (C_{4v}) arrangement of the $M(CO)_5$ carbonyl groups..[15] In the 3800−3200 cm^{-1} region, a hydroxo sharp band at 3576 cm^{-1} that has been attributed to the stretching mode of μ_3OH[16] is accompanied by a broad peak, in the apparent range of the OH stretching bands of water (3350 cm^{-1}), whereas the coordinated β-diketonate ligand exhibits splittings and shifts as well as intensity changes in the 1650−400 cm^{-1} region.

Of the isolated complexes the samarium derivative **1a** provided the most suitable crystals for a single-crystal X-ray analysis. The representative Sm complex can be formulated as $[Sm_9(acac)_{16}(OH)_{10}][Cr_2(CO)_{10}(\mu\text{-}H)]$ according to the crystallographic results presented here.[17] The molecular structure of the Sm cluster in the form of two independent barrels with crystallographic binary symmetry is shown in Figure 1.

The barrels are oriented perpendicularly to each other. Each barrel contains nine Sm(III) ions and sixteen acetylacetonate ligands in addition to 10 hydroxo ligands, and the space between barrels is filled by the $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ anions. The barrels contain two alternative positions of the atoms in the cluster: one is predominant with an occupancy factor of 70%, and the second is rotated about 45° with respect to the axis passing through the central samarium and the oxygens of the μ_4OH moieties as is shown in Figure 2, where only the samarium alternative positions are reported.

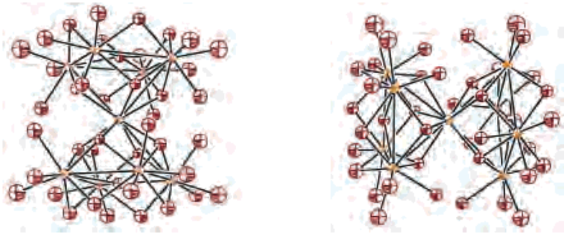

Figure 1. Molecular structure representation of the two samarium clusters (only the coordinated atoms are given: yellow, samarium; red, oxygen).

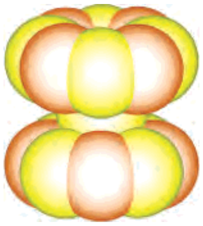

Figure 2. Space-filling representation of the samarium alternative positions (yellow 70%, orange 30% occupancies).

In the main structure the central Sm (which is common to the two alternative positions) has at the top of the barrel four Sm ions in an antiprismatic arrangement with respect to the four of the bottom (a reversed antiprism is formed by the alternative Sm positions). Eight hydroxo groups that also occupy the vertices of a square antiprism form a μ_3OH glue between each samarium on the cylindrical part of the barrel while the top and the bottom are characterized by a μ_4OH group on each side connecting the four samarium ions residing in the two opposite lids of the barrel. Eight acetylacetonate ligands beside the μ_4OH groups represent the connection between the four samarium ions acting as bridging-chelating ligands at the top and at the bottom of the barrel while the remaining eight are chelating on each single samarium ion (Figure 3).

The coordination number of these samarium ions is still eight, but the geometry is not assignable to a well-defined polyhedron (Figure 4).

Then we can envisage two different Sm coordination geometries, one regular square antiprismatic, where the central metal ion is bonded to eight μ_3OH groups with a range of Sm−O bond distances from 2.46(1) to 2.49(1) Å, and the second dealing with the peripheral Sm ions of

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(17) Crystal structure analysis of $C_{90}H_{123}O_{52}Cr_2Sm_9$, $M = 3494$: crystal size, 0.2 × 0.2 × 0.3 mm; monoclinic, space group C_2, $a = 26.303(2)$ Å, $b = 30.602(2)$ Å, $c = 20.151(1)$ Å, $\beta = 130.672(2)°$, $V = 12302(1)$ Å^3, $Z = 4$; $\rho_{calc} = 1.886$ Mg/m^3; $T = 293$ K; $\mu = 4.37$ mm^{-1}. (The alternative tetragonal cell $a = b = 21.627(1)$ Å, $c = 26.303(2)$ Å obtained with the transformation matrix 0.5,−0.5,1; 0.5,0.5,1; −1,0,0 space group $I\bar{4}c2$ gave worse results in the refinement; therefore the monoclinic cell here reported has been adopted.) A total of 56186 reflections of which 21628 are independent ($R_{int} = 0.0838$) were collected on a Bruker-Axs SMART-CCD detector diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (Sir 92: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Gagliardi A. and Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined by full-matrix least squares on F^2 using the SHELXTL/PC package (*Siemens SHELXTLplus Version 5.1 (Windows NT version) Structure Determination Package*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1998). $R = 0.0565$ (on 15894 reflections with $I > 2\sigma(I)$, 1123 parameters), wR2 (all data) = 0.1467; GOF = 1.02; maximum electron density = 1.05.

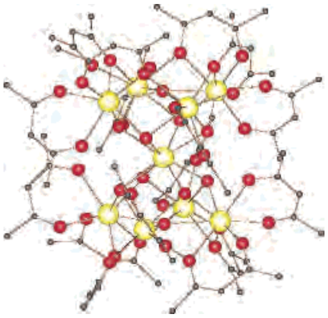

Figure 3. General view of a barrel composed of the acetylacetonate ligands (light black lines).

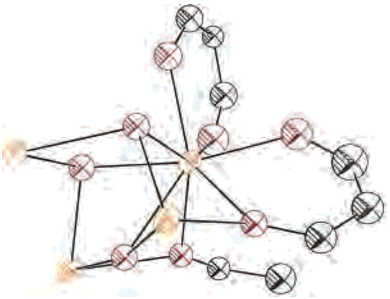

Figure 4. Coordination geometry of samarium in the barrel side position.

irregular geometry, due to the coordination of eight oxygen donor atoms belonging to the different ligands as acetylacetonate, μ_3OH, and μ_4OH.

The range of Sm−oxygen bond distances in the latter is represented by the values 2.33(1)−2.42(1) Å for the chelating acetylacetonate, 2.46(1)−2.48(1) for the chelating bridging acetylacetonate, 2.35(1)−2.37(1) Å for μ_3OH, and 2.63(1)−2.65(1) Å for μ_4OH. In the square antiprismatic geometry Sm1 and Sm2 have contact distances with eight neighboring Sm of about 3.8 Å, while Sm3, presenting irregular coordination geometry, has contact distances with only two other Sm of the order of 3.7 Å. The shorter intercluster distance Sm−Sm is 13.15 Å.

The dinuclear anion $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ is characterized by a bent Cr−H−Cr structure with the carbonyl groups in staggered positions. The nonlinear Cr−H−Cr hydride bond is suggested by the characteristic short Cr−Cr distance 3.28(1) Å (the H position was not detected), according to a neutron diffraction study where the Cr−Cr distance was 3.30 Å[18] and to previous X-ray results.[19]

The ^{1}H NMR spectra of **1a**−**e** in CD_3Cl show a signal around −20 ppm confirming the presence of the hydride species.

All operations were performed under a nitrogen atmosphere. The solvents and $Ln(acac)_3\cdot 3H_2O$ (Ln = Sm, Eu, Gd, Dy, Yb) were reagent grade (Strem, C. Erba, Fluka, Merck) and were used as received. $K[HCr_2(CO)_{10}]$ has been prepared by our published procedure.[20] The identity and purity of the isolated products were checked by analytical determinations: complexometric titration of Ln with EDTA using xylenol orange as indicator, atomic absorption spectroscopy for Cr, and gas-volumetric analysis of CO in samples decomposed by interaction with iodine in EtOH solutions.

Synthesis of **1a** (compounds **1b**−**e** were synthesized by the same procedure): A solution of $Sm(acac)_3\cdot 3H_2O$ (0.50 g, 1 mmol) in EtOH (30 mL) was slowly added to a stirred yellow solution of $K[Cr_2(CO)_{10}(\mu\text{-}H)]$ (1.27 g, 3 mmol) in EtOH (30 mL) at room temperature. From the resulting solution, some yellow crystalline solid soon separated. The stirred mixture was rapidly warmed to 45 °C, stirred at 45−47 °C for 5 h, and then to room temperature for 24 h. The yellow crystalline product separated and was collected by filtration and washed with EtOH (up to colorless filtrate, 3 × 3 mL), in which any nonreacted $K[HCr_2(CO)_{10}]$ or $Sm(acac)_3\cdot 3H_2O$ is very soluble.

The product was then well-dried under high vacuum. Usual yields: 68−72% (based on Sm). It was recrystallized at room temperature from 2:1 v/v $CHCl_3$/toluene mixture (75% yield).[21]

In summary, the present work has shown that the ease of lanthanide ion hydrolysis and consequently the tendency of the hydroxo species to form polynuclear complexes are in this case induced and controlled by a novel system: the dichromium decacarbonyl hydride. The square antiprismatic Sm clusters represent a new assembling process in lanthanide coordination compounds.

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Supporting Information Available: Crystallographic file in CIF format for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] Anal. Calcd for $Sm_9Cr_2C_{90}H_{123}O_{52}$: Sm 38.73, Cr 2.97, C 30.93, H 3.55, CO 8.01. Found: Sm 38.55, Cr 2.93, C 29.91, H 3.04, CO 7.97.