3802 *Inorg. Chem.* **1997,** *36,* 3802−3803

Communications

The New Octanuclear Europium Cluster $Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2$ Comprising Oxo, Hydroxo, and Polyselenido Ligands

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Received April 4, 1997

For both fundamental and technological reasons, interest in polychalcogenometalates has increased markedly in the last decade.[1−6] Whereas the softer, heavier chalcogens (Se and Te) form stable compounds with the equally soft later transition metals, they tend to form less stable compounds with the harder early transition and f-block metals. Indeed, few polychalcogenometalates involving these metals have been synthesized and isolated.

The first molecular species containing Ln−Q (Ln = rare earth; Q = Se and Te) bonds also contains pentamethylcyclopentadienyl rings[7] for electronic and steric stabilization. Soon after, bulky groups[8,9] and simple alkyl groups[10−13] were used as stabilizers of these highly reactive bonds. The oxophilicity of the rare-earth elements and the stability of their compounds in polar, oxygen-containing solvents leaves them unreactive toward the polychalcogenide solutions. In fact, there are no examples of homoleptic chalcogenolanthanate species isolated from solution.[14] However, this same oxophilicity has opened a new area of polychalcogenohydroxolanthanate clusters, as we demonstrate here with the synthesis and structure of the first such cluster $Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2$ (DMF = *N*,*N*-dimethylformamide).

The title compound was prepared in the following manner. A red-brown solution of nominally K_2Se_4 was generated by adding 56 mg (0.36 mmol) of K_2Se and 85 mg (1.1 mmol) of Se to 8 mL of DMF; the solution was stirred for 24 h. $EuCl_3$ (46 mg, 0.18 mmol) was dissolved in 8 mL of tetrahydrofuran with stirring. This solution was added to the polyselenide solution. The resultant solution was stirred for 16 h, was filtered through a fine glass frit, and was then layered with 15 mL of diethyl ether. Bright red rectangular plates of $Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2$ were manually isolated[15] after 1 week. The crystals are extremely air and water sensitive.

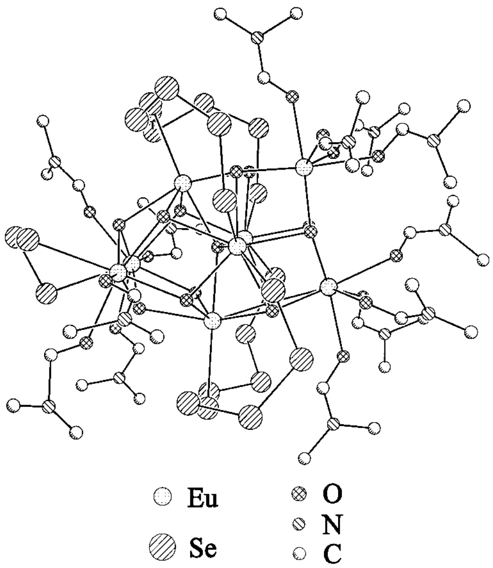

Figure 1. Structural connectivity in $Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2$.

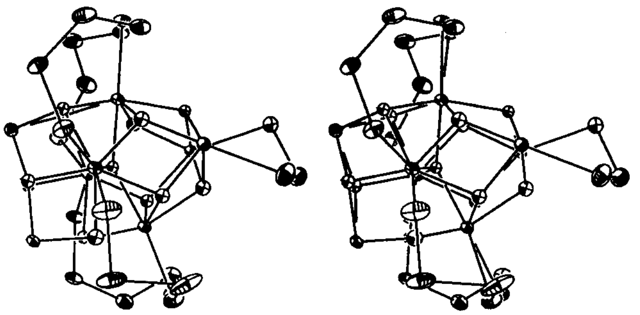

Figure 2. Stereoview of $Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2$. The hydrogen atoms and the coordinated DMF molecules have been removed for clarity. Displacement ellipsoids are drawn at the 30% probability level.

The molecular structure of $Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2$[16] consists of a Eu_8 polyhedron centered by an oxygen atom (Figures 1 and 2). The oxygen atom lies 0.07 Å from the geometrical center of the polyhedron. This polyhedron may be described as a bicapped octahedron or a triangulated dodecahedron. Each of the 12 faces formed by the triangulated dodecahedral core of Eu atoms is capped by a μ_3-hydroxo group.[17] Two Se_5 chains, two Se_4 chains, and one Se_3 chain connect Eu atoms.[18] Thirteen DMF molecules fill the remainder of the Eu coordination spheres. The resultant coordination

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(14) Nor are there examples of homoleptic chalcogenoactinate species isolated from solution, but in the solid state K_4USe_8 comprises isolated K^+ and $[U(Se_2)_4]^{4-}$ ions.[36]
(15) EDAX measurements on a scanning electron microscope gave consistent Eu/Se ratios of about 8:21 on several crystals.

S0020-1669(97)00379-0 CCC: $14.00

numbers are 8 for all but one, which has a coordination number of 7. An alternative and useful description of the cluster geometry comprises a Eu_4 butterfly sandwiched between two perpendicular Eu_2 dimers. The central oxygen atom is bonded to the four atoms of the Eu_4 butterfly. This structure is also seen in the boron closo clusters $B_8H_8^{2-}$ and B_8Cl_8,[19,20] although the boranes have no interstitial atom. Two Se_4 and two Se_5 rings alternate around the centered butterfly to connect adjacent Eu atoms while the Se_3 ring connects the Eu atoms of one of the dimers. DMF molecules are attached to Eu atoms in the following way: two and three to the two atoms respectively of the Se_3 bridged dimer, four to each of the Eu atoms in the other dimer. The hydroxo groups cap the faces of the Eu core. $Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2$ contains two sets of Eu−Eu interactions: four (all in the butterfly) in the range 3.47−3.51 Å and the rest in the range 3.78−3.97 Å. All Eu-Eu interactions are well out of bonding range. The average Eu−OH bond is 2.40(6) Å, the average Eu−O (DMF) bond is 2.41(6) Å, and the average Eu−O(center) bond is 2.36 Å, comparable to other such Eu−O bonds.[21−23]

Whereas triangulated dodecahedral clusters exist for a variety of elements with and without centered atoms,[24−26] centered clusters of this type comprising main-group elements are rare. Such clusters necessarily display two different interactions between the central atom and those of the outer skeleton. These commonly differ by about 15% as, for example, in the boron clusters. In the present instance the difference is greater, 2.36 Å vs 3.74 Å. Although no other examples exist of a face-capped triangulated dodecahedron, the present structure bears a resemblance to those of the rare-earth basic nitrate clusters, such as $\{[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{12}(NO_3)_6](NO_3)_2\}\cdot xH_2O$ (Ln = Y, Gd, Yb),[21] in which there is an octahedral arrangement of Ln atoms with hydroxo groups capping the eight faces.[27]

Although the low yield (<10%) of $Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2$ has thus far precluded any bulk analyses, it is copacetic if one considers the lack of an innocent oxygen source in the synthesis. Examples exist of hard Lewis acids reacting with tetrahydrofuran[28,29] to afford oxides and alkoxides. In addition, DMF, though stored over 4 Å sieves, can contain a measurable amount of water. However, in a series of experiments, specially dried DMF was substituted for tetrahydrofuran and toluene (freshly distilled from Na) was substituted for diethyl ether during layering. This change in procedure did not cause a noticeable change in products. However, the $EuCl_3$, which was purchased from Strem Chemicals, Inc. and used promptly without purification, was found to contain 0.17 H_2O molecules per $EuCl_3$ unit.[30] This amount leads to a maximum theoretical yield based on Eu content of 10.5%. The subtle, often serendipitous, inclusion of oxygen from innocent sources is not uncommon and has led to a multitude of novel chemical structures.[31−35]

Preliminary results indicate that the octanuclear structure of $Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2$ persists throughout the lanthanides.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE95-31232).

Supporting Information Available: Tables providing further crystallographic details, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates (22 pages). Ordering information is given on any current masthead page.

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(16) Crystal data for $Eu_8(DMF)_{13}(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(Se_3)(Se_4)_2(Se_5)_2$: $C_{39}H_{103}Eu_8N_{13}O_{26}Se_{21}$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 14.405(3)$ Å, $b = 24.540(5)$ Å, $c = 29.102(6)$ Å, $\beta = 101.08(3)$, $V = 10096$ Å^3 at 106(2) K. Data were collected from a crystal of dimensions 0.34 mm × 0.10 mm × 0.02 mm in ω scan mode on a CAD4 diffractometer out to θ(Cu Kα) = 46°. The final model was restricted to anisotropic displacement parameters for Eu and Se atoms only in order to maintain a reasonable observation-to-parameter ratio. It converged to $R_w(F^2) = 0.180$ for 7192 observations and 586 variables and to $R(F)$ of 0.102 for those 4534 reflections having $F_o^2 > 2\sigma(F_o^2)$.

(17) The presence of hydroxo as opposed to oxo capping groups is inferred from considerations of charge balance. In the absence of Eu−Eu bonds, an oxidation state of +III has been assumed for Eu.

(18) One Se_4 chain is disordered; two Se atoms are distributed over three sites. This disorder is not shown in the figures. Crystallographic results on an isostructural Gd cluster have resolved the disorder in this Se_4 chain.

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