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A Topological Link between Lanthanide and Alkali-Metal Clusters: Face-Sharing Gadolinium Octahedra Centered by Endohedral Iridium Atoms in $\{Ir_3Gd_{11}\}Br_{15}$

Matthias Brühmann[a] **and Gerd Meyer***[a]

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The oligomeric cluster complex $\{Ir_3Gd_{11}\}Br_{15}$ was first obtained from a reaction of Gd, $GdBr_3$ and Ir in a 3:4:1 molar ratio at 1123 K. The crystals belong to the hexagonal space group $P6_3/m$ with lattice parameters a = 1276.79(14) pm and c = 1286.92(16) pm. The structure features isolated $\{Ir_3Gd_{11}\}$ cluster trimers, which are built up by three face-sharing gadolinium octahedra each centered by an iridium atom. The endohedral iridium atoms form a triangle with Ir–Ir distances of 295.51(11) pm. Thus, the $\{Ir_3Gd_{11}\}$ cluster is topologically equivalent to the suboxide $\{O_3Cs_{11}\}$. The $\{Ir_3Gd_{11}\}$ clusters are encapsulated in a coordination sphere of 30 bromide ions, which act as bridging ligands according to the formulation $\{Ir_3Gd_{11}\}Br^{i-i}{}_{12/2}Br^{i-a}{}_{9/2}Br^{a-i}{}_{9/2}$. In $\{Ir_3Gd_{11}\}Br_{15}$ there are 45 electrons present for intracluster bonding.

Introduction

Octahedral clusters $\{\square R_6\}$ were first recognized for a rare-earth metal halide within the gadolinium sesquichloride[1] forty years ago. Since then the chemistry of reduced rare-earth metal halides has steadily grown and appears to be by no means at an end.

Whereas in Gd_2Cl_3 the octahedral clusters are empty and connected by common *trans* edges and surrounded by chlorido ligands resembling the $\{M_6\}X^{i3}{}_8$-type clusters, almost all of the now known octahedral clusters may be derived from the $\{M_6\}X^{i2}{}_{12}$ type (with i2 = μ_2; i3 = μ_3; a = μ_1).[2] All rare-earth-metal cluster complexes derived from the latter type are centered by a main-group-element atom like B, N, C (or C_2 dumbbells) and, even more frequently, by a transition-metal atom, which contribute to the overall electron count. There are a few cluster complexes that contain isolated clusters as in $\{NSc_6\}Cl_{12}Sc$;[3] the vast majority contains "condensed clusters",[4] as for example edge-connected chains as in $\{CY_4\}I_5$.[5] Oligomeric clusters are also rare; the first dimer detected was $\{(C_2)_2Gd_{10}\}Cl_{18}$ with two octahedral clusters sharing one common edge.[6] Trimers as in $\{(C_2)_3R_{14}\}I_{20}$ (R = La, Ce, Pr)[7] or tetramers as in $\{B_4Tb_{16}\}Br_{23}$[8] and $\{Ru_4Y_{16}\}I_{20}$[9] are also known, but all of them contain edge-connected clusters.

Face-sharing of octahedral rare-earth metal clusters is not known so far, in contrast to the increasing number of monocapped trigonal-prismatic or square-(anti-)prismatic clusters that share common faces resulting in chains, as in $\{RuPr_3\}Cl_3$[10] (seven-coordinate endohedral ruthenium atom) or in $\{OsY_4\}Br_4$[11] and the higher symmetric $\{ReGd_4\}Br_4$[12] as well as $\{Ir_3Sc_{12}\}Br_{16}$,[12] all with eight-coordinate endohedral atoms (Re, Os, Ir).

During attempts to further broaden our knowledge on transition-metal/rare-earth-metal/halide cluster complexes, Z/R/X, we have now observed the first face-sharing trimeric cluster for the example of $\{Ir_3Gd_{11}\}Br_{15}$.[13]

Results and Discussion

In the crystal structure of $\{Ir_3Gd_{11}\}Br_{15}$,[14] there are three iridium-centered gadolinium octahedra connected by common triangular faces to the trimeric cluster $\{Ir_3Gd_{11}\}$ (Figure 1), which has the same topology as is present in solid cesium suboxide $\{O_3Cs_{11}\}$.[16] There are, of course, important differences between the $\{O_3Cs_{11}\}$ and $\{Ir_3Gd_{11}\}$

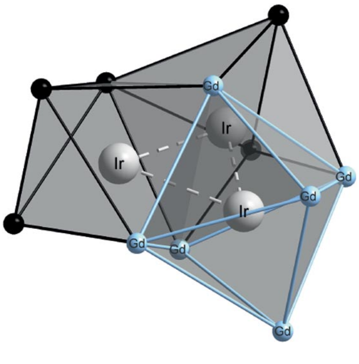

Figure 1. Trimeric $\{Ir_3Gd_{11}\}$ cluster as observed in the crystal structure of $\{Ir_3Gd_{11}\}Br_{15}$.

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[a] Department für Chemie, Institut für Anorganische Chemie, Universität zu Köln,
Greinstraße 6, 50939 Köln, Germany
Fax: +49-221-470-5083
E-mail: gerd.meyer@uni-koeln.de
Homepage: http://www.gerdmeyer.de

clusters, most importantly the repulsion between the oxygen atoms (or better: oxide ions) in the former and some, although not much, bonding attraction between the Ir atoms in the latter.

The Ir_3 triangle in $\{Ir_3Gd_{11}\}Br_{15}$ is even-sided with Ir–Ir distances of 295.51(11) pm. This will not be considered a bonding distance, in the sense of a two-center–two-electron bond, although it is close to the Ir–Ir distance of 283.28(11) pm in $\{Ir_3Sc_{12}\}Br_{16}$,[12] which, in this special case, has been considered a two-electron bonding distance for the following reason: For $\{Ir_3Sc_{12}\}Br_{16}$ we count 47 cluster-based electrons per formula unit; if two electrons are involved in one Ir–Ir bond, there are 45 electrons left for mostly Ir–Sc bonding. For $\{Ir_3Gd_{11}\}Br_{15}$ we count that same number of 45 electrons per formula unit, or 15 when scaled per endohedral iridium atom. All Ir–Gd distances are shorter than the Ir–Ir contacts (see Table 1) and much shorter than Gd–Gd distances, although these are all in the ranges usually observed in these clusters.

Table 1. Selected distances for $\{Ir_3Gd_{11}\}Br_{15}$ in pm.

Ir–Ir	295.51(11)
Ir–Gd	271.64(8)–287.07(11), <d> = 278.9
Gd–Gd	366.34(13)–444.63(16), <d> = 392.3 pm
Gd–Br	287.50(16)–357.6(3), <d> = 310.1

The $\{Ir_3Gd_{11}\}$ clusters are surrounded by a total of 30 bromido ligands with Gd–Br distances ranging from 287.5 to 357.6 pm with an average of 310.1 pm, which is quite consistent with Gd–Br distances ranging from 297.1 to 313.8 pm with an average of 307.3 pm in $\{ReGd_4\}Br_4$.[12] All of the bromido ligands bridge to neighbouring cluster complexes, as attested by the formulation $\{Ir_3Gd_{11}\}Br^{i–i}_{12/2}Br^{i–a}_{9/2}Br^{a–i}_{9/2}$. Figure 2 exhibits how one cluster complex is connected to surrounding clusters. As $\{Ir_3Gd_{11}\}Br_{15}$ crystallizes in the hexagonal space group *P*6_3/*m*, the crystal structure may also be classified as being built in the fashion of a hexagonal closest packing of $\{Ir_3Gd_{11}\}$ clusters.

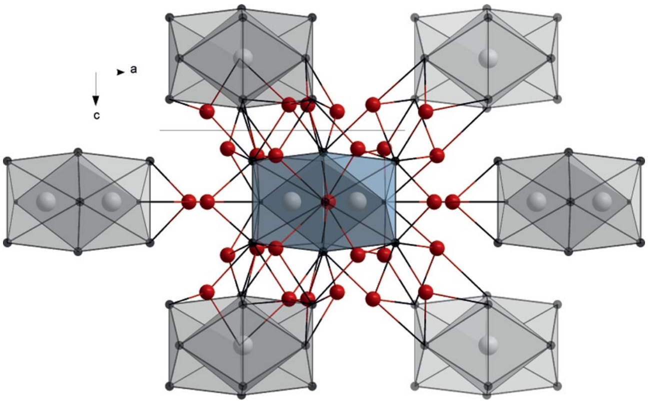

Figure 2. Connection of one $\{Ir_3Gd_{11}\}Br_{30}$ cluster complex with its neighbours, expressed by the formulation $\{Ir_3Gd_{11}\}Br^{i–i}_{12/2}Br^{i–a}_{9/2}Br^{a–i}_{9/2}$.

Conclusions

We have observed in the Ir/Gd/Br system a trimeric cluster $\{Ir_3Gd_{11}\}$ composed of three $IrGd_6$ octahedra sharing common faces. The clusters are packed in the fashion of a hexagonal closest packing and embedded in a surrounding of 30 bromido ligands, which connect these cluster complexes by i-i, i-a and a-i bridges, respectively, in accord with the formulation $\{Ir_3Gd_{11}\}Br^{i–i}_{12/2}Br^{i–a}_{9/2}Br^{a–i}_{9/2}$. A dimeric cluster of face-sharing octahedra as observed in rubidium suboxides, $\{O_2Rb_9\}$,[17] has yet to be detected in rare-earth-metal cluster chemistry.

Experimental Section

Starting materials for the synthesis of $\{Ir_3Gd_{11}\}Br_{15}$ were turnings of Gd metal (Chempur, Karlsruhe, Germany, 99.9%) and Ir powder (Chempur, Karlsruhe, Germany, 99.9%), which were both used as purchased. $GdBr_3$ was synthesized according to the ammonium bromide route and purified as described previously.[18] A molar ratio of 3:1:4 (Gd/Ir/$GdBr_3$, typically 59.4 mg/24.2 mg/200 mg) was applied and the reaction was carried out in an He-arc-welded tantalum container by using the following temperature program: Heat to 1223 K, slowly cool to 1123 K, anneal at this temperature for 13 d, cool with 2 K/h to 973 K and fast to room temperature (quench with ice/water). Reactions with stoichiometric amounts (6:3:5) of the starting materials produce $\{Ir_3Gd_{11}\}Br_{15}$ in much better yield. To prevent oxidation at elevated temperatures, the tantalum container was jacketed in an evacuated silica tube. All manipulations were carried out under strict exclusion of moisture and air under dry nitrogen in a glove-box (MBraun, Garching, Germany). $\{Ir_3Gd_{11}\}Br_{15}$ forms well-faceted, polygonal black crystals (see Figure 3). Minor impurities of GdOBr and unreacted $GdBr_3$ were present in the first reaction, as checked by sight under the microscope and by X-ray powder diffraction (Stadi P, Stoe, Darmstadt). GdOBr impurities are hard to avoid and are thought to originate from the reaction container or from the starting materials.

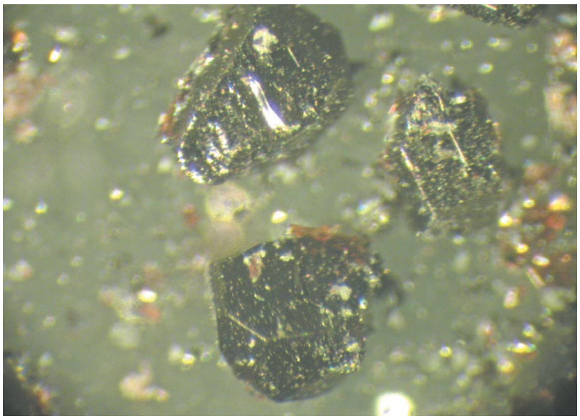

Figure 3. Microscopic view of a few well-facetted crystals of about 0.4 mm in diameter of $\{Ir_3Gd_{11}\}Br_{15}$ (courtesy of Dipl.-Chem. C. Rustige).

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[14] Single crystals of $\{Ir_3Gd_{11}\}Br_{15}$ suitable for X-ray diffraction were selected under a microscope in the dry box. They were inspected by Laue photographs (Mo-K_α radiation, image plate). The best specimen was transferred to a Stoe "Image Plate Diffraction System" (IPDS-II diffractometer, Stoe, Darmstadt, Germany). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data. The programs used in this work are Stoe's X-Area as well as SHELXS-97 and SHELXL-97 for structure solution and refinement.[15] The last cycles of refinement included atomic positions and anisotropic thermal parameters for all atoms. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-421569. $\{Ir_3Gd_{11}\}Br_{15}$: Hexagonal, space group $P6_3/m$ (No. 176); a = 1276.79(14) pm, c = 1286.92(16) pm, V = 1816.9(4) $\times 10^6$ pm^3; $Z = 2$; $1.84° < \theta < 27.32°$; Mo-K_α radiation (graphite monochromator, λ = 71.073 pm); T = 293(2) K; $F(000)$= 2919; μ = 47.180 mm^{-1}; 13338 reflections measured, 1431 unique, 1145 observed; R_{int} = 0.0866, $R1/wR2$ = 0.0367/0.0790 [$I_0 > 2\sigma(I_0)$] and 0.0497/0.0825 (all data); goodness-of-fit on F^2 = 0.998.

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