Isolated and Edge-Connected Tetramers $(\text{C}_2)_2\text{O}_2\text{Dy}_{14}$ in the Crystal Structures of $(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\text{I}_{24}$ and $(\text{C}_2)_2\text{O}_2\text{Dy}_{12}\text{I}_{18}$

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**Isolated and Edge-Connected Tetramers $\{(C_2)_{20}Dy_{14}\}$ in
the Crystal Structures of $\{(C_2)_{20}Dy_{14}\}I_{24}$ and
 $\{(C_2)_{20}Dy_{12}\}I_{18}$**

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Isolated and Edge-Connected Tetramers $\{(C_2)_2O_2Dy_{14}\}$ in the Crystal Structures of $\{(C_2)_2O_2Dy_{14}\}I_{24}$ and $\{(C_2)_2O_2Dy_{12}\}I_{18}$

Kathrin Daub^[a] and Gerd Meyer*^[a]

Dedicated to Professor Bernd Harbrecht on the Occasion of His 60th Birthday

Keywords: Dysprosium; Cluster complexes; Synthesis; Crystal Structure

$\{(C_2)_2O_2Dy_{14}\}I_{24}$ (**1**) and $\{(C_2)_2O_2Dy_{12}\}I_{18}$ (**2**) were obtained by solid state reactions in sealed tantalum containers at a temperature of 1000°C. $\{(C_2)_2O_2Dy_{14}\}I_{24}$ crystallizes in the space group P-1 with $a = 972.97(14)$ pm, $b = 1033.03(13)$ pm, $c = 1677.0(2)$ pm, $\alpha = 101.42(1)^\circ$, $\beta = 92.72(1)^\circ$, $\gamma = 112.75(1)^\circ$ and $V = 1509.3(3) \cdot 10^6$ pm³, $Z = 2$, and is isotypic with the analogous yttrium and erbium cluster complexes. The tetrameric $\{(C_2)_2O_2R_{14}\}I_{32}$ cluster complexes consist of corner-sharing tetrahedra with

endohedral oxygen atoms to which octahedra encapsulating C_2 dumbbells are attached on both sides. The tetramers are connected via iodide bridges yielding, e.g., $\{(C_2)_2O_2Dy_{14}\}I_{24}$. Connection of the tetramers via common cluster edges leads to the one-dimensional polymeric cluster complex $\{(C_2)_2O_2Dy_{12}\}I_{18}$. It crystallizes in the space group $P6/m$ with $a = 2024.18(8)$ pm, $c = 1299.21(4)$ pm, $V = 4610.1(3) \cdot 10^6$ pm³ and $Z = 8$.

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In our attempts to shed more light on the differences of the chemistry of reduced halides of the neighbouring elements dysprosium and holmium, we have also obtained two new iodides whose important structural feature are tetrameric clusters, $\{(C_2)_2O_2Dy_{14}\}$,^[7] on which we report here.

Results and Discussion

All cluster complex compounds of dysprosium hitherto reported contain dicarbon units encapsulated in octahedral clusters. The simplest example is $\{(C_2)Dy_6\}I_{12}Dy$ (see Fig. 1) which has 15 electrons for carbon—dysprosium bonding,^[7] a rather comfortable number for isolated cluster complexes.

Figure 1. Part of the crystal structure of $\{(C_2)Dy_6\}I_{12}Dy$ exhibiting the $\{(C_2)Dy_6\}I_{18}$ cluster and the seventh Dy atom residing in the third coordination sphere in an octahedron of iodide ions. The C_2 dumbbells are disordered and arranged along the (pseudo-)four-fold axes of the dysprosium octahedron.

Introduction

In oxidation states of less than +3, there are two types of lanthanide elements. One group behaves in oxidation state +2 as pseudo-alkaline-earth elements. The second group resembles the early transition elements with their ability to metal-to-metal bond as well as cluster formation.^[1] The reason for this behaviour is the possibility of a configuration crossover, from $[Xe]4f^n5d^06s^0$ to $[Xe]4f^{n-1}5d^16s^0$. The “large” 5d orbitals may delocalize or combine in covalent bonds or overlap with respective orbitals of endohedral atoms in clusters (“lanthanides as d metals”)^[2].

As its homologue praseodymium, with the electronic configuration, for Pr^{2+} , $4f^25d^1/4f^35d^0$, dysprosium is a borderline element, with $4f^95d^1/4f^{10}5d^0$ for Dy^{2+} . Experience shows that the electronic configuration $4f^25d^1$ is more important for Pr^{2+} and $4f^{10}5d^0$ for Dy^{2+} . This knowledge is based, for example, on the crystal structures and properties of PrI_2 ^[3] and DyI_2 ^[4]. Dysprosium(II) iodide crystallizes with the $CdCl_2$ -type of structure with an electronic structure which accounts for an $4f^{10}5d^0$ configuration.^[5] However, clusters have been mentioned, as for Dy_7I_{12} ^[6] which may as well have been $\{(C_2)Dy_6\}I_{12}Dy$ (for the nomenclature used here see ref. [1d]), a compound which has been obtained recently.^[7] Three other dysprosium cluster iodides have been reported, $\{(C_2)_2Dy_{10}\}I_{18}$ with dimeric cluster complexes as well as $\{(C_2)_3Dy_{12}\}I_{17}$ and $\{(C_2)Dy_4\}I_6$ with chains of edge-connected octahedral clusters.^[8] And there is just one bromide, $\{(C_2)_2Dy_{10}\}Br_{18}$,^[9] isostructural with the respective iodide just mentioned.

It was initially intended to synthesize dysprosium cluster complexes with transition metals as endohedral atoms, attempts which have completely failed. One next step was to secure cluster complexes with both carbon and transition metal atoms as interstitials, iron in the present case. Such a reaction yielded single crystals of $\{(C_2)_2O_2Dy_{12}\}I_{18}$ (**2**). Even though no oxygen source was used, as so often ubiquitous oxygen impurities originating

either from atmospheric impurities in the glove box or from contaminated reactants or the reaction containers. In further steps we have then added Dy_2O_3 to the reaction mixtures and obtained hetero-interstitial C_2/O cluster complexes in yields higher than 90%. In order to keep the reaction temperatures low and to grow crystals of better quality, we have used sodium iodide (m. p. 662°C) as a flux. However, reaction temperatures as high as 1000°C gave the best results.

$\{(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\}\text{I}_{24}$ (**1**) crystallizes with a structure that has already been reported for the yttrium and erbium analogues.^[10] This is insofar not surprising as dysprosium, yttrium and erbium have very similar sizes. It also shows that dysprosium which forms a rather stable diiodide, DyI_2 , is capable of forming clusters when the right endohedral atoms/atom groups are available. The crystal structure consists of isolated tetramers of the composition $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\}$ which are composed of two $\{\text{C}_2\text{Dy}_6\}$ octahedra O and two $\{\text{ODy}_4\}$ tetrahedra T, all sharing common edges in the sequence O—T—T—O, see Fig. 2.

Figure 2. $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\}\text{I}_{32}$ tetramers in the crystal structure of $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\}\text{I}_{24}$ and their connection via common iodide bridges.

The Dy-Dy bond lengths lie in the usual range with significantly shorter distances between dysprosium atoms building up the common edges, see Table 1. The bond lengths of the common octahedral/tetrahedral edge of 338.88(5) pm is only marginally shorter than the common edges between the tetrahedra, 339.75(4) pm. The outer Dy-Dy edge does obviously relax with $d = 351.36(5)$ pm. The other Dy-Dy edges of the tetrahedra average to 366.7 pm and those in the octahedra to 382.1 pm, except for the edges that are parallel to the tetramer which are about 348 pm long.

The C_2 dumbbell encapsulated in the octahedron has a C-C bond length of 141.06(2) pm, a value in a range that is often found for such compounds, see also ref. [10c]. The O-Dy bond lengths are between 216.90(3) and 222.73(4) pm and compare rather well with tetrahedra encapsulating an oxygen atom as for example in $\{\text{OLa}_4\}\text{Br}_7$ (240 pm) or $\{\text{OSm}_4\}\text{I}_6$ (241 pm).^[11]

The Dy-I distances all lie in a usual range from 295.44(6) to 333.04(4) pm except for those who are neighbouring the T—T condensation; these are much larger with 369.95(5) and 373.07(6) pm, respectively. The $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\}\text{I}_{32}$ tetramers are connected via I^i and I^a bridges to each other, established parallel to [100] and [001] according to the formulation $\{(\text{C}_2)\text{Dy}_4\text{Dy}_{2/2}\}_2\{\text{ODy}_{4/2}\}_2\text{I}_{16/1}^{i-i}$ $\text{I}_{8/2}^{i-a}\text{I}_{8/2}^{a-i}$, see Fig. 3. Connections between the so established layers which are stacked roughly in the [001] direction can only be of the van-der-Waals type.

The crystal structure of $\{(\text{C}_2)\text{ODy}_6\}\text{I}_9$ (**2**), or $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{12}\}\text{I}_{18}$ for a better comparison with **1**, features, in principle, the same tetrameric building blocks, $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{12}\}\text{I}_{32}$. Two formula units of DyI_3 need to be taken out with respect to $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\}\text{I}_{24}$ to

connect the tetramers via common octahedral edges to a polymeric chain, according to $(\text{O—T—T—O—O—T—T—O})_\infty$, see Fig. 4. An inspection of the Dy-Dy-distances, see Table 1, shows that these are pretty much the same with one obvious difference: the newly established common edge of two octahedra has shortened.

Figure 3. Connection of the $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\}\text{I}_{32}$ tetramers in the crystal structure of $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\}\text{I}_{24}$; view approximately down [001].

Figure 4. Infinite chain of edge-connected $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\}\text{I}_{32}$ tetramers in the crystal structure of $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{12}\}\text{I}_{18}$.

Table 1. Internuclear Dy-Dy distances in the $\{\text{Dy}_{14}\}$ cluster tetramer of $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{14}\}\text{I}_{24}$ (**1**) and $\{(\text{C}_2)_2\text{O}_2\text{Dy}_{12}\}\text{I}_{18}$ (**2**), for the atomic numbering see Scheme 1.

	1	d/pm	2	d/pm
common edges	Dy1-Dy3	351.36(5)	Dy3-Dy3	319.32(15)
	Dy5-Dy6	338.88(5)	Dy2-Dy3	334.33(11)
	Dy7-Dy7	339.75(4)	Dy11-Dy11	336.43(18)
T	Dy5-Dy7	366.68(6)	Dy2-Dy11	370.55(8), 2x
	Dy5-Dy7	368.55(7)	Dy2-Dy11	372.01(8)
	Dy6-Dy7	364.91(4)		
O	Dy2-Dy3	384.08(5)	Dy1-Dy3	392.92(9), 2x
	Dy2-Dy1	376.83(5)	Dy1-Dy3	387.63(8), 2x
	Dy2-Dy5	384.29(4)	Dy1-Dy2	371.06(8), 2x
	Dy2-Dy6	377.44(6)	Dy1-Dy2	372.90(8), 2x
	Dy4-Dy1	385.45(4)		
	Dy4-Dy3	376.08(6)		
	Dy4-Dy5	383.28(5)		
	Dy4-Dy6	389.38(5)		
	Dy3-Dy5	348.50(5)	Dy2-Dy3	364.04(5), 2x
	Dy1-Dy6	347.63(5)		

	2/1			4/1	
3/3		5/2	7/11	6/2	1/3
1/3		6/2	7/11	5/2	3/3
	4/1			2/1	

Scheme 1. Atomic numbering scheme for the $\{\text{Dy}_{14}\}$ O—T—T—O tetramers in **1** (left) and **2** (after the slash).

considerably, from 351.36(5) pm in **1** to 319.32(15) pm in **2**.

Figure 5. View down the infinite chains of edge-connected $\{(C_2)_2O_2Dy_{12}\}I_{32}$ tetramers in the crystal structure of $\{(C_2)_2O_2Dy_{12}\}I_{18}$ exhibiting a packing in the fashion of the hexagonal closest packing of rods.

Even the packing of the chains in $\{(C_2)_2O_2Dy_{12}\}I_{18}$ looks familiar when compared with $\{(C_2)_2O_2Dy_{14}\}I_{24}$, it is in the fashion of a hexagonal closest packing of rods, compare Figs. 3 and 5. One out of four chains is disordered. It has only van-der-Waals contacts to its six neighbouring chains and the threefold axis seem to allow for three orientations parallel [001]. It is situated in a tube of roughly 1300 pm diameter which is created by the six surrounding chains that are connected via i-a bridging. There are three equivalent orientations for the chain enclosed in the tube, see Fig. 5.

Conclusions

Two new dysprosium cluster complexes with O—T—T—O type $\{(C_2)_2O_2Dy_{14}\}$ cluster tetramers, where O stands for a $\{(C_2)Dy_6\}$ octahedron and T for a $\{ODy_4\}$ tetrahedron, have been obtained and structurally characterized for $\{(C_2)_2O_2Dy_{14}\}I_{24}$ (isolated tetramers) and $\{(C_2)_2O_2Dy_{12}\}I_{18}$ (chains of edge-connected tetramers). This adds to a small number of dysprosium clusters, all of which encapsulate C_2 dumbbells in octahedra and, in the cases reported here, O atoms in tetrahedra. The ambivalent character of reduced dysprosium chemistry is thereby clearly established. Dysprosium may be truly divalent as in DyI_2 with a $4f^{10}5d^0$ configuration and also capable to cluster formation that must involve the $4f^95d^1$ configuration for bonding with the endohedral atoms.

Experimental Section

Synthesis. DyI_3 is synthesized from stoichiometric amounts of dysprosium (Chempur, Karlsruhe, Germany) and iodine (Acros, Geel, Belgium), followed by sublimation in high vacuum for purification [12]. Due to air and moisture sensitivity of both reagents and products, all handlings were carried out in an argon-filled glove box (M. Braun, Garching, Germany).

$\{(C_2)_2O_2Dy_{14}\}I_{24}$ (**1**) is obtained from the reaction of 200 mg DyI_3 , 84 mg dysprosium powder, 7 mg Dy_2O_3 ($\geq 99.9\%$ Chempur, Karlsruhe, Germany) and 11 mg graphite powder (p.a. Merck, Darmstadt, Germany) and approximately 1 g NaI (p.a. Acros, Geel, Belgium) as a flux. The reaction mixture was loaded in a tantalum container which was He-arc sealed and heated at $1000^\circ C$ for ten days. The product that was obtained after slow cooling consisted of black, rectangular plates with edge lengths of ca. 0.2 mm which were embedded in the NaI flux.

$\{(C_2)_2O_2Dy_{12}\}I_{18}$ (**2**) was first synthesized using 150 mg DyI_3 , 63 mg dysprosium powder, 8 mg graphite powder and 10 mg iron powder ($\geq 99.9\%$ Merck, Darmstadt, Germany). The reaction

mixture was loaded into a tantalum container, sealed and heated at $1000^\circ C$ for 8 days. The product mixture mostly contained black needles that easily split upon applying mechanical pressure.

Crystal Structure Determination. Single crystals of **1** and **2** were selected in a nitrogen-filled dry box under a microscope and mounted in thin-walled glass capillaries. They were checked for their quality by Laue diffraction patterns. The best specimens were transferred to the image plate diffraction system IPDS-I (Stoe, Darmstadt, Germany) with which complete data sets of X-ray diffraction intensities were collected. The data were corrected for Lorentz and polarization effects. The analysis of the intensity data was performed with the computer programs SIR-92 [13], and SHELX-97 [14, 15] for structure solution and refinement. A numerical absorption correction was carried out with the programs X-RED [16] and X-SHAPE [17].

Crystal data for $\{(C_2)_2O_2Dy_{14}\}I_{24}$ (**1**): Diffractometer IPDS-I, Mo- K_α radiation (graphite monochromator, $\lambda = 71.073$ pm); $T = 293(2)$ K; $2\theta_{max} = 58.88^\circ$; 180 images, $0^\circ \leq \omega \leq 180^\circ$, $\varphi = 0^\circ$; $0^\circ \leq \omega \leq 180^\circ$, $\varphi = 90^\circ$, $\Delta\omega = 1^\circ$; indices: $-13 \leq h \leq 13$, $-13 \leq k \leq 14$, $-23 \leq l \leq 23$; transmission (min, max) = 0.0051, 0.1883; $\rho(\text{calc}) = 5.942$ g/cm $^{-3}$; 29843 reflection intensities measured of which 8305 were symmetrically independent, $R_{int} = 0.1886$, $F(000) = 2236$, $\mu = 29.367$ mm $^{-1}$; triclinic, $P\bar{1}$ (no. 2), $a = 972.97(14)$, $b = 1033.03(13)$, $c = 1677.0(2)$ pm, $\alpha = 101.424(11)^\circ$, $\beta = 92.724(11)^\circ$, $\gamma = 112.745(10)^\circ$, $V = 1509.3(3) \cdot 10^6$ pm 3 , $Z = 1$, R values: R_1/wR_2 for 5659 reflections with $I_0 > 2\sigma(I_0)$: 0.0616/0.1465 and for all data: 0.0876/0.1566; $S_{all} = 0.941$

Crystal data for $\{(C_2)ODy_6\}I_9$ (**2**): Diffractometer IPDS-I; Mo- K_α radiation (graphite monochromator, $\lambda = 71.073$ pm); $T = 293(2)$ K; $2\theta_{max} = 54.14^\circ$; 180 images, $0^\circ \leq \omega \leq 180^\circ$, $\varphi = 0^\circ$; $0^\circ \leq \omega \leq 180^\circ$, $\varphi = 90^\circ$, $\Delta\omega = 1^\circ$; indices: $-25 \leq h \leq 25$, $-25 \leq k \leq 25$, $-16 \leq l \leq 14$; transmission (min, max) = 0.0164, 0.0761; $\rho(\text{calc}) = 6.158$ g/cm $^{-3}$; 62811 reflection intensities measured of which 3526 were symmetrically independent, $R_{int} = 0.1070$, $F(000) = 7064$, $\mu = 31.236$ mm $^{-1}$; hexagonal, $P6/m$ (no.175), $a = 2024.18(8)$, $c = 1299.21(4)$ pm, $V = 4610.1(3) \cdot 10^6$ pm 3 , $Z = 8$, R values: R_1/wR_2 for 5659 reflections with $I_0 > 2\sigma(I_0)$: 0.0344/0.0781 and for all data: 0.0550/0.0830; $S_{all} = 0.941$.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crystdata@fizkarlsruhe.de), on quoting the depository numbers CSD-421641 (**1**) and CSD-421642 (**2**).

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Entry for the Table of Contents

Dysprosium clusters

Two new dysprosium cluster complexes with O—T—T—O type $\{(C_2)_2O_2Dy_{14}\}$ cluster tetramers have been obtained and structurally characterized for $\{(C_2)_2O_2Dy_{14}\}I_{24}$ (isolated tetramers) and $\{(C_2)_2O_2Dy_{12}\}I_{18}$ (chains of edge-connected tetramers). The ambivalent character of reduced dysprosium chemistry ($4f^{10}5d^0 \leftrightarrow 4f^95d^1$) is thereby clearly established.

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Isolated and Edge-Connected Tetramers $\{(C_2)_2O_2Dy_{14}\}$ in the Crystal Structures of $\{(C_2)_2O_2Dy_{14}\}I_{24}$ and $\{(C_2)_2O_2Dy_{12}\}I_{18}$

Keywords: Dysprosium / Cluster Complexes / Synthesis / Crystal Structure

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