Synthesis and Crystal Structures of Two New Reduced Iodides of Erbium with Isolated Monomeric and Dimeric Clusters, $Cs[Er_6C]I_{12}$ and $Cs[Er_{10}(C_2)_2]I_{18}$

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The reduction of erbium triiodide with caesium in the presence of carbon yielded two new ternary reduced iodides of erbium as black single crystals, $Cs[Er_6C]I_{12}$ and $Cs[Er_{10}(C_2)_2]I_{18}$, containing the monomeric unit $[Er_6C]$ and the dimeric unit $[Er_{10}(C_2)_2]$ composed of two $[Er_6(C_2)]$ octahedra sharing a common edge, respectively.

An enormous wealth of reduced halides containing octahedral clusters of the early transition and rare-earth elements has emerged from intensive research during the last forty years.[1–3] Almost all of the rare-earth clusters, $[M_6]$, contain interstitial atoms, from light-element to noble-metal atoms, owing to their electron deficiency.

Most of the synthetic work has followed the conproportionation route.[4] An alternative to this is the metallothermic reduction of rare-earth halides with alkali metals,[5] which has several advantages for crystal growth. First, there is no surface blockage on the reducing metal at the lower reaction temperatures and, secondly, alkali halides may serve as solvents at elevated temperatures. Furthermore, if the respective system contains quaternary halides, *i.e.* that they contain an additional metal, these are detected easily.

Still, quaternary reduced halides of the rare-earth elements are extremely rare. The lithium-intercalated erbium and yttrium monochloride-hydrides, for example $Li_{0.15}ErClH_{0.65}$,[6,7] being almost the only ones. The first hint that there were more was seen when we obtained a few single crystals of $Cs_2Lu[Lu_6Z]Cl_{18}$.[8] This compound with Z being carbon, however, has only 9 electrons for bonding within the $[Lu_6C]$ cluster. Many attempts to prepare pure samples of $Cs_2Lu[Lu_6C]Cl_{18}$ and analogous compounds, which are well known for niobium[9] and zirconium,[10] were unsuccessful. Finally, we are now able to synthesize two new compounds in the Cs–ErI_3–C system, $Cs[Er_6C]I_{12}$ and $Cs[Er_{10}(C_2)_2]I_{18}$.

Caesium, erbium triiodide (ErI_3; from the elements, see ref. 11), and graphite were sealed in 2 : 7 : 1 molar ratios into tantalum containers by He-arc welding,[12] jacketed with an evacuated silica tube and heated in the temperature range from 750 to 1050 °C for 30 days. All handling was carried out under strictly anhydrous/anaerobic conditions in argon dry boxes. The crystals of both compounds are black.

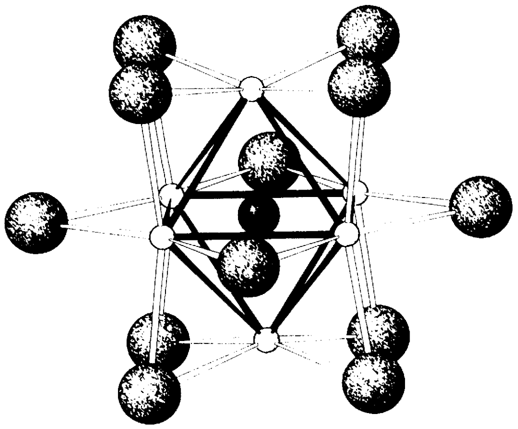

Fig. 1 The monomeric unit $[Er_6C]$ with neighbouring I^- in the crystal structure of $Cs[Er_6C]I_{12}$. Selected atomic distances (pm): Cs···I(1), 419.8(2); Cs···I(2), 416.1(2); Er···I(1), 305.5(2), 308.9(2), 338.2(3); Er···I(2), 298.8(2), 299.9(2); Er···Er, 353.7(2), 359.6(2), 504.5(2); Er···C, 252.2(2).

The monomeric unit, $[Er_6C]$, together with the surrounding sphere of iodide of the crystal structure of $Cs[Er_6C]I_{12}$ is shown in Fig 1.[†] Analogously, the dimeric unit, $[Er_{10}(C_2)_2]$, with its direct iodide neighbours in the crystal structure of $Cs[Er_{10}(C_2)_2]I_{18}$ is shown in Fig 2.[‡]

Following Schäfer's notation,[15] the $[M_6(C)]$ and $[M_{10}(C_2)_2]$ clusters, respectively, are edge-capped by twelve/eighteen 'inner' ligands, ${}^{i}I$ and, in addition, six/eight 'outer' ligands, ${}^{a}I$ ('a' from German; *i.e.* outward pointing), located at the corners. The metal octahedra are connected *via* two different types of ligands (${}^{i-a}I$ and ${}^{a-i}I$) each belonging to two different clusters. Therefore, a useful description of the interconnectivity of the $[Er_6C]I_{12}^-$ and $[Er_{10}(C_2)_2]I_{18}^-$ clusters in these compounds taking the different iodine atom functionalities into account is $Cs\{[Er_6C]{}^{i}I_6{}^{i-a}I_{6/2}\}{}^{a-i}I_{6/2}$ and $Cs\{[Er_{10}(C_2)_2]{}^{i}I_{10}{}^{i-a}I_{8/2}\}{}^{a-i}I_{8/2}$, respectively. In both structures the caesium atoms are surrounded by twelve iodine atoms building a regular cuboctahedron.

Bonding in these clusters can be represented fairly well in MO terms,[16] as they are well isolated in the solid compound. The optimum electron count within the monomeric rare-earth cluster phases with main-group interstitials is 14. With $Cs[Er_6C]I_{12}$ a cluster with 11 electrons was obtained for the first time. The carbon atom certainly does not donate its valence electrons to the cluster but shares them in covalent bonds acquiring a somewhat negative charge.

[†] *Crystal data*: $Cs[Er_6C]I_{12}$, M = 2671.33, trigonal, space group $R\bar{3}$ (No. 148, $R_{int.}$ = 0.069), Z = 3, a = 1112.0(3), c = 2063.8(9) pm, V = 443.71(24) cm^3 mol^{-1}, D_c = 6.02 g cm^{-3}, $F(000)$ = 3315, μ = 307.83 cm^{-1}. Number of data measured 5338, number of unique reflections 1669, number of observed reflections with $|F_o| > 4\ \sigma|F_o|$ 1210 and number of parameters 30. Diffraction data were collected on a Siemens-Stoe AED 2 diffractometer with graphite monochromated Mo-Kα radiation (λ = 71.07 pm, ω-scan) at room temperature to $2\theta_{max.}$ = 64°. Intensity data were corrected for linear isotropic decay, Lorentz and polarization effects, ψ-scan for 20 reflections ($\Delta\psi$ = 10°). The structure was solved by a combination of direct methods (SHELXS 86,[13]) and Fourier techniques, and refined by full-matrix least-squares analysis (SHELX 76,[14]). The final R value was 0.094 (R_w = 0.068).

[‡] *Crystal data*: $Cs[Er_{10}(C_2)_2]I_{18}$, M = 4137.82, triclinic, space group $P\bar{1}$ (No. 2, $R_{int.}$ = 0.036), Z = 1, a = 1105.2(8), b = 1112.0(7), c = 1122.9(8) pm, α = 66.91(3), β = 87.14(3), γ = 60.80(3)°, V = 656.6(8) cm^3 mol^{-1}, D_c = 6.29 g cm^{-3}, $F(000)$ = 1713, μ = 327.05 cm^{-1}. Number of data measured 9684, number of unique reflections 5133, number of observed reflections with $|F_o| > 2\sigma|F_o|$ 4579 and number of parameters 152. Diffraction data were collected on an Siemens-Stoe AED 2 diffractometer with graphite monochromated Mo-Kα radiation (λ = 71.07 pm, ω–2 θ-scan) at room temperature to $2\theta_{max.}$ = 56°. Intensity data were corrected for linear isotropic decay, Lorentz and polarization effects, extinction coefficient g = 0.0001, ψ-scan for 20 reflections ($\Delta\psi$ = 10°). The structure was solved by a combination of direct methods (SHELXS 86,[13]) and Fourier techniques and refined by full-matrix least-squares analysis (SHELX 76,[14]). The final R value was 0.049 (R_w = 0.043). Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Inorganic Crystal Data Base (ICSD), Bonn, Germany. See Notice to Authors, Issue No. 1.

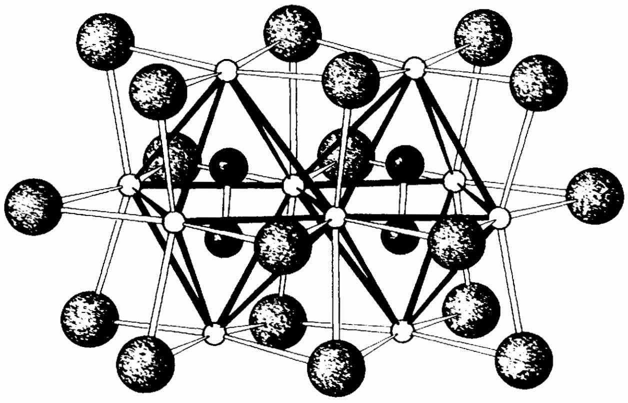

Fig. 2 The dimeric unit $[Er_{10}(C_2)_2]$ with neighbouring I^- in the crystal structure of $Cs[Er_{10}(C_2)_2]I_{18}$. Selected atomic distances (pm): Cs···I(5), 394.7(3); Cs···I(6), 409.3(3); Cs···I(8), 431.1(3); Er(2)···I(3), 289.1(3); Er(5)···I(8), 289.1(2); Er(1)···I(4), 301.8(3); Er(2)···I(2), 341.2(3); Er(3)···Er(3), 316.7(2); Er(2)···Er(5), 339.7(3); Er(2)···Er(3), 356.4(3); Er(1)···Er(2), 368.5(3); Er(3)···Er(4), 393.9(3); Er(1)···C(1), 213.9(2); Er(4)···C(2), 218.1(2); Er(5)···C(1), 243.9(2); Er(2)···C(2), 246.4(2); Er(3)···C(2), 259.4(2); Er(1)···C(2), 361.6(2); C(1)···C(2), 148.0(3).

Chemical bonding in dimeric clusters is more difficult to describe but seems to be predominantly ionic. We expect that the extra electron donated from the caesium atom occupies the metal–metal bond concentrated along the shared edges as was demonstrated for $Gd_{10}Cl_{17}C_4$.[17]

Received, 14th May 1992; Com. 2/02525F

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