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Synthesis, Structure, and Characterization of Lanthanacarboranes. Molecular Structures of [*closo*-1,1,1-(MeCN)$_3$-1,2,4-EuC$_2$B$_{10}$H$_{12}$]$_\infty$ and [1,1-(THF)$_2$-*commo*-1,1′-Eu(1,2,4-EuC$_2$B$_{10}$H$_{12}$)$_2$]$^{2-}$

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The reaction of LnI$_2$(THF)$_2$ with Na$_2$[*nido*-7,9-C$_2$B$_{10}$H$_{12}$] in THF affords lanthanacarborane complexes with the formulation [Ln(C$_2$B$_{10}$H$_{12}$)(THF)$_x$]$_n$ (x = 3, n = ∞, Ln = Sm (**1**) or Eu (**2**); x = 4, n = 1, Ln = Yb (**3**)). The THF ligands in **1**–**3** are labile and can be replaced by other ligands such as MeCN. The latter derivatives have been fully characterized by spectroscopic and analytical techniques. The samarium and europium complexes **1** and **2** are polymeric in the solid state whereas the ytterbium complex **3** is monomeric. The molecular structure of the acetonitrile derivative from **2**, [Eu(C$_2$B$_{10}$H$_{12}$)(MeCN)$_3$]$_\infty$ (**4**), has been established crystallographically. Complex **4** crystallizes in the monoclinic space group $P2_1/n$ with a = 20.146 (6) Å, b = 9.909 (3) Å, c = 20.871 (6) Å, β = 118.838 (7)°, V = 3650 Å^3, and Z = 8. Data were collected on a modified Picker FACS-1 diffractometer at 128 K using Mo Kα radiation, to a maximum 2θ = 50°, giving 6609 unique reflections, and the structure was solved by heavy-atom methods. The final discrepancy indexes were R = 0.041 and R_w = 0.057 for 4745 independent reflections with $I > 3\sigma(I)$. The crystal is composed of two crystallographically inequivalent spiral chains. Each carborane moiety serves as a ligand for two europium atoms, bonded to one through an open six-membered face and to the other via both an upper- and a lower-belt Eu–H–E (where E = B or C) interaction. The coordination sphere about each europium center is completed by three acetonitrile ligands. Complex **2** reacts further with 1 molar equiv of Na$_2$[*nido*-7,9-C$_2$B$_{10}$H$_{12}$] in THF at room temperature to produce a europium carborane sandwich complex formulated as [Eu(C$_2$B$_{10}$H$_{12}$)$_2$(THF)$_2$]$^{2-}$ (**5**). This complex can also be generated by the disproportionation of **2** with 1 molar equiv of NaC$_5$Me$_5$ in THF at room temperature or by the interaction of EuI$_2$(THF)$_2$ with 2 molar equiv of Na$_2$[*nido*-7,9-C$_2$B$_{10}$H$_{12}$]. Reduction of EuCl$_3$ with 2 molar equivalents of Na$_2$[*nido*-7,9-C$_2$B$_{10}$H$_{12}$] also yields complex **5**. The molecular structure of the tetraethylammonium salt, [Eu(C$_2$B$_{10}$H$_{12}$)$_2$(THF)$_2$][NEt$_4$]$_2$ ((NEt$_4$)$_2$(**5**)) has been established crystallographically. The complex ((NEt$_4$)$_2$(**5**)) crystallizes in the monoclinic space group $I2/c$ with a = 18.571 (7) Å, b = 9.396 (3) Å, c = 27.813 (10) Å, β = 103.38 (1)°, V = 4721 Å^3, and Z = 4 (the anion is located on a 2-fold axis). Data were collected on a modified Picker FACS-1 diffractometer at 298 K using Mo Kα radiation, to a maximum 2θ = 35°, giving 1499 unique reflections, and the structure was solved by heavy-atom methods. The final discrepancy indexes were R = 0.050 and R_w = 0.059 for 1201 independent reflections with $I > 3\sigma(I)$. The europium atom is sandwiched by two nonparallel η^6-carborane ligands. The coordination sphere about the europium is completed by two THF ligands, and the coordination geometry around the europium atom can be best described as that of a distorted tetrahedron.

Introduction

The chemistry of the metallacarboranes derived from dicarbollide ligands combined with transition metals[1-12] and the main-group elements[13-20] has been a subject of intense interest for the past 25 years. Structural characterization of many of the compounds clearly demonstrates the isolobal analogy[1] of carborane-derived ligands such as [*nido*-7,8-C$_2$B$_9$H$_{11}$]$^{2-}$ with the cyclopentadienyl ion [η^5-C$_5$H$_5$]$^-$. We have now taken this isolobal analogy to a different part of the periodic table, i.e., the f-block elements. Recently, we reported the dicarbollide complexes of samarium and ytterbium and also probed the nature of the bonding interactions between a lanthanide metal and the dicarbollide ligand using mainly IR spectroscopy.[21,22a] In this paper, we report the synthesis and spectroscopic characterization of new [*nido*-7,9-C$_2$B$_{10}$H$_{12}$]$^{2-}$ complexes of samarium (**1**), europium (**2**), and ytterbium (**3**). The molecular structures of the polymeric europium carborane complex [*closo*-1,1,1-(MeCN)$_3$-1,2,4-EuC$_2$B$_{10}$H$_{12}$]$_\infty$ (**4**) and the monomeric dianionic europium carborane sandwich complex [1,1-(THF)$_2$-*commo*-1,1′-Eu(1,2,4-EuC$_2$B$_{10}$H$_{12}$)$_2$]$^{2-}$ (**5**) are also reported herein. A portion of this work has appeared elsewhere.[22b]

Results and Discussion

The reaction of LnI$_2$(THF)$_2$ (Ln = Sm, Eu, Yb) with equimolar amounts of Na$_2$[*nido*-7,9-C$_2$B$_{10}$H$_{12}$] in THF at room temperature results in the precipitation of a colored complex which has been formulated as [Ln(C$_2$B$_{10}$H$_{12}$)(THF)$_x$]$_n$ (x = 3, n = ∞, Ln = Sm (**1**) or Eu (**2**); x = 4, n = 1, Ln = Yb (**3**)) on the basis of spectroscopic, analytical, and X-ray diffraction studies. The samarium complex **1** is reddish brown, whereas the europium and

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ytterbium species **2** and **3** are yellow and bright purple, respectively. Metallacarboranes **1**–**3** are insoluble in THF but soluble in MeCN, thereby allowing the THF to be replaced by this solvent ligand. Lanthanide species of this type were characterized by IR spectra and X-ray diffraction in the solid state whereas complexometric metal analysis and ^{1}H NMR, ^{11}B NMR, and mass spectroscopic studies provide information regarding their structures in solution.

The IR spectra (Nujol mull) of **1**–**3** exhibit a unique doublet centered around 2490 cm^{-1}, the region normally assigned to the B–H stretching mode. Similar doublets have previously been observed in the IR spectra of other lanthanide[21,22a] and alkaline-earth-metal[23,24] metallacarborane complexes, and they are believed to arise from ionic interactions of a positive metal center and an anionic carborane ligand.[22,24] In addition to this unique B–H doublet, the IR spectra of **1** and **2** also exhibit a medium-intensity B–H stretching band centered at 2390 cm^{-1}, which is assigned to a Ln–H–B stretch (where Ln = Sm or Eu). A similar pattern has previously been observed in the crystallographically characterized polymeric strontium carborane complex[23] [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_\infty$ (**6**). In its solid-state IR spectrum, complex **6** exhibits both a characteristic doublet B–H stretching mode centered at 2498 cm^{-1} and a medium band at 2390 cm^{-1} due to a Sr–H–B stretching mode. On the basis of the observation that complexes **1** and **2** both display a band due to Ln–H–B stretching in their solid-state IR spectra, we propose a polymeric structure similar to that of **6** for complexes **1** and **2** in the solid state. These complexes undoubtedly possess different structures in the solution state. In contrast, ytterbium complex **3** does not show a band due to a Yb–H–B stretching mode in its solid-state IR spectrum. The calcium carborane complex [*closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$] (**7**), which has been shown by an X-ray diffraction study to possess a monomeric structure,[24] resembles **3** in the B–H stretching region of its solid-state IR spectrum. On the basis of these observations, we propose a similar monomeric structure for the ytterbium complex **3**, with $[Yb(THF)_4]^{2+}$ capping the open hexagonal face of the [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ ligand to give a closo 13-vertex polyhedron. We were unable to confirm the monomeric structure of ytterbium complex **3** by X-ray diffraction, since all attempts to obtain suitable single crystals of **3** failed.

It is interesting to note that the ytterbium and calcium carborane complexes **3** and **7** exhibit similar solid-state IR band patterns in the 2300–2600-cm^{-1} region and possess similar monomeric structures, while samarium, europium, and strontium carborane complexes **1**, **2**, and **6** exhibit similar solid-state IR band patterns in the 2300–2600-cm^{-1} region and possess similar polymeric structures. This is not unexpected due to the similarity in ionic radii[25] of Yb^{2+} and Ca^{2+} (1.02 and 1.00 Å, respectively) and of Sm^{2+}, Eu^{2+}, and Sr^{2+} (1.22, 1.21 and 1.22 Å, respectively). The relatively large ionic radii of Sm^{2+}, Eu^{2+}, and Sr^{2+} may be responsible for the polymeric nature of complexes **1**, **2**, and **6**, since this particular arrangement of ligands meets the coordination requirements of the metal atom.

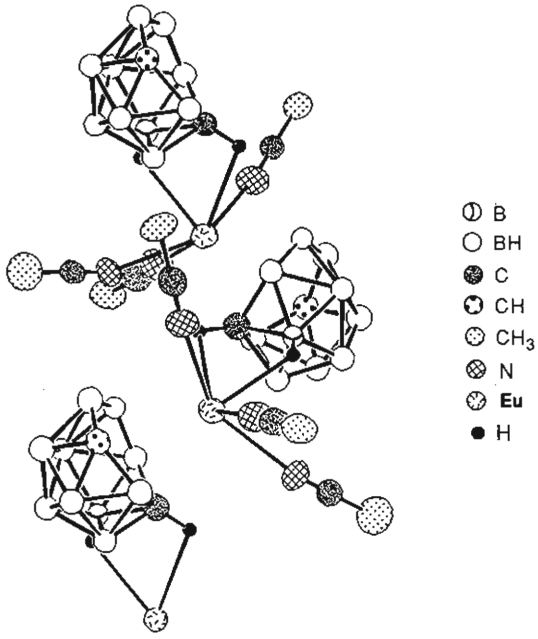

Figure 1. Three units of one of the spiral polymeric chains of [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$EuC_2B_{10}H_{12}]_n$ (**4**).

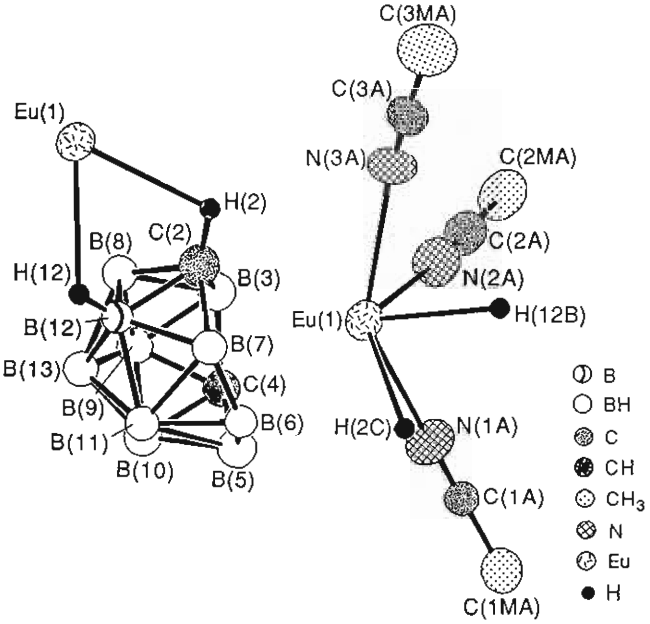

Figure 2. Closer view of the metal to carborane interactions in the polymeric complex [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$EuC_2B_{10}H_{12}]_n$ (**4**). All terminal hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Eu(1)–N(1A), 2.620 (9) [2.662 (9)]; Eu(1)–N(2A), 2.746 (9) [2.692 (9)]; Eu(1)–N(3A), 2.668 (8) [2.672 (9)]; Eu(1)*–C(2), 2.967 (10) [3.019 (10)]; Eu(1)*–B(3), 2.836 (11) [2.881 (11)]; Eu(1)*–C(4), 3.126 (9) [3.116 (9)]; Eu(1)*–B(5), 3.084 (11) [2.987 (11)]; Eu(1)*–B(6), 2.854 (10) [2.791 (10)]; Eu(1)*–B(7), 3.067 (11) [3.061 (11)]; C(2)–B(3), 1.743 (10) [1.742 (15)]; C(2)–B(7), 1.815 (15) [1.805 (15)]; C(4)–B(3), 1.669 (14) [1.663 (14)]; C(4)–B(5), 1.643 (15) [1.616 (15)]; B(5)–B(10), 1.860 (16) [1.849 (16)]; C(2)–B(8), 1.747 (14) [1.765 (15)]; B(3)–B(8), 1.793 (15) [1.807 (15)]; C(2)–B(12), 1.746 (15) [1.759 (15)]; B(7)–B(12), 1.787 (16) [1.818 (16)]; Eu(1)–C(2), 3.075 (9) [3.019 (10)]. Asterisks denote that the Eu(1) is interacting directly with the atoms of the open hexagonal face of the carborane fragment. Distances in brackets are those of a second molecule. Note: Lines are for the purpose of orientation only and do not imply covalent bonding.

In order to confirm the assumed polymeric nature of complexes **1** and **2**, suitable single crystals of the related acetonitrile derivative of **2**, i.e. [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$EuC_2B_{10}H_{12}]_\infty$ (**4**), were successfully grown from $MeCN/Et_2O$ at room temperature. A view of the molecular structure of **4** is presented in Figure 1. The crystal is composed of two crystallographically independent, but structurally similar, spiral chains. Three units of one of the spiral polymeric chains are shown in Figure 1. A detailed view of the metal to carborane interactions can be seen in Figure 2 along with some important interatomic distances. Each carborane moiety serves as a ligand for two europium atoms, being bonded to one via both upper- and lower-belt Eu–H–E (where E = B or C) interactions. The coordination sphere about each europium atom is completed by three acetonitrile ligands. This arrangement of metal and carborane ligands is repeated to give a polymeric structure. The crystal structure of **4** is isomorphous with the

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previously reported strontium carborane complex **6**.[23]

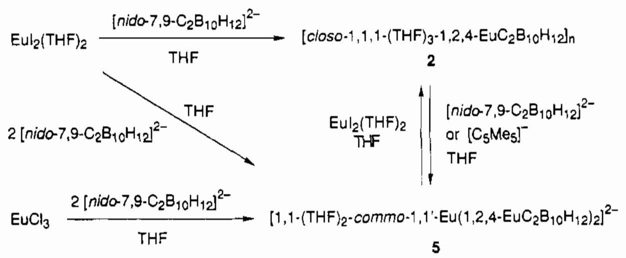
The Eu–N distances in complex **4** range from 2.620 to 2.746 Å and the europium-carborane (η^6) distances fall in the range 2.791–3.126 Å. The Eu–E (bonding face, where E = B or C) distances in complex **4** are very similar to those found in complex **6**.[23] The C_2B_{10} fragment in **4** can be compared with related transition-metal[9-11] and alkaline-earth-metal[23,24] metallacarborane complexes. In complex **4**, the entire upper belt is distorted in order to accommodate the 13-vertex polyhedron. The polyhedron is somewhat similar to that observed in both complexes[23] **6** and [*closo*-1,1,-$(PPh_3)_2$-1-H-1,2,4-$RhC_2B_{10}H_{12}$].[9] The open six-membered C_2B_{10} bonding face in **4** is puckered, and the four boron atoms do not lie in a plane. The maximum deviation from the least-squares plane through the four boron atoms is 0.14 Å. In complex **4**, C(2) and C(4) lie on the same side of this plane in the upper belt of the carborane fragment. This arrangement is similar to that previously reported for complex[23] **6** and is in contrast to the structures of other related metallacarboranes containing the C_2B_{10} unit[10,11,24] where one carbon atom lies above and another lies below the plane defined by the remaining four borons in the upper belt. In complex **4**, B(3) and B(6) lie above the plane defined by C(2), C(4), B(5), and B(7) in the upper belt. The upper belt thus adopts a boatlike shape and closely resembles that observed in complex[23] **6**. Both carbon atoms C(2) and C(4) interact asymmetrically with the adjacent borons in the upper belt [C(2)–B(3), C(2)–B(7), C(4)–B(3), and C(4)–B(5) distances are 1.743 (15), 1.815 (15), 1.669 (14), and 1.643 (15) Å, respectively]. This asymmetry is similar to that reported for both complexes[23] **6** and [*closo*-1,1,-$(PPh_3)_2$-1-H-3-OMe-1,2,4-$IrC_2B_{10}H_{12}$][10] but is in contrast to complex[24] **7**, where the carbon atom which lies above the plane defined by four borons in the upper belt interacts nearly symmetrically with the adjacent borons whereas the other carbon atom, which lies below the plane, interacts asymmetrically with the adjacent borons in the upper belt.

It is interesting to note that in this polymer one of the C–H vertices of each carborane fragment is coordinated to a europium atom to afford this unique M–H–C agostic structural arrangement despite the fact that the B–H vertices of the carborane fragment are traditionally more basic than the C–H vertices. The presence of one Eu–H–C and one Eu–H–B interaction is not yet understood.

In order to study the structures of complexes **1**–**3** in solution, complexometric metal analysis and solution NMR spectroscopic studies were carried out. The hydrolysis of **1** or **3** in CH_3CN-d_3 with a slight molar excess of H_2O and subsequent examination by ^1H NMR spectroscopy reveals the presence of free THF and the known $[C_2B_{10}H_{13}]^-$ ion in the ratio of 4:1. A complexometric metal analysis of complex **1** or **3** (in solution) is consistent with a complex having four metal-coordinated THF molecules, one metal, and one [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ ligand. The IR spectra of complexes **1** and **2** in MeCN solution both exhibit a broad band near 2508 cm^{-1} due to B–H stretching and do not exhibit a band near 2390 cm^{-1} due to Ln–H–B stretching. The IR spectrum of **3** in MeCN solution exhibits a broad band around 2500 cm^{-1} due to B–H stretching and shows no absorption near 2390 cm^{-1} characteristic of Yb–H–B stretching, consistent with the assigned formula of **3**. These studies reveal a general formula [Ln($C_2B_{10}H_{12}$)$(THF)_4$] (Ln = Sm, Eu) for complexes **1** and **2** in solution and suggest that these complexes exist as monomeric species in solution with a structure similar to that of ytterbium and calcium[24] carborane complexes **3** and **7**.

Synthesis and Structural Characterization of the Europacarborane Sandwich. Following the syntheses of the monocage lanthanacarborane complexes described above, we began an investigation of the reactivity of these species. Complexes **1**–**3** do not provide reactions with neutral nucleophiles such as CO, phosphines, alkenes, and alkynes. Complexes **1**–**3**, however, do react with anionic ligands to afford anionic derivatives. We have examined in detail the reaction of complex **2** with the anionic ligand present in Na_2[*nido*-7,9-$C_2B_{10}H_{12}$]. The product was fully characterized as an anionic europacarborane sandwich complex. We here report the synthesis and structural characterization of this complex, which represents the first authentic example of a structurally characterized lanthanacarborane complex containing two [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ ligands.

Scheme I



The yellow complex **2** reacts with 1 molar equiv of Na_2[*nido*-7,9-$C_2B_{10}H_{12}$] in THF at room temperature to produce an orange complex which is soluble in both THF and MeCN. Metathesis of this orange complex with Et_4NCl followed by recrystallization from THF/MeCN/Et_2O provides orange crystals. An X-ray diffraction study showed these orange crystals to be a dianionic monomeric complex formulated as $[Eu(C_2B_{10}H_{12})_2(THF)_2][NEt_4]_2$, (($NEt_4)_2$(**5**)). The sodium salt of **5**, $Na_2[Eu(C_2B_{10}H_{12})_2(THF)_2]$ reacts with 1 molar equiv of $EuI_2(THF)_2$ to yield **2**. As anticipated, the sodium salt of **5** can be obtained more conveniently from the direct reaction of $EuI_2(THF)_2$ with 2 molar equiv of Na_2[*nido*-7,9-$C_2B_{10}H_{12}$] in THF at room temperature followed by metathesis with Et_4NCl. Another alternate route to **5** involves the reaction of $EuCl_3$ with 2 molar equiv of Na_2[*nido*-7,9-$C_2B_{10}H_{12}$] followed by metathesis with Et_4NCl. In the latter case, the [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ ligand reduces Eu(III) to Eu(II). Moreover, we have also noticed that the disproportionation reaction of **2** with 1 molar equiv of NaC_5Me_5 in THF followed by metathesis with Et_4NCl affords crystalline $(NEt_4)_2$(**5**) and presumably the known $(C_5Me_5)_2Eu(THF)_2$. All of these synthesis routes are summarized in Scheme I. It is noteworthy that the expected complex $[(C_5Me_5)Eu(C_2B_{10}H_{12})(THF)_2]^-$ does not result from the reaction of **2** with 1 molar equiv of NaC_5Me_5. Instead, the complex $[Eu(C_2B_{10}H_{12})_2(THF)_2]^{2-}$ is formed via a disproportionation reaction. The reaction of $[Eu(C_2B_{10}H_{12})_2(THF)_2][Na]_2$ with 1 molar equiv of NaC_5Me_5 or the reaction of **2** with different molar ratios of NaC_5Me_5 did not produce the desired complex $[(C_5Me_5)Eu(C_2B_{10}H_{12})(THF)_2][Na]$. It appears that the coordination of two identical ligands around the Eu^{2+} ion is favored.

The molecular structure of $(NEt_4)_2$(**5**), [1,1-$(THF)_2$-*commo*-1,1′-Eu(1,2,4-$EuC_2B_{10}H_{12})_2][NEt_4]_2$, has been established crystallographically and is shown in Figure 3 along with some important interatomic distances and angles. The europium atom is sandwiched by two [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ ligands, and two coordinated THF molecules form the remainder of the coordination sphere about europium. Dianion **5** has a 2-fold axis which passes through europium and relates one carboranyl and one THF ligand to the other two ligands. The Eu–carborane (Eu–C and Eu–B) distances fall in the range 2.89–3.20 Å. The Eu–O(THF) distance is 2.63 (1) Å. The angles around europium which involve the two apical boron atoms B(13) and the two THF oxygen atoms O(1T) are 127.4 (3) and 74.8 (3)°, respectively, and are very similar to those reported previously (ring centroid–Sm–ring centroid angle is 131.9°, O(THF)–Sm–O(THF) angle is 79.5°) for the bis(dicarbollide) samarium sandwich complex[21,22] [3,3-$(THF)_2$-*commo*-3,3′-Sm(3,1,2-$SmC_2B_9H_{11})_2$][PPN]. In the complex $(NEt_4)_2$(**5**), the B(13)–Eu(1)–O(1T) angles are 109.9 (3) and 111.3 (3)°. Thus, the coordination geometry about the europium atom in anion **5** could be viewed as that of a distorted tetrahedron.

The C_2B_{10} fragment in **5** can be compared with related metallacarborane complexes. The interatomic distance B(3)···B(8) in **5** is 2.14 (2) Å and is very similar to that found in the complex[9] [*closo*-1,1-$(PPh_3)_2$-1-H-1,2,4-$RhC_2B_{10}H_{12}$] (2.166 Å) but is longer than that reported for the complex[11] [*closo*-1-(η^5-C_5H_5)-1,2,4-$CoC_2B_{10}H_{12}$] (2.082 Å). The B(9)···C(2) interatomic distance in anion **5** is 2.65 (2) Å and is somewhat shorter than 2.72 Å

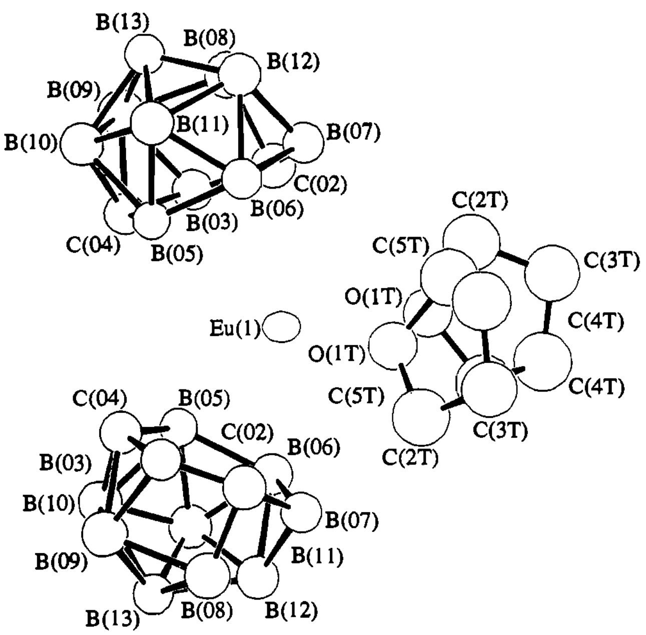


Figure 3. Molecular structure of the anion $[1,1\text{-}(THF)_2\text{-}\textit{commo}\text{-}1,1'\text{-}Eu(1,2,4\text{-}EuC_2B_{10}H_{12})_2]^{2-}$ (**5**). All hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Eu(1)–O(1T), 2.63 (1); Eu(1)–C(2), 2.89 (1); Eu(1)–B(3), 3.09 (2); Eu(1)–C(4), 3.20 (1); Eu(1)–B(5), 2.98 (2); Eu(1)–B(6), 2.99 (2); C(2)–B(3), 1.45 (2); C(2)–B(7), 1.55 (2); C(4)–B(3), 1.60 (2); C(4)–B(5), 1.64 (2). Selected bond angles (deg): B(13)–Cu(1)–B(13), 127.4 (3); O(1T)–Eu(1)–O(1T), 74.8 (3); B(13)–Eu(1)–O(1T), 109.9 (3) and 111.3 (3).

reported for the complex[9] $[\textit{closo}\text{-}1,1\text{-}(PPh_3)_2\text{-}1\text{-}H\text{-}1,2,4\text{-}RhC_2B_{10}H_{12}]$. The C(2)···B(12) interatomic distance (2.83 (2) Å) found in anion **5** is nearly the same as reported for the complex[9] $[\textit{closo}\text{-}1,1\text{-}(PPh_3)_2\text{-}1\text{-}H\text{-}1,2,4\text{-}RhC_2B_{10}H_{12}]$ (2.841 Å) whereas the B(3)···B(10) interatomic distance (2.91 (2) Å) found in **5** is nearly identical to 2.938 Å reported for the complex $[\textit{closo}\text{-}1,1\text{-}(PPh_3)_2\text{-}1\text{-}H\text{-}1,2,4\text{-}RhC_2B_{10}H_{12}]$.[9] In anion **5**, the four boron atoms in the upper belt (bonding face) of the $C_2B_{10}H_{12}$ fragment are coplanar (within 0.002 Å), with C(2) lying above (0.205 Å) and C(4) lying below (0.191 Å) this plane. The five boron atoms of the lower belt of the $C_2B_{10}H_{12}$ fragment are coplanar (within 0.06 Å). The planes defined by the upper and the lower belts of the $C_2B_{10}H_{12}$ fragment are nearly parallel (4.6° between their normals). Both the carbon atoms C(2) and C(4) interact asymmetrically with the adjacent boron atoms in the upper belt [C(2)–B(3), C(2)–B(7), C(4)–B(3), and C(4)–B(5) distances are 1.45 (2), 1.55 (2), 1.60 (2), and 1.64 (2) Å, respectively], in contrast to the case of complex **7**.[24] In the latter complex, the carbon atom which lies above the plane defined by four borons in the upper belt interacts nearly symmetrically with the boron atoms [C(2)–B(3) and C(2)–B(7) distances are 1.519 (8) and 1.510 (7) Å, respectively] whereas the other carbon atom, which lies below the plane, interacts asymmetrically with the adjacent boron atoms [C(4)–B(3) and C(4)–B(5) distances are 1.645 (8) and 1.697 (7) Å, respectively].[24]

The structural characterization of $(NEt_4)_2$(**5**) represents the first example of its kind of lanthanacarboranes which contain two $[\textit{nido}\text{-}7,9\text{-}C_2B_{10}H_{12}]^{2-}$ ligands. The bent sandwich arrangement observed in anion **5** is similar to that observed in the complexes $[3,3\text{-}(THF)_2\text{-}\textit{commo}\text{-}3,3'\text{-}Sm(3,1,2\text{-}SmC_2B_9H_{11})_2][PPN]$,[21,22] $(C_5Me_5)_2Ln$ (Ln = Sm, Eu),[26] $(C_5Me_5)_2Sm(L)$,[27] $(C_5Me_5)_2Sm(THF)_2$,[28] and $[(C_5Me_5)_2Sm(THF)_2]^+[BPh_4]^-$.[29] The reversible transformations between **2** and **5** strongly support our previous observations that the bonding between a lanthanide metal ion center and an anionic carborane ligand is quite ionic in character. This observation is not surprising due to the fact that the 4f orbitals of the lanthanide do not have significant radial extension beyond the filled $5s^25p^6$ orbitals. The restricted radial function[5] of the f orbitals ensures that they are not energetically accessible for significant participation in bonding,[30] and as a result, lanthanide-metal ions resemble the alkali-metal and alkaline-earth-metal ions. In lanthanide chemistry, Coulombic and stereochemical considerations are seemingly more important in determining the stability of a lanthanide complex than the covalent bonding interactions between the lanthanide-metal and ligand orbitals.

Experimental Section

All manipulations were performed under an atmosphere of dinitrogen or argon with the exclusion of air and moisture. Reagents were handled by using a combination of Schlenk, vacuum-line, and glovebox (Vacuum Atmospheres HE-43-2 Dri Lab) techniques.

Materials. The solvents, THF and Et_2O were distilled over Na/benzophenone whereas MeCN was distilled over P_2O_5 prior to use. Traces of O_2 were removed by three freeze–pump–thaw cycles; the solvents were then taken into the glovebox and stored over molecular sieves (4 Å). The direct interaction of $\textit{closo}\text{-}1,2\text{-}C_2B_{10}H_{12}$ (0.5 g, 3.47 mmol) and Na metal (0.35 g, 15.21 mmol) in THF at room temperature over a period of 16 h followed by filtration through Celite gives a THF solution of $Na_2[\textit{nido}\text{-}7,9\text{-}C_2B_{10}H_{12}]$ (0.65 g, 3.42 mmol, 100% conversion). Solutions of $LnI_2(THF)_2$ (Ln = Sm, Eu, Yb) were prepared from excess Ln metal (Research Chemicals, Phoenix, AZ) and 1,2-diiodoethane (Aldrich) in THF at room temperature.[31] $EuCl_3$ was purchased from Cerac Chemicals, Inc., and was used without any further purification.

Characterization Methods. The ^1H and ^{11}B FT NMR measurements were performed on a Bruker AM-500 instrument at 500.13 and 160.463 MHz, respectively. Proton chemical shifts were referenced to residual solvent protons: $CH_3CN\text{-}d_3$, 1.93 ppm. Boron chemical shifts were externally referenced to $BF_3\cdot OEt_2$ in C_6D_6; peaks upfield of the reference are designated as negative. Samples for IR spectroscopy were obtained from a Nujol mull (NaCl; spectra were taken immediately after the mull was prepared in a glovebox) on a Beckman FT IR Fourier Transform spectrometer. Complexometric metal analyses were conducted by titration with EDTA.[32]

$[\textit{closo}\text{-}1,1,1\text{-}(THF)_3\text{-}1,2,4\text{-}SmC_2B_{10}H_{12}]_n$ (1). A THF solution of $Na_2[\textit{nido}\text{-}7,9\text{-}C_2B_{10}H_{12}]$ (0.59 g, 3.1 mmol) was added dropwise to a stirred THF solution of $SmI_2(THF)_2$ (1.69 g, 3.08 mmol) at room temperature over a period of 1.5 h. The reaction mixture was allowed to stir for 20 h. After that time, stirring was stopped and the solid product was allowed to separate. The supernatant was cannulated from the reddish brown solid which had precipitated during the course of the reaction. The solid was washed four or five times with THF and then dried in vacuo to give 0.9 g of $[\textit{closo}\text{-}1,1,1\text{-}(THF)_3\text{-}1,2,4\text{-}SmC_2B_{10}H_{12}]_\infty$ (**1**) in 57% yield. IR (Nujol mull, NaCl): 2530 (s), 2467 (s), 2395 (m), 1210 (w, br), 1180 (w, br), 1031 (s), 968 (w), 915 (w), 881 (s) cm^{-1}. ^1H NMR (ppm, THF-d_8): 4.2 (s, carboranyl CH). Hydrolysis of **1** in $CH_3CN\text{-}d_3$ with a slight molar excess of H_2O and subsequent examination by NMR spectroscopy showed the presence of free THF and $[C_2B_{10}H_{13}]^-$ in the ratio of 4:1. The $^{11}B\{^1H\}$ NMR spectrum consisted of extremely broad, unresolved resonances. The effective magnetic moment (25 °C) was 3.7 μ_B. Complexometric anal. Calcd for $C_{18}H_{44}O_4B_{10}Sm$: Sm, 25.82. Found: Sm, 26.7. This suggests that complex **1** exists in solution as a monomer with the formulation $[Sm(C_2B_{10}H_{12})(THF)_4]$.

$[\textit{closo}\text{-}1,1,1\text{-}(L)_3\text{-}1,2,4\text{-}EuC_2B_{10}H_{12}]_n$ (L = THF (2), MeCN (4)). A THF solution of $Na_2[\textit{nido}\text{-}7,9\text{-}C_2B_{10}H_{12}]$ (0.5 g, 2.6 mmol) was added dropwise to a THF solution of $EuI_2(THF)_2$ (1.5 g, 2.7 mmol) at room temperature over a period of 0.5 h. The reaction was then allowed to stir for 16 h. The orange solution was cannulated from the yellow solid which had precipitated during the course of the reaction. The yellow solid was washed four or five times with THF in order to remove unreacted $Na_2[\textit{nido}\text{-}7,9\text{-}C_2B_{10}H_{12}]$ and then dried in vacuo to give 1.0 g of $[\textit{closo}\text{-}1,1,1\text{-}(THF)_3\text{-}1,2,4\text{-}EuC_2B_{10}H_{12}]_n$ (**2**) (71.5% yield). IR (Nujol mull, NaCl): 2525 (s), 2468 (s, br), 2391 (m), 1066 (s), 883 (m) cm^{-1}. Complex **2**, when dissolved in MeCN, yields $[\textit{closo}\text{-}1,1,1\text{-}(MeCN)_3\text{-}1,2,4\text{-}EuC_2B_{10}H_{12}]_\infty$ (**4**) quantitatively. IR (Nujol mull, NaCl): 2522

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(s, br), 2458 (s, br), 2301 (m), 2267 (s) cm^{-1}. ^1H NMR (CD_3CN, 20 °C, ppm): 3.63 (s, br, carboranyl CH). ^{11}B NMR (in MeCN, 20 °C, ppm; chemical shifts referenced to external $BF_3{\cdot}OEt_2$; peaks upfield of the reference designated as negative; areas given in parentheses): −5.9 br (3), −15.6 br (2). Anal. Calcd for $C_8H_{21}B_{10}N_3Eu$: C, 22.91; H, 5.01; N, 10.02. Found: C, 20.76; H, 4.69; N, 8.07. Combustion analyses of compounds of this type are normally inaccurate.

[*closo*-1,1,1,1-(THF)$_4$-1,2,4-YbC$_2$B$_{10}$H$_{12}$] (3). The THF solution of Na_2[*nido*-7,9-$C_2B_{10}H_{12}$] (0.475 g, 2.5 mmol) was added to a stirred THF solution of $YbI_2(THF)_2$ (1.42 g, 2.49 mmol) at room temperature over a period of 2 h. The reaction mixture was then allowed to stir at room temperature for 20 h. The supernatant was cannulated from the bright purple solid which had precipitated during the course of the reaction. The solid was washed four or five times with THF and then dried in vacuo to give 0.89 g of [*closo*-1,1,1,1-(THF)$_4$-1,2,4-YbC$_2$B$_{10}$H$_{12}$] (**3**) in 59% yield. IR (Nujol mull, NaCl): 2513 (s, br), 2430 (s), 1252 (w, br), 1176 (w), 1028 (s), 983 (w), 914 (w, sh), 872 (s). ^1H NMR (ppm, THF-d_8): 1.6 (s, carboranyl CH). Hydrolysis of **3** in CD_3CN-d_3 with a slight molar excess of H_2O and subsequent examination by NMR spectroscopy showed the presence of free THF and $[C_2B_{10}H_{13}]^-$ in the ratio of 4:1. The $^{11}B\{^1H\}$ NMR spectrum consisted of extremely broad, unresolved resonances. The effective magnetic moment (25 °C) was 0.0 μ_B. Complexometric anal. Calcd for $C_{18}H_{44}O_4B_{10}Yb$: Yb, 28.60. Found: Yb, 28.39.

Synthesis of [1,1-(THF)$_2$-*commo*-1,1′-Eu(1,2,4-EuC$_2$B$_{10}$H$_{12}$)$_2$][NEt$_4$]$_2$ ((NEt$_4$)$_2$(5)). A THF solution of Na_2[*nido*-7,9-$C_2B_{10}H_{12}$] (0.34 g, 1.79 mmol) was added dropwise to a THF solution of [*closo*-1,1,1-(THF)$_3$-1,2,4-EuC$_2$B$_{10}$H$_{12}$]$_\infty$ (**2**) (1.0 g, 1.953 mmol) at room temperature over a period of 1.0 h. The reaction mixture was then allowed to stir for 20 h. Stirring was then stopped and the reaction contents were allowed to stand for 1.0 h. A pale orange supernatant was either cannulated away or filtered through Celite to remove unreacted complex **2**. The solvent was removed in vacuo, yielding 0.8 g of an orange complex [1,1-(THF)$_2$-*commo*-1,1,′-Eu(1,2,4-EuC$_2$B$_{10}$H$_{12}$)$_2$][Na]$_2$ (65% yield). This latter complex can also be prepared by the reaction of $EuI_2(THF)_2$ and excess Na_2[*nido*-7,9-$C_2B_{10}H_{12}$]. In a typical reaction, $EuI_2(THF)_2$ (1.0 g, 1.818 mmol) was dissolved in THF and a THF solution of Na_2-[*nido*-7,9-$C_2B_{10}H_{12}$] (0.66 g, 3.47 mmol) was added dropwise at room temperature over a period of 1.0 h. The reaction was allowed to stir for 20 h. The reaction was then stopped, and the supernatant was filtered through Celite followed by removal of solvent in vacuo to yield 0.78 g of the yellow complex [1,1-(THF)$_2$-*commo*-1,1′-Eu(1,2,4-EuC$_2$B$_{10}$H$_{12}$)$_2$][Na]$_2$ in 70% yield. Metathesis of this complex with Et_4NCl (0.262 g, 1.583 mmol) in MeCN affords an orange solution which upon removal of solvent gives an orange solid. The solid was dissolved in THF, and the solution was filtered through Celite. The volume of the filtrate was then concentrated to approximately 15 mL. Excess Et_2O was added to it, and the resulting solution was then allowed to stand undisturbed at room temperature, affording pale orange crystals of (NEt_4) (**5**). IR (Nujol mull, NaCl): 2484 (s, br), 2417 (s, br) cm^{-1}. FAB MS (*m*/*e*, fragment): found, 845.010 (M^+); calcd, 845.140 (M^+). ^{11}B NMR (THF-d_8, 20 °C, ppm; chemical shifts referenced to external $BF_3{\cdot}OEt_2$; peaks upfield of the reference designated as negative; areas given in parentheses): −9.49 (1), $^1J_{BH}$ = 128 Hz, −0.6 (4), $^1J_{BH}$ = 149 Hz, 3.44 (2), $^1J_{BH}$ = 145 Hz, 9.95 (1), $^1J_{BH}$ = 154 Hz, 29.1 (1), $^1J_{BH}$ = 158 Hz.

Alternate Route to 2 from 5. In a typical reaction, $(NEt_4)_2$(**5**) (0.5 g, 0.82 mmol) was dissolved in THF, and a THF solution of $EuI_2(THF)_2$ (0.46 g, 0.836 mmol) was added at room temperature over a period of 1.0 h. The reaction was then allowed to stir for 16 h. After that time, stirring was stopped, the reaction mixture was allowed to settle, and the supernatant was cannulated from the yellow solid which had precipitated during the course of the reaction. The yellow solid was washed four or five times with THF in order to remove unreacted Na_2[*nido*-7,9-$C_2B_{10}H_{12}$] and then dried in vacuo to give 0.36 g of **2** (86% yield).

Reaction of 2 with NaC$_5$Me$_5$. Complex **2** (1.0 g, 1.9 mmol) was stirred in THF with an equimolar ratio of NaC_5Me_5 (0.30 g, 1.9 mmol) at room temperature for 16 h. The stirring was then stopped, and the reaction mixture was allowed to stand undisturbed for another 1.0 h. The pale orange supernatant was filtered through Celite, followed by removal of solvent in vacuo, to give a yellowish orange solid. Recrystallization of this complex from THF/Et_2O yielded Na_2(**5**) as a crystalline solid.

Collection and Reduction of X-ray Data for 4. An orange crystal, obtained from a MeCN/Et_2O solution, was sealed in a capillary on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of this department. Systematic absences were found for $0k0$ reflections for which $k \neq 2n$ and for $h0l$ reflections for which $h + l \neq 2n$. Unit cell parameters were determined from a least-squares fit of 34 accurately centered reflections ($10.1 < 2\theta < 20.4°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table I. Data were collected at 128 K in the θ–2θ scan mode. Three intense reflections ($12\bar{3}$, $60\bar{4}$, $\bar{6}04$) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (144 h). Of the 6609 unique reflections measured, 4745 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for absorption. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculations and full-matrix least-squares refinement; ABSCOR, locally written absorption program based on ψ scans; SHELX76 (Sheldrick), a crystal structure package; ORTEP (Johnson).

Table I. Details of the Crystallographic Data Collection for **4** and $(NEt_4)_2$(**5**)

compd	**4**	$(NEt_4)_2$(**5**)
chem formula	$C_8H_{21}B_{10}N_3Eu$	$C_{28}H_{80}B_{20}O_2N_2Eu$
fw	418.96	843.96
space group	$P2_1/n$	I2/c^a
a/Å	20.146 (6)	18.571 (7)
b/Å	9.909 (3)	9.396 (3)
c/Å	20.871 (6)	27.813 (10)
β/deg	118.838 (7)	103.38 (1)
V/Å^3	3650	4721
Z	8	4
ρ(calcd)/g cm^{-3}	1.68	1.2
μ/cm^{-1}	34	13.6
no. of unique reflns	6609	1499
no. of obsd ($I > 3\sigma(I)$) reflns	4745	1201
2θ max/deg	50	35
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$
R, R_w, GOF^b	0.041, 0.057, 1.84	0.050, 0.059, 1.89

^{a} Non standard setting. The $C2/c$ parameters are a = 29.655 Å, b = 9.396 Å, c = 18.571 Å, and β = 114.16°. The transform of the I-centered cell to the C-centered cell is

$$\begin{matrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{matrix}$$

The reduced cell (triclinic) is a = 15.554 Å, b = 18.571 Å, c = 9.396 Å, α = 90.00°, β = 107.58°, and γ = 112.96°. ^{b} $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. $R = \sum||F_o| - |F_c||/|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Solution and Refinement of the Structure of 4. Atoms were located by use of heavy-atom methods. All calculations were performed on the VAX 3100 computer of the J. D. McCullough X-ray Crystallography Laboratory. All methyl hydrogens were included in calculated positions as members of rigid groups; C–H = 1.0 Å, H–C–H = 109.5°. All carboranyl hydrogens were kept in located positions. H atoms were assigned u values of 0.05 or 0.04 Å^2 for methyl and carboranyl hydrogens, respectively. Scattering factors for H were obtained from Stewart and co-workers,[33] and those for other atoms were taken from the ref 34. Anomalous dispersion terms were applied to the scattering of Eu. The larger peaks on a final difference electron density map were 0.6 e Å^{-3}.

Collection and Reduction of X-ray Data for (NEt$_4$)$_2$(5). An orange crystal, obtained from a MeCN/Et_2O solution, was sealed in a capillary on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of this department. Systematic absences were found for hkl reflections for which $h + k + l \neq 2n$ and for $h0l$ reflections for which $l \neq 2n$. Unit cell parameters were determined from a least-squares fit of 17 accurately centered reflections ($4.4 < 2\theta < 13.5°$). Strong reflections at higher 2θ values were not found for this very thin crystal; therefore, the maximum value of 2θ was set at the unusually low value of 35°. These dimensions and other parameters, including conditions of data collection, are summarized in Table I. Data were collected at 25 °C in the θ–2θ scan mode. Three intense reflections ($31\bar{4}$, 202, $01\bar{1}$) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay and fluctuated a maximum of ±4.5% during the course of the experiment (60.5 h). Of the 1499 unique reflections measured, 1201 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing),

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peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculations and full-matrix least-squares refinement; ABSCOR, a locally written ψ-scan-based absorption correction calculation; ORTEP (Johnson).

Solution and Refinement of the Structure of $(NEt_4)_2(5)$. Atoms were located by use of heavy-atom methods. All calculations were performed on the VAX 3100 computer of the J. D. McCullough X-ray Crystallography Laboratory. All carboranyl hydrogens were included in located positions. All methyl and methylene hydrogens were included in calculated positions in structure factor calculations (C–H = 1.0 Å), with an assigned u value of 0.06 (carboranyl), 0.10 (THF), or 0.08, 0.10, or 0.11 (cation) Å^2. H parameters were not refined. Scattering factors for H were obtained from Stewart and co-workers,[33] and those for other atoms were taken from ref 34. Anomalous dispersion terms were applied to the scattering of Eu. The largest peak on a final difference electron density map was 1.0 e Å^{-3}.

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Supplementary Material Available: Tables of crystallographic data collection, atom coordinates, bond distances and angles, torsion angles, and positional and thermal parameters for **4** and $(NEt_4)_2(5)$ (14 pages); tables of observed and calculated structure factors for **4** and $(NEt_4)_2(5)$ (34 pages). Ordering information is given on any current masthead page.

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Preparation, Characterization, and X-ray Crystal Structures of $S_2I_4(MF_6)_2$ (M = As, Sb) and the Electronic Structure of the Highly π-Bonded Eclipsed Disulfur Tetraiodine(2+) Cation: Thermodynamic Considerations and the Nonexistence of $SI_3AsF_6(s)$

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Crystalline $S_2I_4(AsF_6)_2$ was prepared quantitatively by the reaction of stoichiometric amounts of S_8, I_2, and AsF_5, in liquid SO_2, and in reactions designed to give $SI_3AsF_6(s)$. It was also a product of reactions designed to give various other related sulfur–iodine cations. Crystalline $S_2I_4(SbF_6)_2$ was prepared essentially quantitatively by the reaction of stoichiometric amounts of S_8, I_2, and SbF_5, designed to give $S_2I_4(SbF_6)_2$ and $5SbF_3{\cdot}3SbF_5$. Crystal data for $S_2I_4(AsF_6)_2$: monoclinic, space group $C2/c$ (No. 15), a = 9.650 (2) Å, b = 12.874 (2) Å, c = 13.644 (1) Å, β = 93.79 (2)°, Z = 4, R = 0.049 (R_w = 0.054) for 948 significant reflections. Crystal data for $S_2I_4(SbF_6)_2$: orthorhombic, space group $Cmcm$ (No. 63), a = 9.850 (4) Å, b = 13.067 (9) Å, c = 13.782 (9) Å, Z = 4, R = 0.051 (R_w = 0.058) for 568 significant reflections. The $S_2I_4(MF_6)_2$ salt consist of $S_2I_4^{2+}$ and MF_6^- [M = As, Sb] with weak cation–anion interactions. The $S_2I_4^{2+}$ cations have distorted right-triangular-prismatic structures, with symmetry C_2 (AsF_6^-) and C_{2v} (SbF_6^-). Each cation consists of two quadrilateral S_2I_2 units joined at the common S–S bond, with interplanar angles of 89.8 (1)° (AsF_6^-) and 91.3 (1)° (SbF_6^-). The S–S distances of 1.818 (10) Å (SbF_6^-) and 1.843 (6) Å (AsF_6^-) are the shortest reported for an isolated compound and correspond to bond orders of 2.7 and 2.4, respectively. The I–I bonds are 2.571 (2) Å (SbF_6^-) and 2.5987 (17) Å (AsF_6^-), corresponding to bond orders 1.4 and 1.3. The S–I bond distances are 2.993 (4) Å (SbF_6^-) and 2.860 (4) and 3.178 (4) Å (AsF_6^-). A simple model for the bonding in $S_2I_4^{2+}$ is proposed in which an S_2 unit is bonded to two I_2^+ units by two mutually perpendicular four-center–two-electron π^*–π^* bonds, with some charge redistribution resulting in a +0.33 charge on each of the six atoms. This model is supported by quantum-mechanical STO-3G ab initio calculations on rectangular Cl_4^{2+}, as a two dimensional model of the bonding in $S_2I_4^{2+}$, and calculations on $O_2Cl_4^{2+}$ of suitable geometry. The enthalpy of the formation of $S_2I_4(AsF_6)_2(s)$ from corresponding amounts of S_8, I_2, and AsF_5 is estimated by a simple model to be much more favorable than that of $2SI_3AsF_6(s)$. In addition, the enthalpy of disproportionation of the hypothetical $2SI_3AsF_6(s)$ to $S_2I_4(AsF_6)_2(s)$ and $I_2(s)$ is estimated to be substantially exothermic and the enthalpy of isomerization of the observed π-bonded $S_2I_4^{2+}$ to the classical σ-bonded $I_2S^+S^+I_2$ is also estimated to be endothermic.

Introduction

Binary compounds of sulfur and iodine were at one time unknown.[2,3] Since then, the formation of S_2I_2 and SI_2 have been demonstrated[4–6] but not binary selenium iodides.[7] However, SeI_6^{2-} has been known for some time,[8] and more recently we have prepared SeI_3MF_6 (M = As, Sb),[9,10] containing SeI_3^+. In fact salts of all possible chalcogen trihalide cations, $M'X_3^+$ (M′ = S, Se, Te; X = I, Br, Cl, F) have all been prepared and characterized,[10] with the exception of SI_3^+. There seemed no obvious reason why SI_3MF_6 should not have been preparable by similar routes. However, all our attempts to prepare $SI_3AsF_6(s)$ by a wide variety of routes, including those using an excess of iodine, led to $S_2I_4(AsF_6)_2(s)$ and $I_2(s)$. Reactions in which larger amounts of sulfur were present led to our discovery of S_7IMF_6,[11] $(S_7I)_2I(SbF_6)_3{\cdot}2AsF_3$,[12a,b] and $(S_7I)_4S_4(AsF_6)_6$.[12a,c] In this paper we give a full account of the various reactions that lead to $S_2I_4(MF_6)_2(s)$, and account for the greater stability of $S_2I_4(AsF_6)_2(s)$ and $I_2(s)$, relative to 2 $SI_3(AsF_6)_2(s)$.

$S_2I_4^{2+}$ has a distorted right-triangular-prismatic structure, the only known example of this type, very different from the isoelectronic classically σ-bonded *trans*-$P_2I_4(s)$.[13a] It contains the shortest sulfur–sulfur bond distance [1.843 (6) Å (AsF_6^-), 1.818

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