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Cubane Clusters Containing Lanthanide Ions: $(py)_8Yb_4Se_4(SePh)_4$ and $(py)_{10}Yb_6S_6(SPh)_6$

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The extensive family of M_4E_4 (E = S, Se, Te) cubane clusters has been expanded to include lanthanide ions, with the synthesis and isolation of $(py)_8Yb_4Se_4(SePh)_4$ (**1**) and $(py)_{10}Yb_6S_6(SPh)_6$ (**2**). The successful inclusion of a redox-active Ln ion into a cubane core establishes the possibility of synthesizing novel magnetic or unusually reactive cubanes, and the presence of labile neutral donor ligands on each Yb(III) ion creates an opportunity for preparing ordered cluster arrays.

Chalcogenido clusters of the p-,[1] d-,[2] and f-block[3] metals continue to attract attention as models for understanding the relationships between molecular and solid state physical properties. The well-documented family of M_4E_4 cubane clusters,[4] which encompass homo- and heterometallic compounds, are particularly well studied. While cubane chemistry spans virtually the entire d block, i.e., from V to Cu or from Cr to W, the analogous f-block derivatives do not exist. Much of the cubane synthetic effort is driven by the interest in understanding the important redox activity of cubane fragments in nitrogenase, but these compounds also show interesting chemical/physical properties and have potential applications in materials synthesis.[5] We report here that chalcogenolate complexes of the smaller lanthanides react with elemental E to form Ln_4E_4 cubes with octahedral Ln(III) ions.

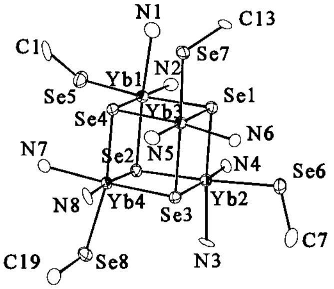

Figure 1. Molecular structure of $(py)_8Yb_4Se_4(SePh)_4$ (**1**) with the C and H atoms removed. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Yb1−Se4, 2.765(1); Yb1−Se2, 2.797(1); Yb1−Se1, 2.812(1); Yb1−Se5, 2.827(2); Yb2−Se1, 2.760(1); Yb2−Se3, 2.770(1); Yb2−Se2, 2.806(1); Yb2−Se6, 2.808(1); Yb3−Se4, 2.767(1); Yb3−Se1, 2.767(1); Yb3−Se3, 2.820(1); Yb3−Se7, 2.863(1); Yb4−Se2, 2.765(1); Yb4−Se3, 2.769(1); Yb4−Se4, 2.773(1); Yb4−Se8, 2.869(1).

The molecular chalcogenolate $(py)_4Yb(SePh)_2$ reduces[6] elemental Se in pyridine to give the cubane cluster $(py)_8Yb_4Se_4(SePh)_4$ (**1**), which can be isolated as deep red crystals in 73% yield.[7] The structure[8] of **1** (Figure 1) contains an alternating array of Yb(III) and Se^{2-} ions at the vertices of a cube, with terminal SePh and two pyridine ligands completing each octahedral Yb(III) coordination sphere. For each of the four Yb atoms, the Yb−selenido bond trans to the terminal SePh ligand is significantly longer than either of the two Yb−Se^{2-} bonds trans to pyridine ligands. Such asymmetric bond lengths were noted previously in the structure of *mer*-$(py)_3Yb(SPh)_3$[9] and can also be found in the structures of the $[(DME)Yb(SePh)_4]$[10] anion and $(py)_3Yb(S\text{-}2,4,6\text{-}{}^iPr_3\text{-}C_6H_3)_3$,[11] all of which suggest the presence of a small but significant trans influence. While a covalent interaction between Ln 4f and chalcogen orbitals seems implausible, the lanthanides do have vacant 5d and 6p shells available, and

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[1] See, for example: (a) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706. (b) Herron, N.; Calabrese, J. C.; Farneth, W. E.; Wang, Y. *Science* **1993**, *259*, 1426. (c) Goldstein, A. N.; Escher, C. M.; Alivisatos, A. P. *Science* **1992**, *256*, 1425. (d) Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 5221. (e) Schreiner, B.; Dehnicke, K.; Fenske, D. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1127.

[2] See, for example: (a) Brennan, J.; Siegrist, T.; Stuczynski, S.; Steigerwald, M. *J. Am. Chem. Soc.* **1992**, *114*, 10334. (b) Dahl, L. F.; Johnson, A.; Whoolery, S. *Inorg. Chim. Acta* **1994**, *227*, 269. (c) Fenske, D.; Fischer, A. *Angew. Chem.* **1995**, *34*, 307. (d) Mathur, P.; Sekar, P. *Chem. Commun.* **1996**, 727.

[3] (a) Evans, W.; Rabe, G.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2110. (b) Cary, D.; Ball, G.; Arnold, J. *J. Am. Chem. Soc.* **1995**, *117*, 3492. (c) Freedman, D.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1997**, *119*, 11112. (d) Melman, J. H.; Emge, T. J.; Brennan, J. G. *Chem. Commun.* **1997**, 2269. (e) Leverd, P. C.; Arliguie, T.; Ephritikhine, M.; Nierlich, M.; Lance, M.; Vigner, J. *New J. Chem.* **1993**, *17*, 769.

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[7] Using standard Schlenk techniques, Yb (0.346 g, 2.00 mmol), PhSeSePh (0.625 g, 2.00 mmol), and Hg (0.05 g, 0.25 mmol) were combined in pyridine (30 mL) to give a solution of $(py)_4Yb(SePh)_2$.[18] After 2 days, Se (0.10 g, 1.25 mmol) was added to the deep purple solution, and within 2 h, the color turned dark red. After an additional 4 h, the volume was concentrated to ca. 20 mL. After 2 weeks, the solution was filtered and layered with hexanes to give dark red crystals (0.58 g, 76% based on Se; the compound does not melt but turns black at ca. 100 °C and eliminates a yellow oil at 170−180 °C). The compound crystallizes with 2.5 isolated pyridine solvate molecules per cluster. Anal. Calcd for $C_{76.5}H_{72.5}N_{10.5}Se_8Yb_4$: C, 37.3; H, 2.97; N, 5.97. Found: C, 36.7; H, 3.14; N, 5.79. ^1H NMR (OC_4D_8, 20 °C) revealed only the pyridine resonances at 8.54, 7.62, and 7.23 ppm. IR (Nujol): 2939 (s), 2857 (s), 2720 (m), 2361 (m), 1911 (w), 1854 (w), 1597 (m), 1578 (m), 1461 (s), 1380 (s), 1263 (w), 1216 (w), 1150 (m), 1068 (w), 1031 (m), 975 (w), 895 (w), 825 (w), 723 (s), 701 (s), 601 (m) cm^{-1}. λ_{max} (THF): 368 nm, with a tail out beyond 600 nm. Cluster **1** can also be prepared by the reaction of $Yb(SePh)_3$ with Se in pyridine,[9] but the product (identified as **1** by mp and unit cell[8]) is isolated in lower (ca. 5%) yield.

[8] **1** crystallizes in the triclinic space group $P\bar{1}$, with $a = 13.752(3)$ Å, $b = 17.059(2)$ Å, $c = 18.548(5)$ Å, $\alpha = 89.45(1)°$, $\beta = 75.97(1)°$, $\gamma = 71.72(2)°$, $V = 3998(1)$ Å^3, $Z = 2$, $\rho_{calc} = 2.046$ g cm^{-3} (Mo Kα radiation at −120 °C; the crystals desolvate within 1 h at room temperature). Full-matrix least-squares refinement of 922 parameters and 1314 restraints with 8134 unique observations $[F > 2\sigma(F)]$ gave $R(F) = 0.045$, $R_w(F^2) = 0.103$. Complete crystallographic details are given in the Supporting Information.

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covalent bonding descriptions involving these orbitals have routinely been applied to Ln_2E_3 solids.[12]

The analogous sulfur compound was targeted next, and because SPh is not abstracted from Ln ions by $Hg(SPh)_2$,[13] the sulfur cube can most easily be prepared by first reducing PhSSPh with a Yb/Hg amalgam in pyridine to form $Yb(SPh)_3$ and then adding elemental S to the mixture. Saturation of the filtered solution gives red crystals of $(py)_{10}Yb_6S_6(SPh)_6$ (**2**) in 59% yield.[14] Cluster **2** (Figure 2) is a cubane fragment with an additional Yb_2S_2 layer capping one of the cube faces.[15] There are three different octahedral Yb(III) coordination environments: four S^{2-} and two py (Yb3, Yb4); three S^{2-}, 2 py, and 1 SPh (Yb2, Yb6); 3 S^{2-}, 1 py, and 2 SPh (Yb1, Yb5). Again, the Yb−S^{2-} bond lengths adopt a range of values that are consistent with a trans influence. The Yb−μ_4-S^{2-} bonds trans to S atoms (Yb1−S4; Yb5−S3) are significantly longer than the corresponding bonds trans to pyridine (Yb6−S4; Yb2−S3); these bonds are also longer than any of the Yb3−S or Yb4−S bonds, all of which are trans to pyridine. Of the μ_3-S^{2-} ligands, Yb−μ_3-S^{2-} bond lengths trans to SPh average 0.010−0.037(1) Å longer than the Yb−μ_3-S^{2-} bonds trans to py.

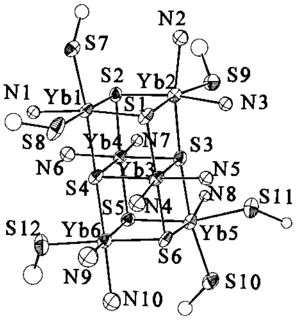

Figure 2. Molecular structure of $(py)_{10}Yb_6S_6(SPh)_6$ (**2**) with the C and H atoms removed. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Yb1−S1, 2.648(7); Yb1−S2, 2.671(6); Yb1−S8, 2.679(7); Yb1−S7, 2.677(7); Yb1−S4, 2.803(7); Yb2−S2, 2.631(7); Yb2−S3, 2.656(7); Yb2−S1, 2.668(7); Yb2−S9, 2.699(7); Yb3−S1, 2.621(7); Yb3−S6, 2.632(7); Yb3−S3, 2.681(6); Yb3−S4, 2.713(7); Yb4−S5, 2.630(6); Yb4−S2, 2.640(7); Yb4−S3, 2.678(7); Yb4−S4, 2.692(6); Yb5−S11, 2.654(7); Yb5−S6, 2.666(6); Yb5−S10, 2.680(7); Yb5−S5, 2.690(7); Yb5−S3, 2.733(7); Yb6−S5, 2.638(6); Yb6−S6, 2.648(7); Yb6−S12, 2.654(7); Yb6−S4, 2.700(7).

The intense colors of **1** and **2** are tentatively attributed to chalcogenido to Yb(III) charge transfer (CT) absorptions. This assignment is based primarily on the visible spectra of redox-active $Ln(ER)_3$ compounds,[9,16] and from more recent observations that $Sm_8S_6(EPh)_{12}$ (E = S[3d], Se[17]) clusters are light yellow while the analogous $Sm_8Se_6(EPh)_{12}$ selenido clusters are deep orange.[3c,17] Each cluster has a broad absorption maximum (**1**, 368 nm; **2**, 361 nm) that is higher in energy than the LMCT absorption in the corresponding $Yb(EPh)_3$ molecules[9] (E = S, $\lambda_{max} = 470$ nm; Se, $\lambda_{max} = 510$ nm). Further studies are currently in progress to confirm these CT assignments and possibly extract more than a single absorption maximum, to determine the factors that govern cubane formation, to further probe the inequivalent Ln−E bond lengths, and to covalently link these paramagnets in polymeric arrays.

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Supporting Information Available: Complete tables of crystallographic details, atomic positions and displacement parameters, bond geometries, and fully labeled ORTEP diagrams for **1** and **2** (31 pages). Structure factor tables are available from the authors.

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(14) Synthesis of **2**: Yb (0.400 g, 2.31 mmol), PhSSPh (0.757 g, 3.47 mmol), and Hg (0.038 g, 0.19 mmol) were combined in 30 mL of pyridine, and the mixture was stirred for 1 day. Sulfur (0.074 g, 2.31 mmol) was added to the red solution, and after 2 days, the solution was filtered and concentrated in vacuo to ca. 25 mL. The resulting red solution was layered with hexane to give red block crystals (0.60 g, 59%; the compound does not melt but darkens continuously between 50 and 157 °C and does not decompose below 330 °C). IR (Nujol): 2900 (s), 2724 (w), 2671 (w), 1598 (w), 1579 (m), 1461 (s), 1377 (s), 1306 (w), 1261 (w), 1215 (w), 1168 (w), 1151 (w), 1081 (w), 1068 (w), 1029 (w), 1008 (w), 990 (w), 973 (w), 892 (w), 875 (w), 849 (w), 801 (w), 742 (m), 723 (m), 701 (m), 628 (w), 601 (w) cm^{-1}. UV−vis (in 4-$^tBuNC_5H_4$): $\lambda_{max} = 361$ nm. The compound was not sufficiently soluble in pyridine, THF, or CH_3CN to permit an NMR analysis. The compound crystallizes with two isolated pyridine solvate molecules per cluster, but the complex desolvates considerably faster than does cluster **1**. Anal. Calcd for $C_{86}H_{80}N_{10}S_{12}Yb_6$: C, 38.6; H, 3.00; N, 5.23. Found: C, 38.0; H, 3.27; N, 4.25.

(15) **2** crystallizes in the monoclinic space group $P2_1/n$, with $a = 13.681(7)$ Å, $b = 31.856(7)$ Å, $c = 22.462(4)$ Å, $\beta = 93.75(4)°$, $V = 9768(6)$ Å^3, $Z = 4$, $\rho_{calc} = 1.928$ g cm^{-3} (Mo Kα at −120 °C). Full-matrix least-squares refinement of 595 parameters with 5034 unique observations [$F > 2\sigma(F)$] gave $R(F) = 0.061$, $R_w(F^2) = 0.119$. Complete crystallographic details are given in the Supporting Information.

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