

A Trivalent Rare Earth Complex of the Heavier Chalcogenolates: Synthesis and Structural Characterization of $[(\text{py})_2\text{Yb}(\text{SeC}_6\text{H}_5)_2(\mu\text{-SeC}_6\text{H}_5)_2\text{Li}(\text{py})_2]$ (py = pyridine)

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Structural characterization of the bimetallic complex $[(\text{py})_2\text{Yb}(\text{SeC}_6\text{H}_5)_2(\mu\text{-SeC}_6\text{H}_5)_2\text{Li}(\text{py})_2]$ shows that phenylselenolato ligands are sufficiently electronegative to function as the only anionic ligands in a Yb^{III} complex.

The synthesis of solid-state compounds from molecular precursors is currently the subject of intense interest, and there have been numerous reports detailing the synthesis of chalcogenate complexes for use in thermolysis experiments.¹ Analogous chalcogenolate complexes of the rare earth elements are scarce.^{1,f,g,h,2} The tendency of chalcogenolate

ligands to span more than one metal centre, combined with the tendency of the rare earth ions to attain larger coordination numbers whenever sterically possible, generally leads to the formation of insoluble polymeric materials³ unless sterically demanding ligands are bound to the metal centre.^{1,f,g,2} Strong donor solvents can also solubilize rare earth chalcoge-

molates; we report here the synthesis and characterization of the trivalent ytterbium complex $[(\text{py})_2\text{Yb}(\text{SeC}_6\text{H}_5)_2(\mu\text{-SeC}_6\text{H}_5)_2\text{Li}(\text{py})_2]$ **1**.

In our initial attempt to establish the stability of trivalent rare earth arylchalcogenates, we reacted YbCl_3 with 3 equiv. of LiSeC_6H_5 in tetrahydrofuran (THF). No crystalline material was isolated from this reaction, but exposure of the pink solid to pyridine gave a red compound, which was initially soluble in toluene. Saturation of the red toluene solution with hexane gave a red oil, but over a period of days large red crystals formed.† These were shown by single crystal X-ray diffraction‡ to be a molecular bimetallic compound **1**. The octahedral rare earth ion is bound to two terminal [Yb–Se 2.754(2) and 2.789(2) Å] and two bridging [Yb–Se 2.813(2) and 2.833(2) Å] phenylselenolate anions (Fig. 1) and two *trans* pyridine ligands bent away (N–Yb–N 160°) from the bridging phenylselenolate ligands. Binding of both lithium and ytterbium to a selenolato ligand results in a competition for ligand electron density, and a lengthening of the bridging Yb–Se bond relative to the terminal Yb–Se bond. The average terminal Yb–Se distance in **1** is 0.19 Å shorter than the terminal Yb–Se distance [2.961(1) Å] found in the low temperature structure of the divalent ytterbium complex⁴ $(\text{py})_4\text{Yb}(\text{SeC}_6\text{H}_5)_2$. Shannon's table of ionic radii lists six-coordinate Yb^{III} as 0.15 Å smaller than six-coordinate Yb^{II} .⁵

Compound **1** is thermally unstable with respect to pyridine dissociation at room temperature. When isolated, the crystals become opaque within a day at room temperature. In the solid state and in pyridine, the complex is intensely coloured, and we attribute this optical absorption to a charge-transfer excitation from a terminal phenylselenolate ligand to the trivalent metal. A pyridine solution of the complex is red, while in THF the complex gives a colourless solution. An NMR spectrum of **1** in $[\text{D}_8]\text{THF}$ contains diamagnetic and paramagnetic phenylselenolate resonances, indicating that all the phenylselenolate ligands are no longer bound to the Yb ion, and that anion exchange between the diamagnetic and paramagnetic metal centres is slow on the NMR timescale. The resonances of ligands bound to the paramagnetic ytterbium ion are considerably broader ($\nu_{1/2} = 50$ MHz for the highest upfield pyridine signal), and there is also substantial

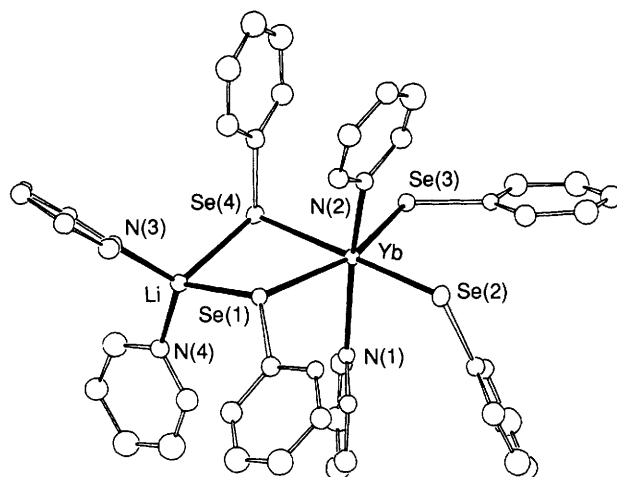


Fig. 1 Molecular structure of $[(\text{py})_2\text{Yb}(\text{SeC}_6\text{H}_5)_2(\mu\text{-SeC}_6\text{H}_5)_2\text{Li}(\text{py})_2]$ **1**. The octahedral Yb^{III} ion is surrounded by *trans* pyridine ligands, two *cis*- $\mu\text{-SeC}_6\text{H}_5$ ligands bridging to the lithium ion and two terminal SeC_6H_5 ligands. The lithium coordination sphere is a distorted tetrahedron. Significant distances (Å): Yb–Se(1) 2.813(2), Yb–Se(2) 2.754(2), Yb–Se(3) 2.789(2), Yb–Se(4) 2.833(2), Yb–N(1) 2.46(2), Yb–N(2) 2.40(2), Li–Se(1) 2.57(3); Li–Se(4) 2.69(3), Li–N(3) 2.00(3), Li–N(4) 1.96(4). Significant angles (°): Yb–Se(1)–C 119.0(6), Yb–Se(2)–C 109.5(6), Yb–Se(3)–C 117.0(6), Yb–Se(4)–C 97.8(7), Se(1)–Yb–Se(4) 78.1(1), Se(2)–Yb–Se(3) 104.3(1), Se(3)–Yb–Se(4) 79.3(1), Se(1)–Yb–Se(2) 98.4(1).

broadening (with no difference in chemical shift) of the THF resonances, indicating that in solution there is a significant amount of THF bound to the metal. This broadening of the THF resonance can result from partial displacement of pyridine from the metal centre as well as displacement of the bridging phenylselenolate ligands by the oxygen donor.

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References

- (a) A. N. MacInnes, M. B. Power and A. R. Barron, *Chem. Mater.*, 1992, **4**, 11–12; (b) W. E. Farneth, N. Herron and Y. Wang, *Chem. Mater.*, 1992, **4**, 916; (c) K. Osakada and A. Yamamoto, *Inorg. Chem.*, 1990, **30**, 2328; (d) K. Osakada and T. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1987, 1117; R. Nomura, S. Fujii, K. Kanaya and H. Matsuda, *Polyhedron*, 1990, **9**, 361; (e) J. Brennan, T. Siegrist, S. Stuczynski, P. Carroll, P. Rynders, L. Brus and M. Steigerwald, *Chem. Mater.*, 1990, **2**, 403; (f) R. D. Cary and J. Arnold, *J. Am. Chem. Soc.*, 1993, **115**, 2520; (g) A. R. Strzelecki, P. A. Timinski, A. B. Hesel and P. A. Bianconi, *J. Am. Chem. Soc.*, 1992, **114**, 3159; (h) M. Berardin, T. Emge and J. Brennan, *J. Am. Chem. Soc.*, 1993, **115**, 8501.
- H. Schumann, I. Albrecht and E. Hahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 985; D. Berg, C. Burns, R. A. Andersen and A. Zalkin, *Organometallics*, 1988, **8**, 1858; M. Welder, M. Noltemeyer, U. Pieper, H. Schmidt, D. Stalke and F. Edelmann, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 894; D. J. Berg, C. Burns, R. A. Anderson and A. Zalkin, *Organometallics*, 1989, **8**, 1865; A. Zalkin and D. J. Berg, *Acta Crystallogr., Sect. C*, 1988, **44**, 1488; K. Tatsumi, T. Amemiya, H. Kawaguchi and K. Tani, *J. Chem. Soc., Chem. Commun.*, 1993, 773; B. Cetinkaya, P. B. Hitchcock, M. F. Lappert and R. G. Smith, *J. Chem. Soc., Chem. Commun.*, 1992, 932.
- K. S. Gharia, M. Singh, S. Mathur, R. Roy and B. S. Sankhla, *Synth. React. Inorg. Metal-Org. Chem.*, 1982, **12**, 337.
- M. A. Buretea, D. V. Khasnis, M. Berardini, T. J. Emge, M. Brewer and J. G. Brennan, submitted to *Inorg. Chem.*
- R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

† Lithium triethylborohydride (9.0 ml of a 1.0 mol dm^{-3} solution in THF, 9.0 mmol) was added by syringe to a solution of diphenyldiselenide (1.4 g, 4.5 mmol) in THF (40 ml). The solution was stirred for 30 min and taken to a white solid which was then redissolved in THF (20 ml) and added to a slurry of YbCl_3 (0.84 g, 3.0 mmol) and triethylphosphine (1.3 ml, 9.0 mmol). The solution was stirred for 18 h and concentrated to a dark-red oil which was then dissolved in toluene (50 ml). The toluene solution was filtered and taken to dryness, and the red oil was redissolved in pyridine (5 ml). The pyridine was removed, and the oil was dissolved in toluene (15 ml) and layered with an equal amount of hexane. An oil quickly formed which over a period of days gave red needles (0.30 g, 12%), m.p. 97–99 °C. Satisfactory elemental analysis was obtained. The compound desolvates at room temperature. IR ν/cm^{-1} (KBr, Nujol): 1594m, 1571m, 1464s, 1441s, 1378s, 1261w, 1217w, 1149w, 1068m, 1035m, 1020m, 1004m, 802w, 755w, 733s, 701s, 690s, 666m, 626m, 467m. ^1H NMR ($[\text{D}_8]\text{THF}$, 24.5 °C) contains broad overlapping resonances ($\nu_{1/2} = 40\text{--}60$ Hz) at δ 8.56 (py), 7.67 (py), 7.45, 7.28 (py) and 6.95, and sharp multiplets centred at δ 7.20 and 7.12. The pyridine resonances were identified by addition of pyridine to the solution. In NC_5D_5 , overlap with solvent peaks precluded analysis of the spectrum.

‡ Crystal data for **1**: the compound rapidly loses pyridine at room temp., and the crystals become amorphous within 48 h at room temp. in an inert atmosphere. For this reason, X-ray data was collected at low temperature. Space group $Pca2_1$, $a = 23.200(4)$, $b = 9.559(2)$, $c = 19.411(4)$ Å, $V = 4305(1)$ Å³, $Z = 4$, and $\rho_c = 1.729$ g cm^{-3} (Mo-K α radiation at -100 °C). Full-matrix least-squares refinement with 3150 unique reflections [$F_o > 4\sigma(F_o)$] gave $R_f = 0.055$ and $wR_f = 0.059$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.