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Tris(methyltrihydroborato)(tetrahydrofuran)ytterbium(III) complex: structure and volatility

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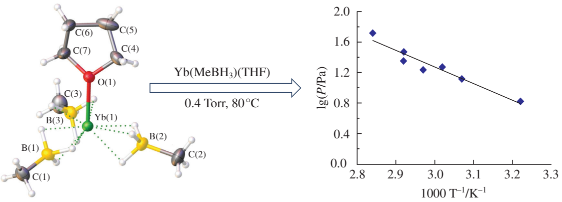
The complex $Yb(BH_3Me)_3(THF)$ has been prepared and characterized by IR and ^1H, ^{13}C and ^{11}B NMR spectroscopy. The crystal and molecular structures of the complex have been solved by single crystal XRD analysis. The vapor pressure as a function of temperature was measured in the batch mode.



The volatile compounds of rare earth elements, including ytterbium, are of interest for the preparation of films and new materials and isotope separation by gas-phase techniques. The volatile alkoxides, fluorinated β-diketonates, cyclopentadienyls, and substituted borohydrides are well known.[1–5] Usually, the saturated vapor pressure of these complexes at 40–100 °C is no higher than 10^{-3} Torr, and their thermal stability is poorly understood. Almost no data on the equilibrium vapor pressures of these compounds were reported, and available information on their volatility is restricted to sublimation under reduced pressure.

As for promising volatile ytterbium compounds, the preparation and structure of Lewis acid adducts of tris(methyltrihydroborato)-complexes, in particular, an adduct of tris(methyltrihydroborato) ytterbium(III) with THF, were published.[5] The expected coordination number of ytterbium(III) in this adduct is 10, and the ligands should effectively shield the central atom thus preventing polymerization and providing high volatility.

Here, we report the preparation, crystal structure, and volatility of tris(methyltrihydroborato)(tetrahydrofuran)ytterbium(III) **1**.

Complex **1** was synthesized from (methyltrihydroborato)lithium and anhydrous ytterbium(III) chloride in an argon atmosphere using a standard Schlenk technique in a glove box.

The lithium salt was prepared from trimethylboroxine and lithium aluminum hydride using a slightly modified published procedure[†,6] with the formation of a by-product of aluminum oxohydride Al(O)H:

$$(B_3O_3)Me_3 + 3\,LiAlH_4 \rightarrow 3\,LiBH_3Me + 3\,Al(O)H. \qquad (1)$$

The resulting solution of $LiBH_3Me$ containing THF was used to prepare the ytterbium complex **1** by the reaction:[‡]

$$YbCl_3 + 3\,LiBH_3Me + THF \rightarrow Yb(BH_3Me)_3(THF) + 3\,LiCl. \qquad (2)$$

The synthetic procedure is simpler than the previously developed one[5] because, in our case, the neutral ligand present in the reaction mixture made it possible to eliminate the step of the replacement of diethyl ether in $Yb(BH_3Me)_3{\cdot}(Et_2O)$ by THF. Note that the low solubility of Al(O)H in diethyl ether and its rapid sedimentation allowed us to prepare $LiBH_3Me$ in a quantitative yield.

The vapor pressure of **1** was measured in a 0.5 dm^3 flask, where a 1 ml glass with the test sample was placed in an atmosphere of argon. The flask was sealed, evacuated to a residual pressure of ~10^{-3} Torr, and heated in an air thermostat to a desired temperature (to within ±1 °C) for 4 h. Then, the flask was rapidly cooled to 0 °C to condense the vapor phase on the walls and filled with argon, and the glass with residual sample was removed. The sublimate was washed out from the walls with 3 M HNO_3. The metal content of the resulting solution was determined by ICP OES. The vapor pressure of **1** was calculated using the Clapeyron–Mendeleev equation $P = nRT/(V_f - V_s)$, where n is the number of moles of the complex deposited on the flask walls and outer walls of the source glass; V_f is the flask volume; V_s is the source volume; R is the gas constant; and T is the temperature.

To check the reliability of this procedure, we measured the vapor pressures of naphthalene and iron(III) hexafluoroacetylacetonate (the tabulated temperature dependences of their vapor pressures are similar to that of the test adduct in a range of 40–80 °C). In the case of naphthalene, the sublimate was washed out with hexane, the solvent was removed, and the residue was weighed.

To determine the equilibration time of vapor pressure at a given temperature, we studied the dependence of the vapor pressure P on the heating time. These times were about 2.5 and 4 h for naphthalene

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[†] See Online Supplementary Materials for the synthetic procedures.

[‡] *Synthesis of* **1**. A lithium methylborohydride (3.14 g, 0.088 mol) solution containing THF was added to anhydrous ytterbium(III) chloride (3.3 g, 0.012 mol). The reaction mixture was stirred at room temperature under argon for two days. Under these conditions, adduct **1** was formed by reaction (2). The solvent was removed under reduced pressure, and the residue was sublimed at 70–80 °C *in vacuo* onto a water-cold finger. The product was obtained as colorless prismatic crystals in a yield of ~41% (1.6 g).

Complex **1** was extremely sensitive to atmospheric moisture. IR (ν/cm^{-1}): 2100 (s), 2190 (sh), 1270. ^1H NMR (400 MHz, CD_2Cl_2) δ: –47.46 (br., 9H, BH_3), –3.15 (br., 9H, Me), 5.34 (br., 12H, CH_2, THF), 15.92 (br., 12H, CH_2, THF). ^{13}C NMR (100 MHz, CD_2Cl_2) δ: –70.86 (Me), 29.41 (CH_2, THF), 77.75 (CH_2, THF). ^{11}B NMR (128 MHz, CD_2Cl_2) δ: –138.60 (BH_3). Found (%): Yb, 54.5; C, 26.32; H, 6.71. Calc. for $C_7H_{26}B_3YbO$ (%): Yb, 52.2; C, 25.34; H, 7.91. For more details, see Online Supplementary Materials.

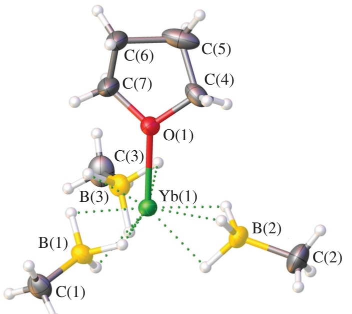

Figure 1 Molecular structure of **1**. Thermal ellipsoids are drawn at a 50% probability level.

and $Fe(hfa)_3$, respectively, and about 4 h for adduct **1**. The differences between the published vapor pressures of reference compounds and those determined experimentally were within 5–10%; thus, the above procedure can be used to determine the vapor pressures of volatile compounds in the indicated temperature range.

Complex **1** was characterized by single-crystal X-ray diffraction analysis (Figures 1 and 2; Tables S1 and S2, see Online Supplementary Materials).§ One crystallographically nonequivalent Yb atom is arranged at the center of a trigonal pyramid with the base formed by three $MeBH_3$ molecules involved in B–H···Yb(1) bonding [2.03(7)–2.24(5) Å], and the apical vertex of the pyramid is arranged by a tetrahydrofuran molecule [Yb(1)–O(1) = 2.251(3) Å]. The Yb pyramids are arranged in dimers around an inversion center *via* van der Waals interactions. The tridentate mode of ligation is confirmed by the IR spectra with a large broad peak at 2100 cm^{-1} with a shoulder at about 2190 cm^{-1} (B–H bridging stretch) and an additional peak at 1270 cm^{-1} (bridge deformation). A similar structure was reported[5] for tris(methyltrihydroborato)-ytterbium(III)(OEt_2). In this complex, the metal is surrounded by three tridentate methyltrihydroborates and one ether group in an approximately tetrahedral arrangement with the methyltrihydroborates bent slightly towards the ether group. All Yb–B–C angles are close to 180°, indicative of tridentate ligation. The average Yb–B distance is 2.45 ± 0.04 Å.

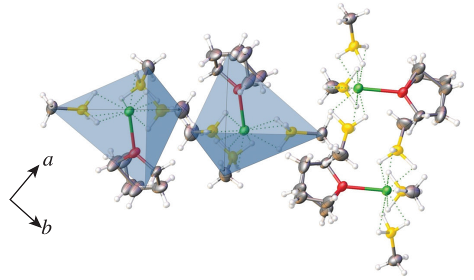

Figure 2 Crystal structure of **1**. Thermal ellipsoids are drawn at a 50% probability level.

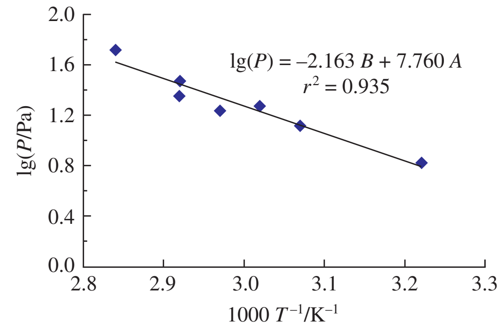

Figure 3 Temperature dependence of the vapor pressure of **1**.

The temperature dependence of vapor pressure characterizes the volatility of a substance as its ability to transfer into a gas phase (Figure 3). For complex **1**, the dependence is fitted well by the integral Clausius–Clapeyron equation $\lg(P) = A - B/T$.

The enthalpy of sublimation of **1** is 40 ± 2 kJ mol^{-1}, as calculated from the temperature dependence of the vapor pressure. Note that the enthalpies of sublimation of the ytterbium β-diketonates $Yb(DPM)_3$ and $Yb(HFDMD)_3$ (where DPM is dipivaloylmethanate, and HFDMD is heptafluorodimethyloctanedionate) are significantly higher, 163 and 137 kJ mol^{-1}, respectively. At 80 °C, the vapor pressure of $Yb(HFDMD)_3$ (3.6×10^{-4} Torr) is lower by three orders of magnitude than that of $Yb(BH_3Me)_3{\cdot}THF$ (0.4 Torr). These data suggest that the ytterbium ion in **1** is much more effectively shielded by ligands than in the β-diketonates due to the tridentate coordination of the borohydride ligands and the presence of the THF oxygen atom in the coordination sphere. Furthermore, low hydrocarbon content of the adduct results in weak van der Waals interactions between its molecules in a solid state to decrease its enthalpy of sublimation. Figure 1 shows that a high coordination number of ytterbium and its effective shielding by the ligands prevent coordination polymerization in complex **1**.

Thus, we have found that the vapor pressure of the complex $Yb(BH_3Me)_3(THF)$ in a range of 40–80 °C is higher by three orders of magnitude than that of well-known volatile ytterbium β-diketonates. The results could be important for material scientists working on ytterbium film deposition.

The NMR and XRD measurements were performed using the equipment of the X-ray Diffraction Research Centre and Centre for Magnetic Resonance at St. Petersburg State University.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.11.032.

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§ *Crystal data for* **1**. The data were collected at 100 K using a Bruker SMART APEX II diffractometer operated with monochromatic MoKα radiation. Empirical absorption correction was applied in CrysAlisPro[7] using spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm. The unit cell parameters [orthorhombic, space group *Pbca*, a = 13.1239(5), b = 14.7655(5) and c = 14.7931(4) Å, V = 2866.63(16) $Å^3$, Z = 8] were determined and refined by the least-squares techniques on the basis of 29492 reflections with 2θ in a range of 4.98–55.00°. The structure was solved by direct methods and refined to $R_1 = 0.033$ ($wR_2 = 0.059$) for 2644 reflections with $|F_o| \geqslant 4\sigma_F$ using the SHELXL program[8] incorporated in the OLEX2 program package.[9]

CCDC 1538682 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.