

Synthesis and Molecular Structures of a Redox-related Pair of Lanthanide Complexes

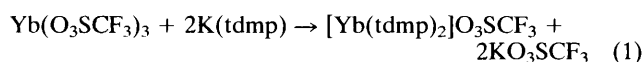
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The syntheses and X-ray crystal structures of the isoelectronic ytterbium complexes $[\text{Yb}(\text{tdmp})_2]\text{O}_3\text{SCF}_3$, **1**, and $[\text{Yb}(\text{tdmp})_2]$, **2**, are reported [tdmp = hydridotris(3,5-dimethylpyrazol-1-yl)borate]; the average metal to ligand distance increases by 0.16 Å (ca. 7%) upon reduction.

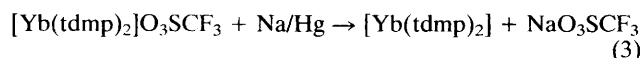
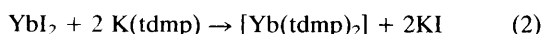
There is increasing interest in the lower oxidation states of the lanthanides.^{1,2} However, much remains to be learned about the detailed factors controlling their structure, bonding, and reactivity. The absence of directional bonding interactions due to the poor radial extension of the 4f valence orbitals is well documented for the trivalent state. However, there is mounting evidence that as the oxidation state is lowered, the 5d orbitals become energetically accessible.^{3,4} Thus, there is a need for detailed structural information on isoelectronic lanthanide complexes in both high and low oxidation states. However, even in the trivalent state the lanthanide ions are large enough to make coordinative saturation of the metal centre difficult to achieve and the associated counter-ions usually bind to the metal centre. Indeed, we are unaware of any reports of effectively isoelectronic pairs of compounds of the type $[\text{LnL}_2]^+\text{X}^-$ and $[\text{LnL}_2]$. The use of the poly(pyrazol-1-yl)borate ligands to bind a wide range of metals has flourished recently as their steric versatility has come to be recognized and a number of trivalent rare earth complexes have been reported.⁵ While this work was in progress Jones and Evans communicated the preparation of the divalent compounds $[\text{Ln}(\text{tdmp})_2]$ (Ln = Sm, Eu and Yb) although no structural information was reported [tdmp = hydridotris(3,5-dimethylpyrazol-1-yl)borate].⁶ Recently, however, the structure of $[\text{Sm}(\text{tdmp})_2]$ has been reported in the literature.⁷

Reaction of two equivalents of $\text{K}(\text{tdmp})$ with $\text{Yb}(\text{O}_3\text{SCF}_3)_3$ in tetrahydrofuran solution gives moderately moisture-sensitive $[\text{Yb}(\text{tdmp})_2]\text{O}_3\text{SCF}_3$, **1**, in good yields [eqn. (1)].[†]



The complex is very soluble in polar solvents such as dichloromethane, but only sparingly so in toluene, suggesting an ionic structure. This observation is in contrast to that made on the lighter members of the lanthanide series which behave as if the CF_3SO_3^- group were coordinated.⁸ Single crystals of **1** were obtained by slow diffusion of pentane into an acetonitrile solution of **1** and the structure was determined by X-ray diffraction.[‡] The molecular structure of **1** consists of well-separated discrete cations and anions, with the metal atom in the $[\text{Yb}(\text{tdmp})_2]^+$ unit being approximately octahedrally coordinated. The anions are disordered about the crystallographic twofold axis and this was successfully modelled by 50% occupancy of CF_3 and SO_3 over the two sites. A view of the cation in **1** is shown in Fig. 1. Although such a low coordination number is at first sight unusual for a lanthanide ion, this observation must reflect the sterically demanding nature of the tdmp ligand together with the fact that Yb is one of the smallest lanthanides.

Compound **2** can be prepared both by direct metathesis of $\text{K}(\text{tdmp})$ with $\text{YbI}_2(\text{thf})_n$ in thf solution and by sodium-mercury reduction of **1** [eqns. (2) and (3)].[§]



As has been previously reported⁶ the compound is only moderately air sensitive as a dry solid, is remarkably insoluble, and was therefore purified by sublimation under dynamic vacuum. Solid state MAS ¹³C NMR studies of the bulk solid confirm **2** as being diamagnetic; resonances associated with

only a single pyrazole environment were observed.[¶] A single crystal of **2** was obtained by slow sublimation of the bulk material in a temperature gradient, and its X-ray crystal structure determined.[‡] The molecular structure of **2** is shown in Fig 2. Consistent with the solid state NMR spectrum the molecule has S_6 symmetry. As with the corresponding samarium complex,⁷ the metal lies at the origin (a site with $R\bar{3}$ symmetry) and the boron atoms lie on a threefold axis. The explanation for the poor solubility of **2** is unclear since no significant intermolecular interactions or contacts are present in the solid state structure. However, since the molecules are approximately spherical, the hexagonal close packed structure may lead to a particularly high lattice energy.

In comparing the two structures we note that although both are six-coordinate they differ in subtle ways. In the case of compound **1** the metal coordination sphere may be regarded as being approximately octahedral with small distortions arising from the crystallographically imposed symmetry. The cation lies on a site of $2/m$ symmetry with a mirror plane running through two of the pyrazole rings. The Yb–N distances of the two independent pyrazole ligands are 2.304(5) and 2.347(6) Å.^{||} The N–B–N angles are approximately 110°, consistent with an effectively tetrahedral geometry. In com-

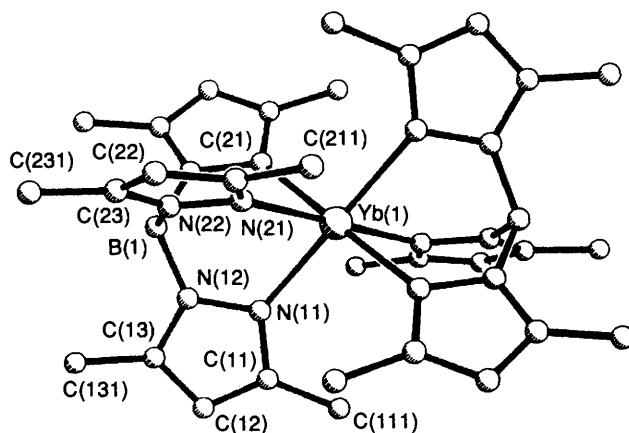


Fig. 1 Ball and stick view of the cation of **1** (hydrogen atoms omitted for clarity)

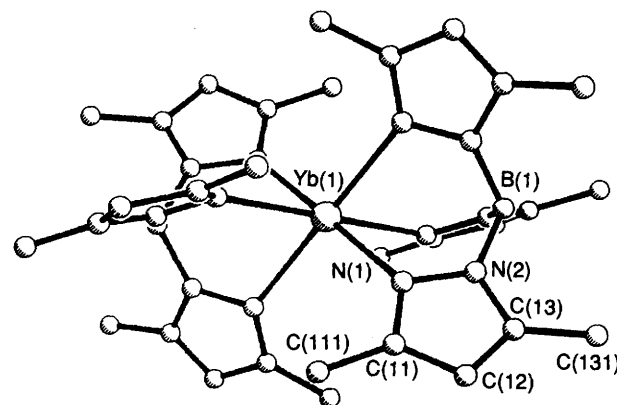


Fig. 2 Ball and stick view of **2** (hydrogen atoms omitted for clarity)

plex **2** the considerably longer Yb–N distance, 2.480(4) Å, is not matched by a corresponding change in geometry at the boron. This is presumed to be the result of the rigidity of the sp³ hybridised boron atom together with the unfavourable steric interactions between the 5-methyl substituents on the pyrazole rings. Thus the expansion of the metal is accommodated essentially by a slippage of the ligand along the threefold axis. The Yb–B distances increase from 3.348(4) in **1** to 3.468(4) Å in **2**. We note that the metal–nitrogen distances in the isostructural complexes [Sm(tdmp)₂]⁷ and [Ba(tdmp)₂]¹¹ are 2.617(4) and 2.754(3) Å respectively, in accord with the lanthanide contraction. In both **1** and **2**, the presence of the effectively gear-locked 3-methyl groups on the tdmp ligands prevents the entry of additional ligands. Thus, it is clear that the ionic radius of Yb increases by ca. 0.16 Å upon reduction.

In a further paper we will discuss the photoelectron spectra of **2** and the corresponding samarium and europium complexes.¹²

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Footnotes

† ¹H NMR (400 MHz, CDCl₃): δ 3.30 (s, 18 H), (brs 18 H), 6.19 (s, 6 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 11.9, 17.9, 111.3, 158.8, 176.2; IR (KBr, ν/cm⁻¹): 2560 (B–H), 1275, 1190, 1030, 640 (CF₃SO₃⁻). Elemental analyses were satisfactory.

‡ *Crystal data* for **1**: C₃₁H₄₄N₁₂B₂F₃O₃SYb, *M* = 916.59, crystal size 0.32 × 0.34 × 0.75 mm, monoclinic, space group C2/m, *a* = 16.593(7), *b* = 13.671(5), *c* = 8.746(2) Å, β = 91.66(3)°, *U* = 1983(1) Å³, *Z* = 2, *F*(000) = 922, *D*_c = 1.53 Mg m⁻³, μ(Mo–Kα) = 2.46 mm⁻¹; 3725 reflections were collected with 5 ≤ 2θ ≤ 50° at 295 K; of these 1888 were unique and the 1807 in which *F* ≥ 6σ(*F*) were used in structural analysis; refinements converged to *R* = 0.0406, *R*_w = 0.0416 [*w*⁻¹ = σ²*F*² + 0.002662(*F*)²] for 137 variables.

Crystal data for **2**: C₃₀H₄₄N₁₂B₂Yb, *M* = 767.52, crystal size 0.35 × 0.22 × 0.15 mm, trigonal, space group R $\bar{3}$ (No. 148), *a* = *b* =

11.063(1), *c* = 25.006(4) Å, *U* = 2650(1) Å³, *Z* = 3, *F*(000) = 1164, *D*_c = 1.44 Mg m⁻³, μ(Mo–Kα) = 2.67 mm⁻¹; 3580 reflections were collected with 5 ≤ 2θ ≤ 50 at 295 K; of these 1273 were unique and the 1038 in which *F* ≥ 6σ(*F*) were used in structural analysis; refinements converged to *R* = 0.0402, *R*_w = 0.0405 [*w*⁻¹ = σ²*F*² + 0.000510(*F*)²] for 69 variables.

All measurements were made on a Nicolet R3mV four circle diffractometer using Mo–Kα (λ = 0.71073 Å) radiation. Corrections for Lorentz, polarization and extinction effects as well as empirical correction for absorption were applied. Crystallographic calculations were carried out with the SHELXTL PLUS suite of programs on a Microvax II computer. Structures were solved by Patterson methods and developed using alternating cycles of Fourier syntheses and full-matrix least-squares calculations. Anisotropic thermal parameters were used in the final model for all non-hydrogen atoms while the hydrogens were placed in idealized positions. Atomic coordinates, bond lengths, angles and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ IR (KBr, ν/cm⁻¹): 2600 (B–H). Elemental analyses were satisfactory.

¶ Solid state MAS ¹³C NMR (75.47 MHz): δ 12.6, 105.2, 146.8, 147.7 ppm.

|| These distances are significantly shorter than those observed in related, but eight-coordinate Yb³⁺ complexes.^{9,10} The contraction in **1** must reflect the reduced coordination number.

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