

HETEROLEPTIC TRISPYRAZOLYLBORATE COMPLEXES OF YTTRIUM: THE SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF A BINUCLEAR *o*-PHENANTHROLINE COMPLEX $[Y(HBpz_3)(NCS)(\mu-OH)(phen)]_2$

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Abstract—The reaction between $[Y(NCS)_3(phen)_3]$ (*phen* = 1,10-phenanthroline) and $K(HBpz_3)$ (*pz* = pyrazol-1-yl) afforded the binuclear hydroxo-bridged complex $[Y(HBpz_3)(NCS)(\mu-OH)(phen)]_2$, the crystal structure of which reveals that the eight-coordinate yttrium atoms have a distorted square antiprismatic geometry with a non-linearly nitrogen-bonded thiocyanate $[Y-N-C(S) = 149.0(6)^\circ]$ ligand.

Yttrium and the lanthanide elements form a range of heteroleptic complexes having the general formula $[LnTp_2(X)]$ (Tp^- = hydrotrispyrazol-1-ylborate; Ln = a lanthanide element or yttrium; X = a uninegative bidentate ligand such as β -diketonate,^{1,2} tropolonate,³ oxalate,⁴ acetate³ or benzoate³). These complexes are remarkably stable towards disproportionation to the homoleptic species $[LnTp_3]$,⁵ despite the fact that they undergo quite rapid intermolecular ligand exchange reactions.⁶ Examples of complexes containing the $\{YTp_2\}^-$ moiety bound to other co-ligands have also been reported and include the monomeric chloride complexes $[YTp_2Cl]_x$ ($x = 1$ or 2 in solution), $[YTp_2Cl(OH_2)]$ and $(YTp_2(Hpz)Cl)$.⁷ However, with the carboxylate ligand, medium-sized ions such as Sm^{3+} and Y^{3+} have been shown to form dimeric species such as $[SmTp_2(\mu-O_2CPh)]_2$ ⁸ and $[YTp(\mu-O_2CMe)_2]_2$.⁹

In an extension of our work on heteroleptic com-

plexes of yttrium and the lanthanides, we have now explored the possibility that neutral bidentate ligands such as 1,10-phenanthroline (*phen*) might function as co-ligands with Tp^- . Lanthanide ion complexes of 1,10-phenanthroline are most commonly prepared by the reaction of a hydrated lanthanide salt with 1,10-phenanthroline and the appropriate anion. The number of phenanthroline ligands coordinated to the lanthanide ion depends upon the coordinating ability of the anion present.¹⁰ If the anion is a strongly bound chelating anion such as 2-formylphenolate, acetate or acetylacetonate, then the mono-substituted complexes $[Ln(phen)(OC_6H_4CHO)_3]$ (Ln = La, Pr, Nd, Sm, Eu or Tb), $[Ln(phen)(O_2CCH_3)_3]$ (Ln = Ce, Pr, Nd, Sm to Lu) or $[Ln(phen)(acac)_3]$ (Ln = Eu or Tb) are obtained.^{11–14} The bis complexes $[Ln(phen)_2Cl_3]$ (Ln = Ce, Pr, Nd, Sm to Lu), $[Ln(phen)_2(NO_3)_3]$ [Ln = La, Ce, Pr, Nd or Sm] or $[Ln(phen)_2(OHC_6H_4COO)_3]$ (Ln = La, Pr, Nd, Sm, Eu or Tb) are obtained when the anion is chloride, nitrate or salicylate,^{15–20} whilst the dinuclear complexes $[Ln_2(phen)_2(SO_4)_3]$ (Ln = Ce,

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Pr, Nd, Sm to Lu) are obtained with sulfate.¹⁸ In the presence of thiocyanate or selenocyanate, it is possible to isolate the tris complexes $[\text{Ln}(\text{phen})_3(\text{SCN})_3]$ (Ln = La, Pr, Nd, Sm, Eu or Tb) and $[\text{Ln}(\text{phen})_3(\text{SeCN})_3]$ (Ln = La, Ce, Pr, Nd, Sm, Eu or Gd).^{13,15,21,22} X-ray powder diffraction studies indicate that these complexes are isostructural and nine-coordinate.²² Recently, the cationic complexes $[\text{Ln}(\text{phen})_3(\text{H}_2\text{O})(\text{SCN})](\text{SCN})_2$ (Ln = La to Yb but excluding Pm) have also been reported.²³ Maximum coordination by phenanthroline is achieved only when the anion is the weakly coordinating perchlorate, and the complexes $[\text{Ln}(\text{phen})_4](\text{ClO}_4)_3$ (Ln = La, Ce, Pr, Nd, Dy or Er) have been isolated.^{24,25} In this paper we report our findings on the complexation of lanthanide ions by phenanthroline in the presence of Tp^- .

RESULTS AND DISCUSSION

Synthetic studies

Attempts to produce heteroleptic complexes of formula $[\text{LnTp}_2(\text{L}-\text{L})]^+$ (L—L = phen, 2,2'-bipyridine) under aqueous conditions similar to those which afford the complexes $[\text{LnTp}_2(\text{X})]$ have not been successful with these neutral ligands and only $[\text{LnTp}_3]$ could be isolated from the reaction mixtures. Reactions in non-aqueous media also produced products contaminated with LnTp_3 . However, fractional crystallization of the product mixture obtained from the reaction between $[\text{Y}(\text{NCS})_3(\text{phen})_3]$ ²² and KTp in non-aqueous media afforded a purer product. The IR spectrum of this material contained bands at 2068 and 2462 cm^{-1} attributable respectively to NCS and BH, in addition to other bands characteristic of phenanthroline and Tp^- . The ¹H NMR spectrum of the new complex contained signals attributable to both the phenanthroline and Tp^- ligands, with integrations which were consistent with these ligands being present in a 1:1 ratio. The mass spectrum contained ions at m/z 515 (100%), 648 (82%) and 1102 (1%). The ion at m/z 515 corresponds with $\{\text{Y}(\text{Tp})_2\}^-$ and that at 648 with $[\text{Y}(\text{Tp})_2(\text{NCS})_2(\text{OH})]^+$, but the presence of an ion at m/z 1102, albeit weak, was surprising and suggested a dimeric formulation. In order to fully characterize this compound a single crystal X-ray diffraction study was undertaken.

Structural studies

The gross features of the crystal structure characterize the new complex as a hydroxyl-bridged dimer

$[\text{Y}(\text{HBpz}_3)(\text{NCS})(\mu\text{-OH})(\text{phen})]_2$ (Fig. 1), which consists of symmetry-related halves (operator' = $1-x, -y, 1-z$). The bonding modes of the ligands therein are κ^3 -, η -N, μ - and κ^2 -, respectively, giving each yttrium centre a formal coordination number of eight. The coordination geometry is best described as square antiprismatic by both Dollase's method²⁶ and that of polytopal analysis.²⁷ Shape parameters, δ and φ , for the latter determination are presented in Table 1, alongside their ideal values. The square faces of the polyhedron are defined by N(4)—N(5)—N(31)—N and N(11)—N(21)—O—O'. The former face is reasonably regular, and the slight deviation from ideal square antiprismatic geometry is caused by the necessarily short O—O' separation, and by a puckering of the N(11)—N(21)—O—O' face due to the shortness of the Y—O bonds relative to the Y—N bonds. This is, however, insufficient to warrant a description of bicapped trigonal prismatic.

The four-membered Y—O—Y'—O' ring is crystallographically planar but the hydroxyl bridge is asymmetric, with bond distances of 2.218(5) and 2.274(5) Å to Y and Y', respectively. These are within the range observed for comparable inversion-centred (YO)₂-containing structures, of 2.218(3) Å in $[\text{Y}(\mu\text{-OH})(\text{H}_2\text{O})_2(\text{phen})_2]_2\text{Cl}_4 \cdot 2\text{phen} \cdot \text{CH}_3\text{OH}$ ²⁸ to 2.36(2) Å in $[\text{Y}(\text{C}_5\text{H}_5)_2\text{OH}]_2 \cdot \text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$.²⁹ The Y—O—Y' angle in the title compound is 120.3(2)°. This is somewhat larger than the previously determined values of 110.2(2) and 100.4(7)° respectively for the foregoing structures,^{28,29} or the 109.1(1)° found in $[\text{Y}(\text{OH})(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{O}]_2$.³⁰ $[\text{Y}(\mu\text{-OH})(\text{H}_2\text{O})_2(\text{phen})_2]_2\text{Cl}_4 \cdot 2\text{phen} \cdot \text{CH}_3\text{OH}$ ²⁸ is the only other Y—phen complex known to us which has been structurally characterized, and bonding Y—N distances therein range from 2.543(3) to 2.587(3) Å. The corresponding distances in the title compound, 2.532(5) and 2.586(5) Å, fall close to either extreme of this range. Coordination distances to the Tp ligand are unremarkable, falling within the range 2.470(6)—2.550(5) Å. Corresponding values from the three other Y—Tp complexes structurally characterized to date^{9,31} range from 2.456(5) to 2.546(4) Å. Finally, the NCS ligand is placed 2.408(6) Å from the yttrium centre.

The ligand set as a whole appears to be oriented so as to bring the phenanthroline ligand into approximate co-planarity with the pyrazolyl ring containing N(21). The reason for this may possibly be in order to maximize interaction between the phenanthroline ligand and the pyrazolyl ring of the symmetry-related half of the molecule. The best plane through N(22')—N(21')—C(21')—C(22')—C(23') and the best plane through the non-

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