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Ternary lanthanide complexes of hydrotris-[3-(2-pyridyl)pyrazol-1-yl]borate (Tp^{Py}) and anionic *O,O*-bidentate chelates: [Tb(Tp^{Py})-(dbm)$_2$] and [Eu(Tp^{Py})(trop)(NO$_3$)] (Hdbm is dibenzoylmethane and Htrop is tropolone)

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Abstract

The reaction of lanthanide(III) salts with the potentially hexadentate podand ligand hydrotris[3-(2-pyridyl)-pyrazol-1-yl]borate (Tp^{Py}) and either dibenzoylmethane (Hdbm) or tropolone (Htrop) afforded bis(1,3-diphenyl-1,3-propanedionato-*O,O'*){hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate}terbium(III), [Tb(C$_{24}$H$_{19}$BN$_9$)(C$_{15}$H$_{11}$O$_2$)$_2$], and {hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate}(2-hydroxycyclohepta-2,4,6-trien-1-onato-*O,O'*)(nitrato-*O,O'*)-europium(III) dichloromethane solvate, [Eu(C$_{24}$H$_{19}$-BN$_9$)(C$_7$H$_5$O$_2$)(NO$_3$)]·CH$_2$Cl$_2$, respectively. The former complex is eight-coordinate involving two bidentate dbm ligands and one Tp^{Py} ligand which is only tetradentate with one bidentate arm pendant. In contrast, the latter complex is ten-coordinate, with Tp^{Py} coordinated in its usual hexadentate mode, with, in addition, one bidentate nitrate ion and one bidentate tropolonate anion.

Comment

We have been interested in the structures and luminescence properties of complexes of lanthanide(III) ions, especially Tb^{III} and Eu^{III}, with podand ligands based on poly(pyrazolyl)borates (Jones *et al.*, 1997; Bardwell *et al.*, 1997; Armaroli *et al.*, 1997; Harden *et al.*, 1998; Reeves *et al.*, 1999). Generally, the complexes contain two types of ligand: one or two of the poly(pyrazolyl)-borate ligands (depending on its denticity) and additional nitrate ligands which complete the coordination sphere and render the complexes neutral.

We thought that a simple way to extend the chemistry of these complexes would be to replace the nitrate ions with other chelating anionic O-donor ligands; obvious possibilities are carboxylates, catecholates, acetylacetonates and related ligands. A particular appeal of this is that binucleating bridging ligands containing two separate bidentate chelating sites based on these donor types are well known, so if we could attach one such bidentate chelating ligand to the {Ln(Tp^{Py})}$^{2+}$ core then, in principle, use of an appropriate bridging ligand containing two such binding sites might lead to dinuclear complexes. Accordingly, we investigated the reactions of lanthanide(III) salts with Tp^{Py} in the presence of either dibenzoylmethane (Hdbm) or tropolone (Htrop) to investigate the possible formation and structures of new ternary complexes.

The reaction of terbium(III) chloride hydrate, K[Tp^{Py}] and Hdbm (1:1:2 molar ratio), and a few drops of triethylamine in aqueous MeOH afforded a pale yellow precipitate. The fast atom bombardment (FAB) mass spectrum showed a strong peak at *m/z* = 826, corresponding to loss of one dbm ligand from the molecule to give the fragment {Tb(Tp^{Py})(dbm)}$^+$. X-ray quality crystals were grown by recrystallization from a CH$_2$Cl$_2$/hexane mixture; the structure of the complex is shown in Fig. 1, confirming the formulation of the complex as [Tb(Tp^{Py})(dbm)$_2$], (1).

(1)   (2)
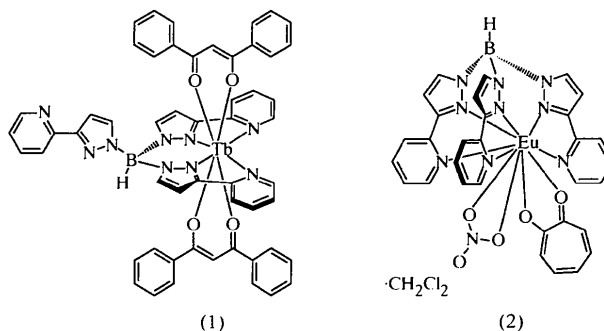
The Tb^{III} centre is in an eight-coordinate N$_4$O$_4$ environment arising from two bidentate dbm ligands and one Tp^{Py} ligand which is only tetradentate with one bidentate arm being pendant (this behaviour is called 'hypodentate'). In all of its previously structurally characterized complexes with lanthanides, Tp^{Py} has

coordinated as a hexadentate chelate (Jones *et al.*, 1997), although this tetradentate coordination mode has been seen in complexes of Tp^{py} with copper(II) (Bardwell *et al.*, 1995) and the uranyl dication (Amoroso *et al.*, 1996). The Tb—O distances [from 2.299 (3) to 2.340 (3) Å] and the Tb—N distances [from 2.501 (3) to 2.543 (3) Å] are unremarkable (Jones *et al.*, 1997; Reeves *et al.*, 1999). The coordination geometry may be described as approximately square antiprismatic, with one square plane defined by N51, N61, O111 and O112 [the average deviation of these atoms from the best-fit mean plane through them is 0.305 (2) Å] and the other defined by N31, N41, O211 and O212 [average deviation 0.172 (2) Å]. The angle between these two mean planes is 7.8 (1)°. The four N-donor atoms form a near-perfect plane [average deviation 0.005 (1) Å], and the structure can also be viewed as having an equatorial belt of four N atoms in a plane, with the bidentate dbm ligands occupying pseudo-axial positions. The pendant bidentate 'arm' has an approximately *transoid* conformation, with an angle of 14.7 (3)° between the two aromatic rings.
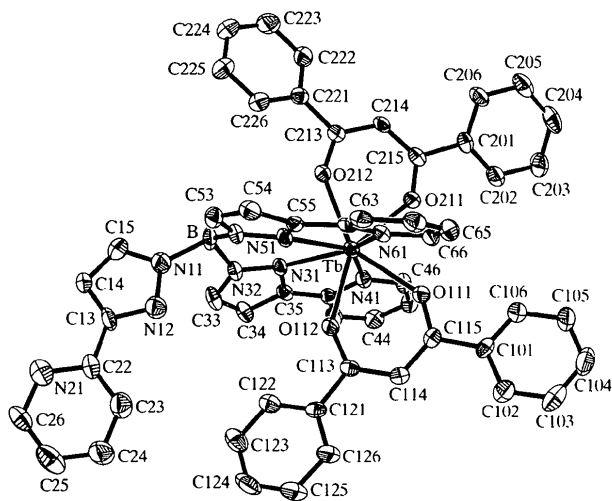

Fig. 1. The molecular structure of [Tb(Tp^{py})(dbm)$_2$] with 40% probability displacement ellipsoids.

Reaction of the known complex [Eu(Tp^{py})(NO$_3$)$_2$] with excess tropolone in MeOH afforded a pale yellow precipitate whose FAB mass spectrum showed a strong peak at $m/z = 718$, corresponding to the fragment {Eu(Tp^{py})(trop)}$^+$. X-ray quality crystals were grown by recrystallization from a CH$_2$Cl$_2$/hexane mixture; the structure of the complex is shown in Fig. 2, confirming the formulation of the complex as [Eu(Tp^{py})(trop)-(NO$_3$)] (as its CH$_2$Cl$_2$ monosolvate), (2).

The Eu^{III} centre is in a ten-coordinate N$_6$O$_4$ environment arising from one Tp^{py} ligand coordinated in its conventional hexadentate manner, one bidentate nitrate ion and one bidentate tropolonate ligand. The structure is basically similar to that of [Eu(Tp^{py})(NO$_3$)$_2$], with
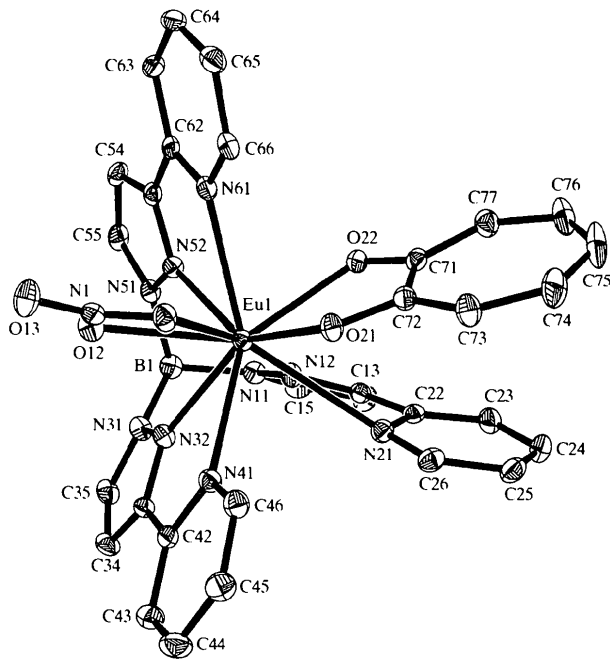

Fig. 2. The molecular structure of [Eu(Tp^{py})(trop)(NO$_3$)]·CH$_2$Cl$_2$ with 40% probability displacement ellipsoids. The dichloromethane solvate molecule is not shown.

one nitrate ion replaced by the tropolonate anion. A significant consequence of the presence of the tropolonate ligand is a stacking interaction between the tropolonate ring (C71–C77) and one of the pyridyl rings (N21–C26), which results in these two rings being pulled towards each other at the cost of some lengthening of the relevant metal–ligand bonds; thus, Eu1—N21 at 2.865 (2) Å is considerably longer than the other five Eu—N bonds [from 2.526 (2) to 2.650 (2) Å]. The angle between the mean planes through these two stacked rings is 26.2 (1)°, and in the overlapping region, the separation between them is in the region of 3.5 to 4.0 Å. Whilst complexes of the tropolonate ion with transition metal cations are well known, there is only one other example of a structurally characterized lanthanide(III) complex of tropolonate (Moss & Jones, 1989).

Experimental

crude product afforded a mixture of crystals with two distinct habits: some of unreacted [Eu(Tp^{py})(NO$_3$)$_2$] and some of what appeared to be [Eu(Tp^{py})(trop)(NO$_3$)] by mass spectroscopic analysis (details in the *Comment*). The yield of this was low because of the necessity of separating the two types of crystalline material manually (*ca* 10%).

In each case, a suitable crystal was quickly removed from the mother liquor, coated with paraffin oil and mounted in a stream of cold N$_2$ (173 K) on the diffractometer for subsequent analysis.

Compound (1)

Crystal data

[Tb(C$_{24}$H$_{19}$BN$_9$)-
  (C$_{15}$H$_{11}$O$_2$)$_2$]
$M_r = 1049.69$
Triclinic
$P\bar{1}$
$a = 11.4944\,(17)$ Å
$b = 14.1547\,(18)$ Å
$c = 16.292\,(2)$ Å
$\alpha = 108.284\,(9)°$
$\beta = 92.329\,(13)°$
$\gamma = 110.712\,(11)°$
$V = 2319.7\,(6)$ Å^3
$Z = 2$
$D_x = 1.503$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 210
  reflections
$\theta = 3.0–27.4°$
$\mu = 1.583$ mm^{-1}
$T = 173\,(2)$ K
Block
$0.24 \times 0.12 \times 0.06$ mm
Colourless

Data collection

Siemens SMART area-
  detector diffractometer
ω rotation with narrow
  frames
Absorption correction:
  empirical (*SADABS*;
  Sheldrick, 1996)
  $T_{min} = 0.768$, $T_{max} = 0.928$
21 541 measured reflections
10 457 independent
  reflections

7337 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 27.48°$
$h = -14 \to 14$
$k = -18 \to 16$
$l = -20 \to 21$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.083$
$S = 0.970$
10 457 reflections
622 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 1.058$ e Å^{-3}
$\Delta\rho_{min} = -0.597$ e Å^{-3}
Extinction correction: none
Scattering factors from
  *International Tables for
  Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Tb—O212	2.299 (3)	Tb—N31	2.501 (3)
Tb—O112	2.309 (3)	Tb—N51	2.510 (3)
Tb—O211	2.335 (3)	Tb—N41	2.520 (3)
Tb—O111	2.340 (3)	Tb—N61	2.543 (3)
O212—Tb—O112	143.12 (9)	N31—Tb—N51	74.75 (11)
O212—Tb—O211	71.38 (9)	O212—Tb—N41	107.80 (11)
O112—Tb—O211	145.35 (10)	O112—Tb—N41	83.09 (10)
O212—Tb—O111	144.46 (9)	O211—Tb—N41	80.73 (10)
O112—Tb—O111	71.60 (10)	O111—Tb—N41	77.57 (10)
O211—Tb—O111	75.08 (9)	N31—Tb—N41	65.43 (11)

O212—Tb—N31	81.34 (10)	N51—Tb—N41	139.64 (11)
O112—Tb—N31	71.29 (10)	O212—Tb—N61	92.10 (11)
O211—Tb—N31	127.02 (10)	O112—Tb—N61	93.11 (10)
O111—Tb—N31	129.75 (11)	O211—Tb—N61	86.98 (10)
O212—Tb—N51	70.99 (10)	O111—Tb—N61	74.54 (10)
O112—Tb—N51	78.15 (10)	N31—Tb—N61	139.62 (11)
O211—Tb—N51	131.78 (10)	N51—Tb—N61	65.52 (11)
O111—Tb—N51	127.73 (10)	N41—Tb—N61	151.60 (11)

Compound (2)

Crystal data

[Eu(C$_{24}$H$_{19}$BN$_9$)(C$_7$H$_5$O$_2$)-
  (NO$_3$)]·CH$_2$Cl$_2$
$M_r = 864.30$
Triclinic
$P\bar{1}$
$a = 10.2193\,(19)$ Å
$b = 10.9574\,(12)$ Å
$c = 15.994\,(3)$ Å
$\alpha = 85.895\,(9)°$
$\beta = 72.163\,(10)°$
$\gamma = 78.536\,(8)°$
$V = 1670.8\,(5)$ Å^3
$Z = 2$
$D_x = 1.718$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 264
  reflections
$\theta = 3.0–27.4°$
$\mu = 2.095$ mm^{-1}
$T = 173\,(2)$ K
Needle
$0.22 \times 0.16 \times 0.05$ mm
Pale yellow

Data collection

Siemens SMART area-
  detector diffractometer
ω rotation with narrow
  frames
Absorption correction:
  empirical (*SADABS*:
  Sheldrick, 1996)
  $T_{min} = 0.685$, $T_{max} = 0.928$
17 128 measured reflections
7546 independent reflections

6396 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.48°$
$h = -13 \to 13$
$k = -14 \to 14$
$l = -20 \to 20$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.058$
$S = 0.976$
7546 reflections
479 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.759$ e Å^{-3}
$\Delta\rho_{min} = -0.883$ e Å^{-3}
Extinction correction: none
Scattering factors from
  *International Tables for
  Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (2)*

Eu1—O21	2.3784 (18)	Eu1—O12	2.596 (2)
Eu1—O22	2.414 (2)	Eu1—N41	2.611 (2)
Eu1—N52	2.526 (2)	Eu1—N61	2.650 (2)
Eu1—N32	2.536 (2)	Eu1—O11	2.663 (2)
Eu1—N12	2.588 (2)	Eu1—N21	2.875 (2)
O21—Eu1—O22	64.89 (7)	N12—Eu1—N61	119.04 (8)
N52—Eu1—N32	73.36 (8)	N41—Eu1—N61	134.86 (7)
N52—Eu1—N12	69.72 (8)	O21—Eu1—O11	64.28 (6)
N32—Eu1—N12	63.61 (8)	N52—Eu1—N21	126.90 (7)
N52—Eu1—N41	131.38 (7)	N32—Eu1—N21	91.98 (7)
N32—Eu1—N41	62.32 (7)	N12—Eu1—N21	58.34 (7)
N12—Eu1—N41	104.70 (8)	N41—Eu1—N21	75.58 (7)
N52—Eu1—N61	62.18 (7)	N61—Eu1—N21	136.50 (7)
N32—Eu1—N61	127.57 (7)		

In (1), the H and Cl atoms of the CH$_2$Cl$_2$ solvent molecule are disordered over two sites, with fractional site occupancies of 0.84 and 0.16. Similarity restraints were applied to all four C—Cl distances to keep the geometry of the solvent molecule reasonable; this requirement, together with the refined U_{ij} values, indicates that the disorder model is only approximate.

For both compounds, data collection: *SMART* (Siemens, 1995*a*); cell refinement: *SAINT* (Siemens, 1995*a*); data reduction: *SAINT*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL* (Siemens, 1995*b*); software used to prepare material for publication: *SHELXTL*.

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Acetylferrocene thiosemicarbazone

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Abstract

The thiosemicarbazone moiety of the title compound, [Fe(C$_5$H$_5$)(C$_8$H$_{10}$N$_3$S)], shows an *E* configuration and exists in the thione tautomeric form. The molecules are linked together by a pair of N—H···S hydrogen-bonding interactions to form an infinite chain.

Comment

There is considerable interest in non-linear optical materials because of their potential use in device applications related to telecommunications, optical computing, optical storage and optical information processing (Williams, 1984; Chemla & Zyss, 1987; Long, 1995). The polarizability and hyperpolarizability of ferrocene and its derivatives have been the subject of some recent studies (Green *et al.*, 1987; Togni & Rihs, 1993; Ghoshal *et al.*, 1990). As part of our work in this area (Tian *et al.*, 1997; Duan *et al.*, 1998), we report here the structure of the title compound, (I).

(I)
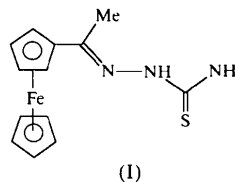
The thiosemicarbazone moiety of (I) (Fig. 1) shows an *E* configuration about both the C2—N3 and C1—N2 bonds, as found in most thiosemicarbazides and thiosemicarbazones. The C—S bond distance of 1.693 (3) Å agrees very well with those in related compounds, being intermediate between 1.82 Å for a C—S single bond and 1.56 Å for a double bond (Sutton, 1965). The shortening of the N—N bond distance of 1.387 (4) Å, compared with the corresponding N—N distance of 1.411 (2) Å for unsubstituted thiosemicarbazide (Andretti *et al.*, 1970), indicates that there is delocalized character in the whole molecule.

The intermolecular hydrogen bonds that link the molecules together in the crystal feature an infinite chain consolidated by hydrogen bonds of the type N1—H1N*B*···S1^{i} [symmetry code: (i) $\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$],