DALTON
COMMUNICATION

Hydrotris[3-(carboxypyrrolidido)pyrazol-1-yl]borate, the first proven N_3O_3-hexadentate homoscorpionate ligand

Arnold L. Rheingold, Christopher D. Incarvito and Swiatoslaw Trofimenko *

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

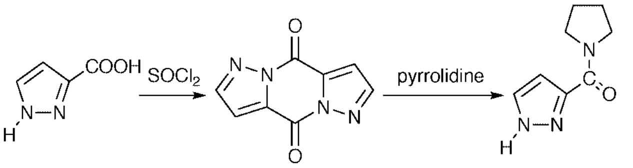
Received 29th February 2000, Accepted 2nd March 2000

The new homoscorpionate ligand, hydrotris[3-(carboxypyrrolidido)pyrazol-1-yl]borate, $[\mathrm{Tp^{cpd}}]^-$, was synthesized, and it formed with lanthanide(III) ions La, Nd and Sm, structurally characterized $[\mathrm{M(Tp^{cpd})_2}]\mathrm{PF_6}$ complexes, where the lanthanide ion was in a ten-coordinate enviroment consisting of one N_3O_3 hexadentate $\mathrm{Tp^{cpd}}$ ligand, and one N_2O_2 tetradentate $\mathrm{Tp^{cpd}}$ ligand.

Although over 170 different scorpionate ligands are known,[1] their maximum denticity is usually equal to the number of pyrazolyl rings bonded to boron, except for the instance of oxidative addition of the *ortho*-CH of a 3-phenyl substituent from $\mathrm{Tp^{Ph}}$ to Rh(I).[2] The only example where higher denticity, including κ^6, has been realized in a $\mathrm{Tp^x}$ ligand, was with $\mathrm{Tp^{Py}}$, where the 3-(2-pyridyl) substituent on each pyrazolyl ring was also capable of coordination.[3–5] No other examples of $\mathrm{Tp^x}$ hexadenticity are known, although ligands such as $\mathrm{Tp^{\mathit{o}\text{-}An}}$ (*o*-An = anisole, *ortho*-methoxyphenyl),[6] and $\mathrm{Tp^{2,4\text{-}(OMe)_2Ph}}$,[7] might be capable of exhibiting additional coordination, up to κ^6, through the *ortho*-methoxy groups. However, the structurally characterized Tl complexes of $\mathrm{Tp^{\mathit{o}\text{-}An}}$,[8] and of $\mathrm{Tp^{2,4\text{-}(OMe)_2Ph}}$ showed the *ortho*-methoxy groups not only uncoordinated, but actually turned away from the metal ion.

Our approach to N_3O_3 hexadentate $\mathrm{Tp^x}$ ligands consisted of choosing 3-C(O)NR_2 as the pyrazolyl 3-substituent, which would coordinate through the oxygen, bearing a partial negative charge *via* the contributing form $R_2N^+{=}C{-}O^-$. As we did not want the 3-substituent to be overly bulky, we selected as NR_2 the pyrrolidido group, $N(C_4H_8)$, in which the N-substituents were tied back into a relatively inflexible five-membered ring, leading to the ligand $\mathrm{Tp^{cpd}}$ ("cpd" standing for carboxypyrrolidido). The five-membered N,O-chelate ring formed by this substituent per $\mathrm{pz^{cpd}}$ unit (pz = pyrazolyl) would be more compact than the twisted six-membered one, which might form in the case of an *ortho*-methoxyphenyl 3-substituent (Fig. 1).

3-(Carboxypyrrolidido)pyrazole, $\mathrm{Hpz^{cpd}}$, was synthesized by the reaction of diketopiperazine (the tricyclic anhydride of pyrazole-3-carboxylic acid),[9,10] with excess pyrrolidine, as shown in Scheme 1.† Upon reaction with KBH_4 in refluxing 4-methylanisole it was converted to hydrotris[3-(carboxypyrrolidido)-pyrazol-1-yl]borate, $\mathrm{Tp^{cpd}}$, which was purified and characterized as the Tl salt, $\mathrm{TlTp^{cpd}}$. An X-ray crystallographic structure determination (Fig. 2) showed Tl to be symmetrically coordinated to the three N atoms.‡ In addition, all three carbonyl oxygens were pointed at the Tl ion, although being out of the bonding range. The N–Tl bond lengths averaged 2.709 Å, which was slightly longer than the pyrazolyl N–Tl distances in $\mathrm{Tl[Tp^{Py}]}$ (2.670 Å), while the Tl–O distances averaged 3.004 Å, thus being moderately shorter than the pyridyl N–Tl distances in $\mathrm{Tl[Tp^{Py}]}$ (3.176 Å).[9]



Scheme 1

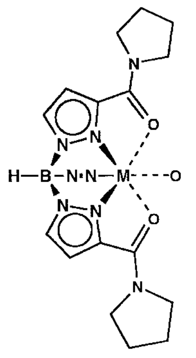


Fig. 1 $\mathrm{Tp^{cpd}M}$ where –N=N– and – – –O represents the third, hidden, $\mathrm{pz^{cpd}}$ ring.

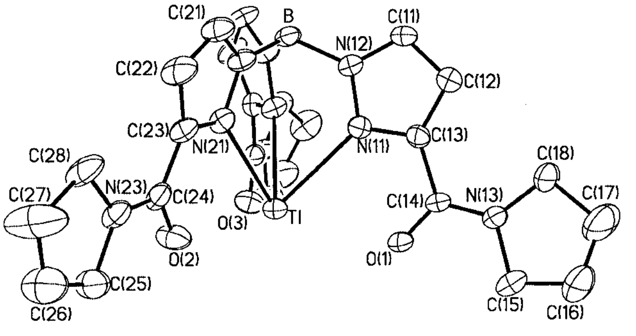


Fig. 2 Structure of the complex $\mathrm{Tl(Tp^{cpd})}$. Selected bond lengths (Å) and angles (°): Tl–N(11) 2.713(7), Tl–N(21) 2.710(7), Tl–N(31) 2.704(7); N(11)–Tl–N(31) 67.2(2), N(11)–Tl–N(21) 69.4(2), N(21)–Tl–N(31) 72.4(2).

The reaction of $\mathrm{Tp^{cpd}}$ with trivalent lanthanide ions (La, Nd, Sm) in 2 : 1 mol ratio yielded cationic species $[\mathrm{M(Tp^{cpd})_2}]^+$,† which were isolated as their PF_6 salts, and structures of all three were determined by X-ray crystallography.‡ They were essentially identical, and of the type shown in Fig. 3 for the Sm(III) complex, except that their average M–N and M–O bond lengths decreased in the La–Nd–Sm series, in line with the "lanthanide contraction" of their ionic radii. Thus, the average M–N bond lengths were 2.720, 2.663, and 2.635 Å, respectively, while the corresponding M–O bonds were 2.594, 2.538 and 2.510 Å.

In each case the lanthanide ion was in a ten-coordinate environment, being bonded to the three N and three O atoms of one κ^6 $\mathrm{Tp^{cpd}}$ ligand, and to two N and two O atoms of the second $\mathrm{Tp^{cpd}}$ ligand, bonded only in κ^4 fashion, and containing the uncoordinated $\mathrm{pz^{cpd}}$ arm positioned roughly at right angles to the B–M axis. Counting the N,O-donor set from each $\mathrm{pz^{cpd}}$ arm as a unit, one could describe the coordination of La as "octahedral" with one vacant site. Looking down the B–M bond, viewed as having a square of oxygens in the equatorial belt, and three capping nitrogens at one apex, and two nitrogens

DOI: 10.1039/b001651i

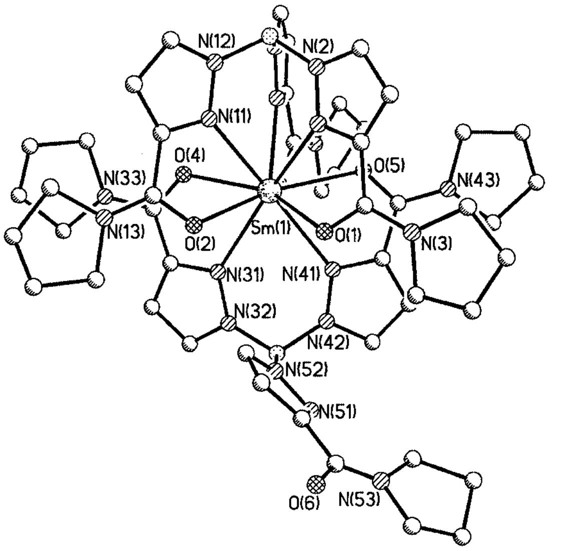


Fig. 3 Structure of the complex cation $[Sm(Tp^{cpd})_2]^+$. Selected bond lengths (Å) and angles (°): Sm–N(1) 2.596(7), Sm–N(11) 2.673(8), Sm–N(21) 2.533(8), Sm–N(31) 2.651(7), Sm–N(41) 2.701(7), Sm–O(1) 2.484(7), Sm–O(2) 2.579(7), Sm–O(3) 2.481(7), Sm–O(4) 2.482(6), Sm–O(5) 2.523(6); N(1)–Sm–N(11) 60.9(2), N(11)–Sm–N(21) 68.9(2), N(21)–Sm–N(31) 128.5(2), N(31)–Sm–N(41) 67.1(2), O(1)–Sm–O(2) 77.9(2), O(2)–Sm–O(3) 135.4(2), O(3)–Sm–O(4) 70.9(2), O(4)–Sm–O(5) 136.3(2).

and one oxygen at the other. All the La–N bond distances were almost identical, those of the κ^6 ligand averaging 2.694 Å. The shortest bond (2.644 Å) was *trans* to the vacant site. The La–O distances were also almost identical, and averaged 2.694 Å in the κ^3 ligand, and 2.760 Å in the κ^2 ligand.

In the related icosahedral cation $[Sm(Tp^{Py})_2]^+$, the pyrazole N–M bond lengths averaged 2.658 Å, while the pyridyl N–M bonds were 2.950 Å.[11] These values should be compared with those of $[Sm(Tp^{cpd})_2]^+$, which were 2.635 Å for Sm–N, and 2.510 Å for Sm–O bonds. The fact that the latter distance is shorter by 0.44 Å as compared with the corresponding Sm–N distance to the pyridyl nitrogen in $[Sm(Tp^{Py})_2]^+$, points to much tighter κ^6 chelation by the Tp^{cpd} ligand, as compared with Tp^{Py}. It is possible that this compactness precluded the accommodation of κ^6 chelation by the second Tp^{cpd} ligand in the $[La(Tp^{cpd})_2]^+$ complexes, at least in the crystal. At the same time, the ^1H and ^{13}C NMR spectra of the diamagnetic $[La(Tp^{cpd})]^+$ complex cation showed only one type of pz^{cpd} present, implying a rapid exchange of the coordinated and uncoordinated pz^{cpd} arms on the NMR time scale, as the presence of a rigid 12-coordinate structure, with two κ^6 Tp^{cpd} ligands, was thought to be less likely. No attempts were made to freeze out the static structure.

In summary, we have synthesized the first proven N_3O_3-hexadentate homoscorpionate ligand, Tp^{cpd}, modifications of which can be readily visualized, and have demonstrated that it is capable of coordinating in both, κ^4 N_2O_2 and κ^6 N_3O_3 fashion.

Notes and references

† Syntheses: 3-(carboxypyrrolidido)pyrazole (Hpz^{cpd}). This pyrazole was synthesized by refluxing diketopiperazine[9,10] in THF with a large excess of pyrrolidine. After stripping the low-boilers, the product was distilled *in vacuo*, bp 215–220 °C at 3 Torr (58% yield). Mp 145–147 °C (from toluene–heptane). IR: CO 1589 cm^{-1}. ^1H NMR (ppm): 7.61 (d, $J = 2.2$ Hz, 1H, H-5), 6.69 (d, $J = 2.2$ Hz, 1H, H-4), 3.84 (m, 2H, CH_2), 3.70 (m, 2H, CH_2), 1.95 (4H, CH_2). ^{13}C NMR (ppm): 23.9 and 26.5 (NCH_2CH_2), 47.0 and 48.5 (NCH_2CH_2), 107.0 (C-4), 134.1 (C-5), 142.5 (C-3), 161.0 (CO). These, and all the other NMR spectra were determined in chloroform-*d*. Anal. Calc. for $C_8H_{11}N_2O$: C, 63.6; H, 7.28; N, 18.5; Found: C, 63.3; H, 7.49; N, 18.2%.

$Tl[Tp^{cpd}]$. A mixture of Hpz^{cpd} and KBH_4 (3.5 : 1 mol ratio) was refluxed in 4-methylanisole until the theoretical amount of hydrogen was evolved. After distilling the solvent *in vacuo*, the residue was dissolved in THF–DMF (10 : 1) and treated with excess aqueous $TlNO_3$. After dilution with much water, the product was extracted with methylene chloride, the extracts were filtered through alumina, stripped, and the residue yielded 69% of the product, mp 263–265 °C, upon trituration with ethyl acetate; IR: BH 2500, CO 1606 cm^{-1}. ^1H NMR (ppm): 7.62 (d, $J = 2.2$ Hz, 1H, H-5), 6.36 (d, $J = 2.2$ Hz, 1H, H-4), 3.56 (m, 4H, CH_2), 1.85 (m, 4H, CH_2). ^{13}C NMR (ppm): 23.5 and 26.2 (NCH_2CH_2), 46.4 and 47.8 (NCH_2CH_2), 105.2 (C-4), 135.3 (C-5), 147.1 (C-3), 162.9 (CO). Anal. Calc. for $C_{24}H_{31}BN_9O_3Tl$: C, 43.2; H, 4.65; N, 12.6; Found: C, 43.1; H, 4.78; N, 12.4%.

$[La(Tp^{cpd})_2][PF_6]$. A mixture of $TlTp^{cpd}$ and $La(NO_3)_3$ (2 : 1 mol ratio) was stirred with excess NH_4PF_6 in DMF until a clear solution resulted, which was diluted with much water, and extracted with chloroform. The extracts were passed through a layer of alumina, and the residue from evaporation of the eluate was crystallized from nitromethane–EtOAc. Mp 296–298 °C, decomp.; IR: BH 2474, CO 1592 cm^{-1}. ^1H NMR (ppm): 7.83 (1H, H-5), 6.43 (1H, H-4), 3.61 (2H, NCH_2), 2.92 (2H, NCH_2), 1.87 (2H, CH_2), 1.63 (2H, CH_2). ^{13}C NMR (ppm): 23.4 and 26.4 (NCH_2CH_2), 47.0 and 47.7 (NCH_2CH_2), 105.3 (H-4), 136.1 (H-5), 147.0 (H-3), 163.8 (CO). Anal. Calc. for $C_{48}H_{62}B_2F_6LaN_{12}O_6P$: C, 47.7; H, 5.13; N, 13.9; Found: C, 48.0; H, 5.28; N, 13.7%.

The isostructural $[Nd(Tp^{cpd})_2]PF_6$ and $[Sm(Tp^{cpd})_2]PF_6$ complexes were prepared similarly.

‡ Crystal data. For $C_{24}H_{31}BN_9O_3Tl$: orthorhombic, *Pbcn*, $a = 34.899(4)$, $b = 9.26(1)$, $c = 17.409(3)$ Å, $V = 5605(4)$ $Å^3$, $Z = 8$, $T = 298(2)$ K, $D_{calc} = 1.680$ g cm^{-3}, colorless rod, GOF = 0.625, μ(Mo-Kα) = 0.71073 Å, $R(F) = 4.03\%$ for 6329 observed independent reflections ($4° \le 2\theta \le 55°$).

For $C_{48}H_{62}B_2F_6LaN_{18}O_6P{\cdot}2EtOAc$: monoclinic, *C*2/*c*, $a = 25.7439(3)$, $b = 19.9574(2)$, $c = 25.7150(3)$ Å, $\beta = 101.1056(5)°$, $V = 12964(3)$ $Å^3$, $Z = 8$, $T = 173(2)$ K, $D_{calc} = 1.470$ g cm^{-3}, colorless block, GOF = 2.205, μ(Mo-Kα) = 0.71073 Å, $R(F) = 7.81\%$ for 10194 observed independent reflections ($4° \le 2\theta \le 50°$).

For $C_{48}H_{62}B_2F_6N_{18}NdO_6P{\cdot}CH_2Cl_2{\cdot}CHCl_3$: monoclinic, *C*2/*c*, $a = 26.0247(4)$, $b = 19.8463(3)$, $c = 26.3284(4)$ Å, $\beta = 103.9329(7)°$, $V = 13198(5)$ $Å^3$, $Z = 8$, $T = 173(2)$ K, $D_{calc} = 1.512$ g cm^{-3}, purple block, GOF = 2.040, μ(Mo-Kα) = 0.71073 Å, $R(F) = 8.52\%$ for 12673 observed independent reflections ($4° \le 2\theta \le 52°$).

For $C_{48}H_{62}B_2F_6N_{18}O_6PSm{\cdot}1/2H_2O{\cdot}1/2Me_2CO$: monoclinic, *C*2/*c*, $a = 25.7018(2)$, $b = 19.6629(2)$, $c = 25.5878(3)$ Å, $\beta = 100.4362(8)°$, $V = 12717.4(2)$ $Å^3$, $Z = 8$, $T = 173(2)$ K, $D_{calc} = 1.463$ g cm^{-3}, colorless plate, GOF = 1.168, μ(Mo-Kα) = 0.71073 Å, $R(F) = 8.16\%$ for 10364 observed independent reflections ($4° \le 2\theta \le 50°$). CCDC reference number 186/1885. See http://www.rsc.org/suppdata/dt/b0/b001651i/ for crystallographic files in .cif format.

1 S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, UK, 1999.
2 R. Krentz, PhD Dissertation, University of Alberta, Edmonton, 1989.
3 A. J. Amoroso, A. M. Cargill Thompson, J. C. Jeffery, P. L. Jones, J. A. McCleverty and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1994, 2751.
4 A. J. Amoroso, J. C. Jeffery, P. L. Jones, J. A. McCleverty, L. Rees, A. L. Rheingold, Y. Sun, J. Takats, S. Trofimenko, M. D. Ward and G. P. A. Yap, *J. Chem. Soc., Chem. Commun.*, 1995, 1881.
5 A. J. Amoroso, J. C. Jeffery, P. L. Jones, J. A. McCleverty and M. D. Ward, *Polyhedron*, 1996, **15**, 2023.
6 P. L. Jones, K. L. V. Mann, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *Polyhedron*, 1997, **14**, 2435.
7 A. L. Rheingold, B. S. Haggerty, L. M. Liable-Sands and S. Trofimenko, *Inorg. Chem.*, 1999, **38**, 6306.
8 A. J. Amoroso, J. C. Jeffery, P. L. Jones, J. A. McCleverty, E. Psillakis and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1995, 1175.
9 C. Musante and P. Pino, *Gazz. Chim. Ital.*, 1947, **77**, 199.
10 H. Brunner and T. Scheck, *Chem. Ber.*, 1992, **125**, 701.
11 P. L. Jones, A. J. Amoroso, J. C. Jeffery, J. A. McCleverty, E. Psillakis, L. H. Rees and M. D. Ward, *Inorg. Chem.*, 1997, **36**, 10.