Hydrotris(methimazolyl)borate, a soft analogue of hydrotris(pyrazolyl)borate. Preparation and crystal structure of a novel zinc complex

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The synthesis of a new ligand, hydrotris(methimazolyl)borate,† a soft analogue of hydrotris(pyrazolyl)borate, is reported; to demonstrate the coordination chemistry of this novel ligand, complexes of Cu^I and Zn^{II} are prepared and characterised.

The hydrotris(pyrazolyl)borate anion (Tp) has become widely accepted as a tridentate trigonal six-electron donor ligand in metal coordination systems. Part of the usefulness of Tp as a ligand is derived from the fact that it can be considered as isolobal with the ubiquitous cyclopentadienyl anion (Cp).[1] Substitutions on the pyrazolyl ring allow control over the steric environment of the binding site. Tp has thus found favour in coordination chemistry for investigating the relationship between structure and reactivity in metal complexes.[2] However, unlike Cp, it is more difficult to alter the donor/acceptor properties of Tp and therefore the reactivity of metal complexes derived from the electronic effects of the Tp ligand.

Recently this group has focused on designing ligands to change the nature and bonding of systems analogous to Tp by attempting to replace the hard nitrogen donor with softer sulfur donors. It came to our notice from our biological studies that there is a significant difference between the biological activity and function of thiols, thioethers and thiones. It has been shown that 2-sulfanyl-1-methylimidazole, known by the trivial name 'methimazole' and widely regarded as existing in the thiol form is in fact better represented as its thione tautomer Scheme 1.[3]

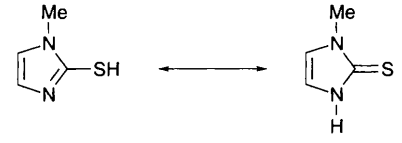
The realisation that the acidic hydrogen on methimazole resides on nitrogen rather than sulfur led us to consider the condensation of methimazole with borohydride (Scheme 2) to produce the novel metal coordinating soft tridentate trigonal 6e$^-$ donor ligand, sodium hydrotris(methimazolyl)borate (Tm) **1** which is analogous to Tp.§

The ligand Tm is prepared in an analogous manner to Tp from the reaction of sodium borohydride and methimazole in the melt.§

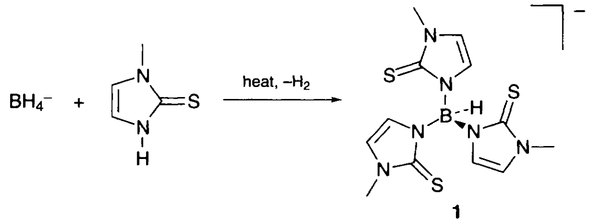
Treatment of zinc bromide with excess ligand leads to the preferential formation of the 1 : 1 complex [Zn(Tm)Br].¶ The X-ray crystal structure|| of [Zn(Tm)Br] (Fig. 1) reveals the coordination geometry expected of this ligand. The molecule has a crystallographic threefold rotation symmetry with the H–B and Zn–Br bonds located on the crystallographic axis. The zinc binds to the three sulfur donors and one bromine atom with a Zn–S bond length of 2.355(3) Å and a Zn–Br bond length of 2.364(2) Å. The zinc ion has a slightly distorted tetrahedral environment with slight compression of the S–Zn–S angle to 105.35(8)°. The Br–Zn–S bond angle is 113.33(7)°. In contrast to Tp which forms three six-membered rings with the metal at the apex, the extra carbon–sulfur double bound in Tm gives rise to three eight-membered rings. In order to relieve the associated strain the methimazole fragments of the ligand adopt a propeller twist of 45.6° measured along the imaginary torsion angle S–Zn···B–N.

Tm offers a slightly different metal binding geometry to that found in Tp, as demonstrated by the comparison of [Zn(Tm)Br] with the analogous Tp complex $[\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{ZnBr}]$.[2a] The coordinated zinc ion is observed to move deeper into the plane of the donor ligands (S–Zn–S 105°) in the methimazolyl complex than in the analogous pyrazolyl complex (N–Zn–N 95°). In contrast to the marked change of the position of the metal ion in the chelate, there is only a relatively small extension of the Zn–Br bond lengths from 2.325 Å in Tp to 2.364 Å in Tm.

The reaction of copper(I) chloride with Tm was conducted under a carbon monoxide atmosphere in an attempt to prepare the carbonyl complex analogous with the classic [TpCuCO] species.[4] However, in contrast to Tp the Tm complex** failed to coordinate carbon monoxide, generating a complexes consistent



Scheme 1



1

Scheme 2

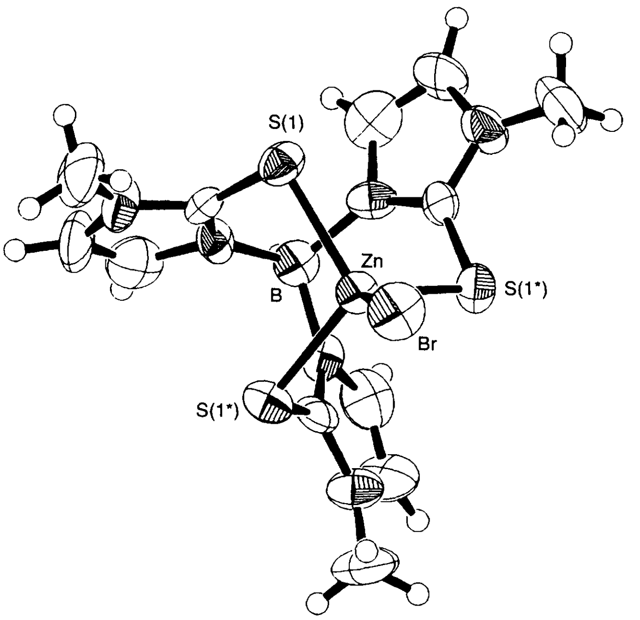


Fig. 1 The structure of [Zn(Tm)Br]. Selected bond lengths (Å) and angles (°): Zn–S 2.355(3), Zn–Br 2.364(2); S–Zn–S 105.35(8)°, S–Zn–Br 113.33(7)°.

with the formation of [Cu(Tm)]. As discussed above, the movement of the metal into the plane of the ligand has already been demonstrated for Tm. Thus it is postulated that the copper(I) complex formed allows the metal ion to sit deeper into the plane of the chelating sulfurs adopting a trigonal-planar geometry. This motif is consistent with the well known 'thione'–copper complex $[\mathrm{Cu(SPMe_3)_3}]^+[\mathrm{ClO_4}]^-$[5] and the recently reported $[\mathrm{Ag(methimazole)_3}]^+\ \mathrm{NO_3}^-$.[6]

The use of thiones as donors in coordination chemistry has significant advantages when compared to thiols. One of the main difficulties in using thiols in coordination chemistry is the redox instability of metal–thiolate bonds. These bonds may readily undergo homolysis causing reduction of the metal ion and formation of a disulfide [eqn. (1)].

$$2\mathrm{Cu^{II}} + 2\mathrm{RSH} \rightarrow 2\mathrm{Cu^{I}} + \mathrm{RSSR} + 2\mathrm{H^+} \qquad (1)$$

Incorporation of readily oxidisable sulfur groups in coordination chemistry can cause severe problems due to facile oxidation of the sulfur ligand and this problem is usually solved by using bulky, sterically hindered thiols to try to prevent autooxidation. In contrast the thione donors in Tm are resistant to oxidation by metals.

Tp can be considered to be harder than Cp. This new ligand is the first example of a soft, singly charged, tridentate trigonal six-electron donor analogue. It is clear that Tm offers different donor/acceptor properties to its cousin Tp thus suggesting that this new species, along with the mixed pyrazole/methimazole donor ligands, has great potential for tuning the electron density at the metal centre and hence the redox properties, a factor which is of great importance when exploiting the coordination chemistry of organometallic compounds in catalysis and material science.

Footnotes

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‡ Tm = Hydrotris(methimazolyl)borate = hydrotris(3-methyl-1-imidazolyl-2-thione)borate.

§ The microanalysis and spectroscopic characterisation obtained for Tm are consistent with expected values. Found: C, 38.30; H, 4.20; N, 21.95; S, 25.61. Calc. for $\mathrm{C_{12}H_{16}BN_6NaS_3}$: C, 38.51; H, 4.31; N, 22.45; S, 25.70%. ^{1}H NMR [400 MHz, $(\mathrm{CD_3})_2\mathrm{SO}$], δ 3.38 (s, 3 H, Me), 6.40 (d, 1 H, CH), 6.79 (d, 1 H, CH, *J* 2.2 Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR; δ 33.6 (Me), 116.5 (CH), 120.8 (CH), 163.4 ($\mathrm{C_{quat}}$). IR ν(B–H) 2480 cm^{-1}.

¶ The microanalysis and spectroscopic characterisation obtained for [Zn(Tm)Br] are consistent with expected values. Found: C, 31.44; H, 3.92; N, 15.71; S, 17.30. Calc. for $\mathrm{C_{12}H_{16}BBrN_6S_3Zn}$: C, 29.03; H, 3.25; N, 16.92; S, 19.37%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$); δ 3.60 (s, 3 H, Me), 6.74 (d, 1 H, CH), 7.07 (d, 1 H, CH, *J* 2.0 Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR; δ 77.2 (Me), 119.3 (CH), 123.5 (CH), 162.0 ($\mathrm{C_{quat}}$). IR ν(B–H) 2475 cm^{-1}.

‖ *Crystal data* for [Zn(Tm)Br]: $\mathrm{C_{12}H_{16}BBrN_6S_3Zn{\cdot}2.25CHCl_3}$; M = 765.17, trigonal, space group $R3(h)$ (no. 146), a = 13.295(2), c = 16.394(3) Å, U = 2509.8(4) Å^3, Z = 3, D_c = 1.519 g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, $F(000)$ = 1135.50, μ = 26.72 cm^{-1}. The room-temperature diffraction data were collected on a Rigaku AFC7S diffractometer using graphite-monochromated Mo-Kα radiation. 1946 reflections were measured (1752 unique, R_{int} = 0.047) of which 1115 with $I > 3\sigma(I)$ were used in the refinement. A semiempirical ψ-scan absorption correction was made ($T_{\min}$ = 80.02%, $T_{\max}$ = 100%) along with a correction for decay (7.73%) and an L_p correction. The structure was solved by direct methods which unambiguously revealed the metal complex ion. Some problems were encountered modelling the $\mathrm{CHCl_3}$ molecule satisfactorily. The occupation number for each of the atoms was set at 0.75 and the chlorine atoms were subject to severe thermal disorder. Full-matrix least-squares refinement led to a model with R = 0.053, R_w = 0.061, GOF = 1.95 with all non-hydrogen atoms anisotropic (108 variables). Residual electron density was in the range 0.80 to −0.39 e Å^{-3}. All calculations used the TeXsan Crystallographic Software Package (Molecular Structure Corp., The Woodlands, TX, 1985 & 1992). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/169.

** The microanalysis and spectroscopic characterisation obtained for [Cu(Tm)] are consistent with expected values. Found: C, 33.77; H, 3.59; N, 19.25. Calc. for $\mathrm{C_{12}H_{16}N_6BCuS_3}$: C, 34.74; H, 3.89; N, 20.26%. IR ν(B–H) 2360 cm^{-1}, No C≡O stretch is observed.

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