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Sodium hydrotris(methimazolyl)borate, a novel soft, tridentate ligand: preparation, structure and comparisons with sodium hydrotris(pyrazolyl)borate †

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The hydrotris(methimazolyl)borate anion (Tm), a soft analogue of the hydrotris(pyrazolyl)borate anion (Tp), has been synthesized. This novel ligand system has been designed to maintain the tripodal geometry around the boron while allowing the replacement of the three nitrogen donor atoms by three sulfur (thione) donor atoms, thus providing a complementary soft, tridentate, face capping ligand system. The two ions, Tm and Tp were compared by X-ray analysis and *ab initio* calculations in an attempt to explore the effects of exchanging the hard donor atoms for soft donor atoms in this type of ligand. The compound NaTm is essentially salt like with discrete anions and hydrated sodium cations. The structure of NaTp crystallised under identical conditions is observed to be an infinite ribbon containing monodentate, bridging and pendant pyrazolyl units. The co-ordination sphere of the sodium cation in NaTp is completed by two water molecules. *Ab initio* calculations at the Hartree–Fock level using a 6-31G* basis set on these anions and their sodium complexes suggested that while both ions are in general similar in nature, there are subtle differences which will influence their chemistry. *Ab initio* calculations were also used to provide a rational analysis of the formation of the two sodium salts obtained and on the analogous copper complexes further to clarify the hard and soft nature of the two ligand systems.

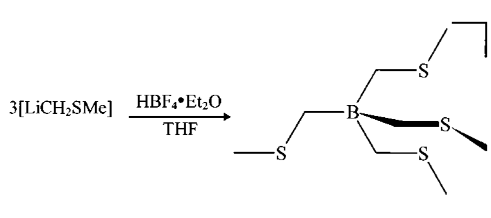
Introduction

Transition metal complexes are a rich source of a diverse range of catalysts, reagents and "smart" materials. Although the reactivity of these compounds is based on the metal, and it is the choice of metal which provides the basic reactive profile, the exact properties exhibited by a metal arise from the symbiotic relationship between the metal and its ligands. At a gross level, modulation of the reactivity of a metal complex by a ligand involves a modification of solubility and charge. At a more subtle level, ligands control the number and position of vacant co-ordination sites, the size or shape of the substrate admitted to a metal centre and the stability of electron rich or electron poor metal centres. Considering the number of factors involved, it is unsurprising that the design of new metal complexes is approached in a systematic manner using homologous series of ligands in an attempt to engineer a graded change in chemistry.[1] However, the utility of a ligand is not just determined by its properties and those of its metal complexes but also by the ease with which it can be prepared. The more successful ligand systems (*e.g.* phosphines) tend to be those which can be constructed relatively simply through one, or two step, high yield reactions.[1]

On occasions a ligand system is developed which is capable of dramatically altering the behaviour of a metal. This was the case with the hydrotris(pyrazolyl)borate anion (Tp),[2,3] which, for instance, once complexed with copper generated a unique carbonyl complex.[4,5] Consistent with the above, pyrazolylborates are relatively simple to prepare and have been found to produce complexes with a vast array of metal ions spanning the wider disciplines of classical co-ordination chemistry, organometallic chemistry and inorganic biochemistry.[3,6–8] As a ligand system, Tp has found great favour amongst synthetic chemists as a facial tridentate six electron donor sometimes compared with and used as an alternative to the isoelectronic cyclopentadienyl anion (Cp).[3]

While it is possible to alter the steric requirements of the three donor nitrogens in Tp by placing substituent groups (*e.g.* Me, ^{t}Bu or Ph)[3,9] on the pyrazole ring adjacent to the donor nitrogens, it is more difficult to alter the electron donor properties of the ligand. Thus, the pyrazolylborate ligand system (*cf.* phosphines) is somewhat restricted should a markedly softer ligand be required. Soft tridentate sulfur containing macrocycles such as trithiacyclononane have been prepared[10] which offer a six electron bonding set comparable with that found for Cp and Tp. However, since thioether macrocycles do not naturally carry an overall charge, they are not readily able to offer a controlled, graded alteration of the chemistry of a metal in conjunction with Cp and Tp.

Clearly it would be of some value to extend the scope of the existing structural motif simply by changing the donor set. This problem has been addressed by Riordan and co-workers[11–14] whose elegant chemistry produced soft tripodal borate ligands based on thioethers, eqn. (1). Subsequent complexation of this tridentate sulfur based system with molybdenum carbonyl produced a similar structural motif to Tp.[11] The existence of these species confirms that soft ligands based on the tetrahedral borate anion can be prepared and furthermore that they can generate the structural types observed with the more popular Tp and



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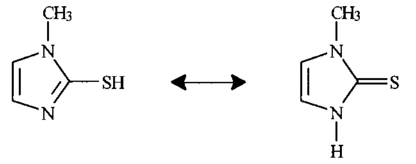
† Methimazolyl = 3-methyl-2-thioimidazolinyl.

Cp ligand systems. However, these soft aliphatic species lack the extended conjugated system which is present in the pyrazolyl moieties thus mitigating against a wider distribution of the electron density within the ligand. Furthermore, due to the orientation of the electron pairs around the sulfur it is difficult to generate a protected pocket around the metal centre *via* the incorporation of bulky groups adjacent to the donor atom.

We envisaged that any expansion of the Tp ligand system would be best achieved by using the traditional high yield reaction of Trofimenko[2] but employing an alternative organic ring fused to the boron. Our previous work[15] had highlighted that in species such as methimazole the acidic hydrogen lay on the nitrogen rather than on the sulfur and that consistent with other workers[16,17] these species are best described as amine thiones, eqn. (2). This suggested to us that species such as



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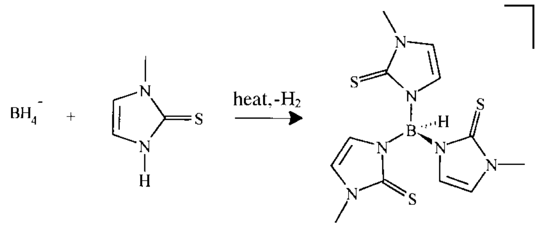
methimazole could undergo an elimination of hydrogen on reaction with the BH_4^- anion in a melt to generate a soft analogue of Tp, eqn. (3).[18]



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We have recently demonstrated this to be the case[18] and hence report in full the synthesis and structure of our soft tripodal ligand, the hydrotris(methimazolyl)borate anion, Tm. As much of the utility of this anion is likely to be driven by its chemical analogy with Tp, we have also synthesized and crystallised the parent Tp system under identical conditions. Furthermore, both anions have been subjected to *ab initio* calculations to try and provide an insight into the subtle chemical differences which may be expected as a result of progressively replacing methimazole for pyrazole in these systems.

Experimental

All chemicals were commercially obtained and used without further purification. All NMR spectra were recorded on a Bruker AMX 400 spectrometer operating at 400.1 MHz for ^1H and 100 MHz for ^{13}C.

Preparation

Sodium hydrotris(pyrazolyl)borate (NaTp). The preparation of sodium hydrotris(pyrazolyl)borate follows that of Trofimenko.[2] Briefly, sodium tetrahydroborate (1.5 g, 0.040 mol) and pyrazole (10 g, 0.15 mol) were placed in a 50 ml round bottom flask and the temperature gently raised to 160 °C. The melt gently evolved hydrogen gas, which was collected and its volume measured. The reaction was stopped when 3 mole equivalents (≈0.12 mol, ≈2.7 l) of hydrogen had been collected signifying that the dominant product would be the tris(pyrazolyl)borate. The mixture was allowed to cool and washed with hexane. The resulting white powder was recrystallised from hexane–toluene at −4 °C. Crystals for structure determination were obtained directly from the liquors, prior to the retrieval and drying (dehydration) of the bulk material. Spectroscopic properties were consistent with literature values[2] (Found: C, 45.50; H, 4.15; N, 35.08. Calc. for $C_9H_{10}BN_6Na$: C, 45.80; H, 4.27; N, 35.61%).

Sodium hydrotris(methimazolyl)borate (NaTm). 3-Methylimidazoline-2-thione (methimazole, 13.2 g, 0.115 mol) and sodium tetrahydroborate (1.1 g, 0.029 mol) were mixed together in a 50 ml round bottom flask, which was fitted with an air jacket condenser. The vessel was placed in an oil-bath and the temperature raised slowly to 160 °C. The mixture melted at approximately 136–140 °C (mp methimazole = 144 °C) whereupon the vigorous evolution of hydrogen gas began. This was collected as above and the reaction allowed to proceed until 3 mole equivalents (≈0.090 mol, 2.0 l) of hydrogen gas had evolved. Excessive heating (>180 °C) led to the mixture turning deep pink/purple indicative of undesirable products forming. Once the reaction was complete the mixture was allowed to cool. The resulting solid was washed with hexane to remove excess of methimazole and Soxhlet extracted into chloroform. The resulting white powder was filtered off and dried, yielding anhydrous NaTm (65%) (Found: C, 38.30; H, 4.22; N, 21.78; S, 25.61. $C_{12}H_{16}BN_6NaS_3$ requires C, 38.51; H, 4.31; N, 22.45; S, 25.70%). δ_H (400.1 MHz; solvent $(CD_3)_2SO$) 3.38 (s, 3 H, Me), 6.40 (d, 1 H, CH) and 6.79 (d, 1 H, CH, *J* 2.2 Hz). δ_C (100.1 MHz; solvent $(CD_3)_2SO$) 33.6 (CH_3), 116.5 (CH), 120.8 (CH) and 163.4 (C_{quat}). $\tilde{\nu}/cm^{-1}$ (Nujol mull): 2478 (B–H).

The compound thus obtained is sufficiently pure for further use. However, it can be recrystallised from methylene chloride at −4 °C in the presence of moist air to yield a hydrated form (Found: C, 31.31; H, 5.33; N, 18.34; S, 21.21. $C_{12}H_{25}BN_6NaO_{4.5}S_3$ requires C, 31.65; H, 5.53; N, 18.45; S, 21.12%).

Thallium(I) hydrotris(methimazolyl)borate (TlTm). Anhydrous NaTm (0.50 g, 1.3 mmol) in 75 ml of acetone was added to $TlNO_3$ (0.35 g, 1.3 mmol) suspended in 25 ml of acetone and the mixture was refluxed for 4 h. The solid formed was filtered off, washed with water to remove $NaNO_3$ and any residual $TlNO_3$ filtered and dried (0.61g, 81%) (Found: C, 26.56; H, 2.90; N, 15.25. $C_{12}H_{16}BN_6S_3Tl$ requires C, 25.94; H, 2.90; N, 15.12%). $\tilde{\nu}/cm^{-1}$ (Nujol mull): 2475 (B–H). δ_H (400.1 MHz; solvent $(CD_3)_2SO$, 313 K) 3.98 (s, 9 H, CH_3), 6.44 (d, *J* = 3, 3 H, CH) and 6.81 (d, *J* = 3, 3 H, CH).

Crystal structure determinations

Crystals of $NaTp\cdot 1H_2O$ and $NaTm\cdot 4.5H_2O$ were obtained by slow evaporation of methylene chloride solutions in the presence of moist air. In both cases colourless crystals were obtained. They were mounted on glass fibres and all measurements performed at room temperature using graphite monochromated Mo-Kα radiation. Accurate cell dimensions were obtained from 25 accurately centred reflections. Details of the data collection and refinement are given in Table 1. The structure was solved by direct methods[19] and expanded using Fourier techniques.[20] The non-hydrogen atoms were refined anisotropically[21] and in both cases the refinement converged satisfactorily. The structure of NaTm was somewhat problematic since the sodium ions and their associated water molecules are badly disordered. It has not been possible to obtain an entirely satisfactory model for this part of the structure and as a consequence the *R* factors are a little higher than one would wish. Nevertheless, the Tm anion is well defined and the separation of anion and cation is unambiguous. Selected bond lengths and angles are shown in Tables 2 and 3.

CCDC reference number 186/1451.

See http://www.rsc.org/suppdata/dt/1999/2119/ for crystallographic files in .cif format.

Ab initio calculations

Ab initio calculations at the Hartree–Fock level using the 6-31G* basis set[22–24] were carried out on the Tm and Tp anions and their corresponding sodium derivatives using the GAUSSIAN 94 computational package.[25] No symmetry constrictions were applied during the geometry optimisation procedures and frequency calculations were subsequently performed to verify that the optimised structures corresponded to a local minimum. Selected calculated parameters are shown in Table 4.

In order to make a simple qualitative assessment of the relative hardness/softness of the Tm and Tp anions, calculations were carried out on the respective copper(I) complexes (*cf.* sodium) using the DZ (14,11,5)/[8,6,2] copper basis sets of Ahlrichs and co-workers.[26]

Results and discussion

The synthesis of the poly(pyrazolyl)borate anions is driven by the elimination of dihydrogen from the reaction of the tetrahydroborate anion with the acidic proton commonly found in pyrazoles. The extension of this synthetic route to the preparation of softer species became possible once it was realised that many 1,2 imine thiols such as methimazole are better formulated as their thione tautomer.[15–17] The acidic hydrogen on the amine group should allow species such as methimazole to react in an analogous manner to pyrazole, eqns. (2) and (3), yielding species in which soft sulfur donors will be available for metal co-ordination. However, there will be a small modification to the ligand architecture around the donor atoms. In particular, in the hydrotris(methimazolyl)borate anion the boron is separated from the donor atoms by three bonds in comparison to two bonds in Tp. Thus, when the Tm anion chelates to metals such as zinc,[18] three eight-membered rings form rather than the three six-membered rings found with the Tp anion.[9]

From the location of the acidic hydrogen the binding of methimazole to boron is expected to be *via* a B–N linkage. However, it is possible that thiol–thione tautomerisation, eqn. (2),[27,28] while not dominant at room temperature, could occur in the melt prior to coupling. Alternatively a 1–3 shift might occur after the initial coupling reaction. Consequently, concern existed that under the prevailing reaction conditions the boron might migrate from the nitrogen to the sulfur. Spectroscopic evidence for the desired B–N coupling in the Tm anion relied heavily on the chemical shift of the thione carbon (δ 163.4) in the NMR spectrum and the identification of the $>$C=S stretch ($\approx$730 cm^{-1}) in the infrared spectrum neither of which could be considered as conclusive. Definitive evidence for the desired arrangement in the form of a crystal structure was sought. Suitable crystals proved elusive until it was observed that crystallisation occurred more readily if moist air was allowed to contact the liquors during the process. Single crystals were thus obtained.

Crystal structures

The structure of our new system consists of discrete Tm anions and disordered one-dimensional chains of hydrated sodium cations, thus rationalising the need for water during the crystallisation process. The anion (Fig. 1) has approximate C_3 symmetry, with each methimazolyl group twisted about the B–N bond to minimise the steric effects of the methyl groups. This results in a "propeller-like" conformation of the rings. The soft nature of the ligand is manifest in the total lack of interaction of the donor atoms with the sodium cation. It is also notable that the ligand is not prearranged for complexation. The rotation about the B–N bond results in an "inverted" configuration, with the three sulfur atoms on the same side as the B–H bond.

A viable comparison of Tm with Tp required that the Tp anion be crystallised in an analogous manner to the Tm anion, *i.e.* in the presence of moist air. The structure of the compound thus obtained reveals infinite one-dimensional chains (Fig. 2) in which five-co-ordinate sodium ions (Fig. 3) are bridged by a pyrazolyl nitrogen and a water molecule. The co-ordination sphere of the sodium ion is completed below the plane by an interaction with a second pyrazolyl nitrogen, while the vacant sixth co-ordination site (above the plane) is protected by a pyrazolyl ring. It is tempting to invoke a weak η^5-π interaction although the Na–C_3N_2 ring centroid distance, at 3.01 Å, is somewhat longer than in genuine documented examples such as Na(η^5-C_5H_5)·TMEDA (2.65 Å)[29] and $[Na(\eta^5\text{-}C_5H_5)_2]^-$ (2.336(3) Å).[30]

Table 1 Experimental details of the crystal structure determination of NaTp·H_2O and NaTm·4.5H_2O

	NaTp·H_2O	NaTm·4.5H_2O
Molecular formula	$C_9H_{12}BN_6NaO$	$C_{12}H_{25}BN_6NaO_{4.5}S_3$
M	254.03	455.37
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)
a/Å	8.508(2)	9.962(2)
b/Å	20.730(3)	14.790(2)
c/Å	7.062(1)	8.217(2)
α/°		83.55(10)
β/°		78.08(2)
γ/°		72.65(1)
V/Å^3	1245.5	1129.0(4)
Z	4	2
μ(Mo-Kα)/cm^{-1}	1.23	3.78
T/K	293	293
Reflections measured	1692	5227
Unique reflections	1692	4935 (R_{int} = 0.044)
Observed reflections	1212 ($I > 1.00\sigma(I)$)	2299 ($I > 3.00\sigma(I)$)
R	0.046	0.067
R′	0.043	0.087

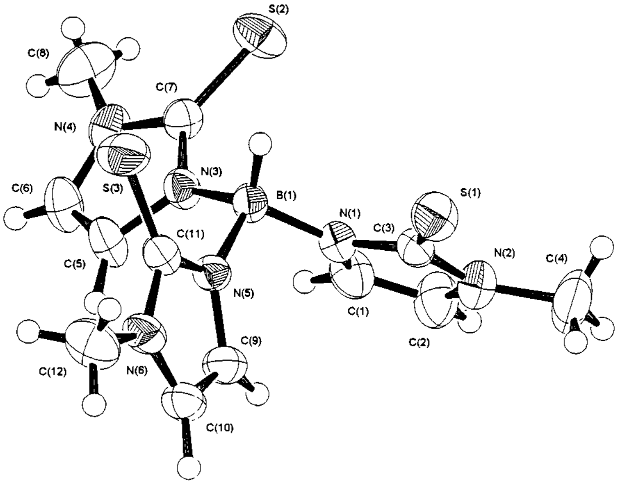


Fig. 1 The structure of the Tm anion showing the atom numbering scheme. The thermal ellipsoids are drawn at the 40% level.

The conformation of the Tp anion is markedly different to the Tm anion. It co-ordinates as a didentate ligand to one sodium, with one of the co-ordinated pyrazolyl groups bridging to the second sodium centre. The third, pendant, pyrazolyl group is weakly hydrogen bonded (*d*N(6)–H(12) = 1.8 Å) to the bridging water ligands (Fig. 3). A number of structures of substituted poly(pyrazolyl)borate ligands have been previously determined. Unlike our structure, alkali metal salts of perfluoroalkyl substituted Tp ligands form mono- or di-nuclear structures with significant M–F interactions,[31–33] while hydrotris(3,4,5-trimethylpyrazolyl)borate forms a mononuclear complex with three trimethylpyrazoles completing the potassium co-ordination sphere.[34] Potassium salts of the related compounds hydrotris(1,2,4-triazolyl)borate[35] and

Table 2 Selected bond lengths (Å) and angles (°) for $Na[HB(MeC_3H_2N_2S)_3]\cdot 4.5H_2O$

	X-Ray	*Ab initio*[a]		X-Ray	*Ab initio*[a]
S(1)–C(1)	1.706(9)	1.704	N(4)–C(7)	1.37(1)	
S(2)–C(5)	1.699(8)		N(4)–C(8)	1.45(1)	
S(3)–C(9)	1.695(8)		N(5)–C(9)	1.351(9)	
N(1)–C(1)	1.354(9)	1.345	N(5)–C(10)	1.38(1)	
N(1)–C(2)	1.37(1)	1.382	N(5)–B(1)	1.55(1)	
N(1)–B(1)	1.55(1)	1.579	N(6)–C(9)	1.36(1)	
N(2)–C(1)	1.36(1)	1.351	N(6)–C(11)	1.35(1)	
N(2)–C(3)	1.36(1)	1.385	N(6)–C(12)	1.46(1)	
N(2)–C(4)	1.48(1)	1.442	C(2)–C(3)	1.35(1)	1.331
N(3)–C(5)	1.37(1)		C(6)–C(7)	1.33(1)	
N(3)–C(6)	1.393(9)		C(10)–C(11)	1.34(1)	
N(3)–B(1)	1.54(1)	1.579	B(1)–H(1)	0.97(6)	1.180
N(4)–C(5)	1.341(9)				
C(1)–N(1)–C(2)	108.2(7)	108.2	C(9)–N(5)–C(10)	108.8(6)	
C(1)–N(1)–B(1)	123.7(7)	126.4	C(9)–N(5)–B(1)	124.8(6)	
C(2)–N(1)–B(1)	128.1(7)	125.1	C(10)–N(5)–B(1)	126.3(6)	
C(1)–N(2)–C(3)	108.8(7)	109.4	C(9)–N(6)–C(11)	109.4(7)	
C(1)–N(2)–C(4)	124.3(9)	124.9	C(9)–N(6)–C(12)	123.7(7)	
C(3)–N(2)–C(4)	126.8(9)	125.8	C(11)–N(6)–C(12)	126.9(7)	
S(1)–C(1)–N(1)	126.9(6)	129.3	S(2)–C(5)–N(3)	127.0(6)	
S(1)–C(1)–N(2)	125.7(6)	123.6	S(2)–C(5)–N(4)	125.4(6)	
N(1)–C(1)–N(2)	107.4(7)	107.1	N(3)–C(5)–N(4)	107.6(7)	
N(1)–C(2)–C(3)	107.9(8)	108.8	N(3)–C(6)–C(7)	109.6(7)	
N(2)–C(3)–C(2)	107.6(8)	106.4	N(4)–C(7)–C(6)	106.7(7)	
N(1)–B(1)–N(3)	108.3(6)	107.6	S(3)–C(9)–N(5)	127.2(6)	
N(1)–B(1)–H(1)	112(3)	111.3	S(3)–C(9)–N(6)	126.5(6)	
N(3)–B(1)–H(1)	106(3)		N(5)–C(9)–N(6)	106.3(7)	
C(5)–N(3)–C(6)	106.2(6)		N(5)–C(10)–C(11)	107.6(7)	
C(5)–N(3)–B(1)	126.3(7)		N(6)–C(11)–C(10)	107.9(7)	
C(6)–N(3)–B(1)	127.5(7)		N(1)–B(1)–N(5)	108.1(6)	
C(5)–N(4)–C(7)	109.9(7)		N(3)–B(1)–N(5)	108.7(6)	
C(5)–N(4)–C(8)	125.1(8)		N(5)–B(1)–H(1)	113(3)	
C(7)–N(4)–C(8)	125.0(7)				

[a] The calculated bond lengths and angles are identical for the three methimazolyl rings in NaTm and the three pyrazolyl rings in NaTp. Thus for clarity *ab initio* data are provided for a single representative ring system for each anion only.

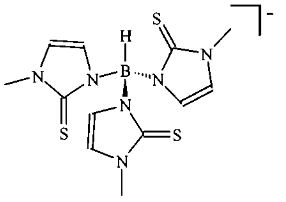
tetrakis(pyrazolyl)borate[36] both form polymeric structures more reminiscent of our structure, in which two water molecules bridge between each potassium ion and the heterocyclic nitrogens only bond terminally. In the case of $M[B(pz)_4]$ an η^5 interaction is also observed, with the M^+–ring centroid distances being 3.097(6) (M = K) and 3.257(4) Å (M = Na).

Ab initio calculations

The scope of the co-ordination chemistry of Tm is vast and can be estimated from the volume of available information on Tp. In order further to understand the analogy between these two systems and to probe their electronic structures and their relative complexing abilities both anions (Tm/Tp) and their sodium and copper(I) complexes were subjected to geometry optimisation procedures by *ab initio* calculations. Initially, however, it was thought instructive to begin the *ab initio* studies of this novel system by analysing the stability of the two possible conformers of Tm; namely that including a B–N linkage (**I**) and that possible *via* a B–S linkage (**II**). Consistent with the experimental results, the structure using a B–N linkage was found to be the more stable by 40.4 kcal mol^{-1}.

Having established that calculations can identify the most stable conformer of the Tm anion, a viable comparison of the two tripodal ligands, as free anions, using *ab initio* calculations could be made. Their optimised geometries are shown in Fig. 4. The most noticeable features are that both ions have approximately C_3 symmetry and that the rings have twisted about the B–N bonds with the result that the donor atoms are no longer prearranged for complexation. Instead the molecules have "inverted" such that the donors lie in a plane on the same side of the molecule as the B–H bond. It is particularly satisfying that the calculations are able to predict this conformational change. The angles of twist from the plane of the B–H axis are 43 (Tm) and 49° (Tp). Also of interest are the calculated parameters for the five-membered methimazole and pyrazole rings. The rings are planar and the bond lengths lie in the range 1.31–1.41 Å, consistent with extensive delocalisation. The calculated C–S distance is 1.704 Å and may be compared with the values of 1.686 Å for the parent thione structure 3-methylimidazoline-2-thione and 1.766 Å for the corresponding thiol tautomer calculated in a similar manner.[15] The charge distribution (as obtained from a Mulliken population analysis) shows that each ring in the Tm anion carries a charge of −0.62 electron compared with −0.57 electron in the Tp anion. This is compensated by changes in charge on the B–H unit, B being more positive and H less negative in the Tm anion. Thus in the Tm anion we have a ligand behaving as an anionic thione with the charge delocalised across the whole ligand. Overall the agreement of the calculated and observed data (Table 4) is good and deviations can on the whole be ascribed to the effects of co-ordination. The calculated Tm structure closely parallels that determined by X-ray crystallography (in which anion–cation separation is observed).

A direct comparison of the calculated structure of the free Tp anion with the crystal structure is not strictly meaningful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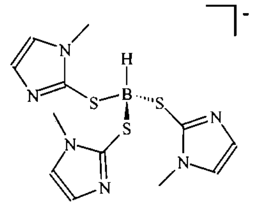
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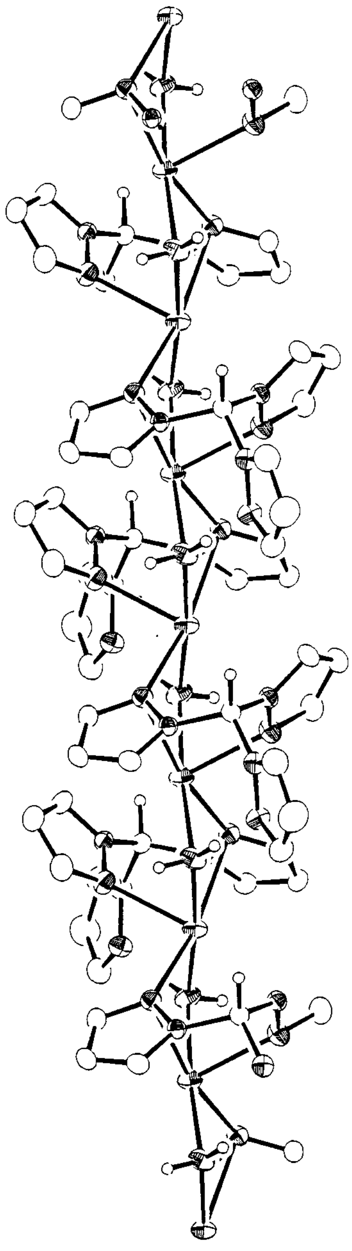

Fig. 2 The structure of the polymeric ribbon of NaTp·H_2O.

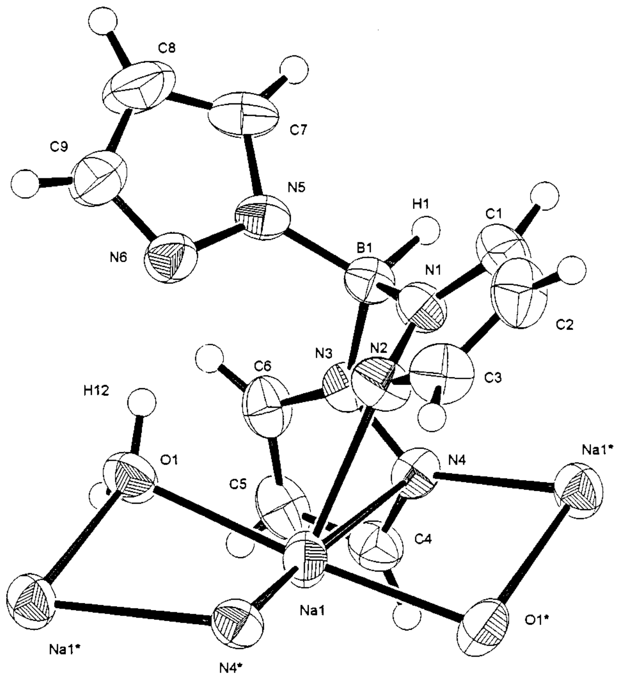

Fig. 3 The local structure of NaTp·H_2O showing the atom numbering scheme and the thermal ellipsoids at the 40% level.

since in the crystal the Tp is co-ordinated to the sodium ions (see above). Indeed, so far as we can ascertain, there are no examples of non-co-ordinated Tp in the literature. However, the structures of the anhydrous sodium salts of Tm and Tp were calculated (Fig. 4). In both cases the anions act as tridentate ligands, in contrast to the crystal structures. We ascribe this observation to the lack of competing solvent molecules, which forces ion pairing and thus co-ordination to the metal as the most stable arrangement. The two structures differ somewhat. Most noticeable is that the pyrazole rings in NaTp lie parallel to the Na–B axis, giving approximately C_{3v} symmetry, while in NaTm the methimazole rings lie at an angle of 40° to the Na–B axis, resulting in a lower, C_3, symmetry (similar to the geometry observed in Zn(Tm)Br[18]). Despite the twist of the rings, the Na···B distance in NaTm (3.72 Å) is much larger than that in NaTp (3.13 Å) and reflects the increase in size (from six to eight) of the chelate rings formed on complexation. The sodium ion in NaTp carries a greater positive charge (+0.76) than that in NaTm (+0.59) and since the charge on the B–H unit is identical in both species the greater negative charge is localised on the pyrazole rings.

Since the effect of solvent is clearly significant we then calculated the effect of addition of one molecule of ammonia to the complex (Fig. 4, Table 4). In both cases the overall enthalpy of formation was more negative than for the unsolvated species. The stabilisation is greater for NaTp(NH_3) than for NaTm(NH_3) (-15.3 *vs.* -13.9 kcal mol^{-1}) which is in line with the greater charge carried by the sodium in NaTp. The Na–N and Na–S bond lengths increased by 0.039 and 0.055 Å respectively and the Na···B distances also increased by 0.071 (NaTp) and 0.141 Å (NaTm). It is clear that solvent addition has a markedly greater effect on the Tm complex, pulling the metal out of the ligand cavity. It can be envisaged that the addition of further molecules of solvent will further weaken the co-ordination of Tp and Tm to sodium. The ultimate structures observed in the solid state would seem to represent the "ideal" situation for each ligand, the generally less stable interaction of Tm and sodium leading to a pentahydrate and complete decomplexation, while the more tightly bound NaTp complex only takes up two water molecules, retaining some of the Na–N linkages.

The impetus for the preparation of Tm was given by the desire to generate a soft tripodal ligand analogous to Tp and so the relative hardness of the ligands was also probed by our *ab initio* calculations. Co-ordination to the hard anion, Na^+, has already been shown to favour Tp, with calculated complexation energies of -153.4 kcal mol^{-1} for NaTp and -146.9 kcal mol^{-1} for NaTm, in line with the expected hardness of the ligands, *i.e.* Tp is harder than Tm. Further to confirm this hypothesis required replacement of Na^+ with a softer cation. In this case the Cu^+ ion was chosen. The structures of CuTp and CuTm were optimised‡ (Table 4) and the resulting complexation energies (calculated using the DZ basis set for Cu) were -169.7 and -174.0 kcal mol^{-1} for CuTp and CuTm respectively, confirming that Tm is indeed the softer ligand. It is interesting that these calculations are in line with experimental evidence in predicting that CuTm is more stable than CuTp; CuTm is air stable and is resistant to complexing CO, while CuTp is prone to aerobic oxidation and readily forms adducts with π-acid ligands.[18] This pattern of reactivity is also consistent with the observations of Riordan and co-workers[11–14] on other soft tripodal ligands.

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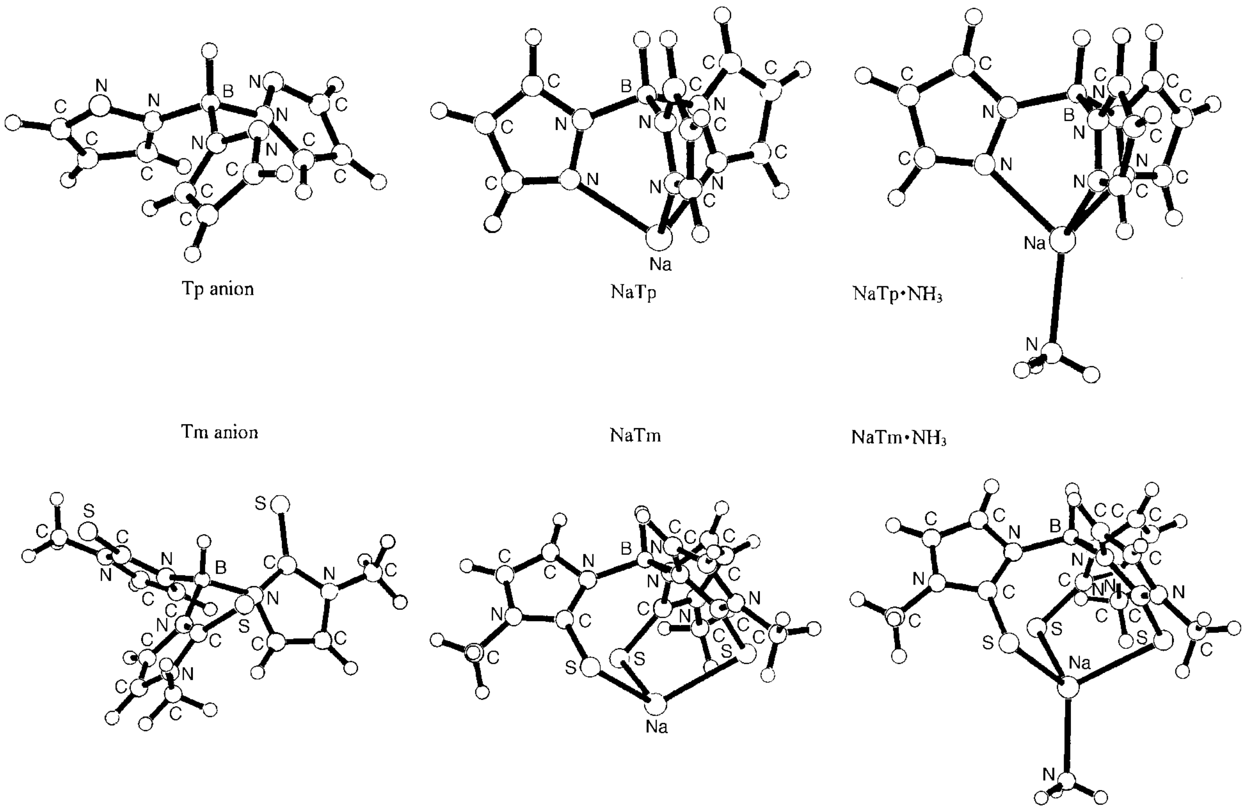
‡ The more appropriate copper basis set DZ (14,11,5)/[8,6,2] of Ahlrichs and co-workers[26] was used for these calculations.

Table 3 Bond lengths (Å) and angles (°) for Na[HB($C_3H_3N_2$)$_3$]·H_2O

	X-Ray	*Ab initio*[a] (for Tp$^-$)		X-Ray	*Ab initio*[b] (for Tp$^-$)
Na(1)–O(1)	2.392(4)		N(4)–C(4)	1.339(5)	
Na(1)–O(1)	2.389(4)		N(5)–N(6)	1.362(5)	
Na(1)–N(2)	2.476(4)		N(5)–C(7)	1.343(5)	
Na(1)–N(4)	2.427(4)		N(5)–B(1)	1.532(6)	
Na(1)–N(4)	2.749(4)		N(6)–C(9)	1.324(5)	
N(1)–N(2)	1.365(5)	1.336	C(1)–C(2)	1.369(7)	1.371
N(1)–C(1)	1.337(5)	1.337	C(2)–C(3)	1.374(7)	1.406
N(1)–B(1)	1.543(5)	1.561	C(4)–C(5)	1.384(6)	
N(2)–C(3)	1.338(6)	1.306	C(5)–C(6)	1.367(6)	
N(3)–N(4)	1.366(4)		C(7)–C(8)	1.361(8)	
N(3)–C(6)	1.339(5)		C(8)–C(9)	1.367(7)	
N(3)–B(1)	1.549(5)	1.561	H(1)–B(1)	1.08(3)	1.196
O(1)–Na(1)–O(1)	174.73(10)		Na(1)–N(4)–C(4)	127.5(3)	
O(1)–Na(1)–N(2)	84.0(1)		Na(1)–N(4)–N(3)	90.9(2)	
O(1)–Na(1)–N(4)	91.3(1)		Na(1)–N(4)–C(4)	94.2(3)	
O(1)–Na(1)–N(4)	80.7(1)		N(3)–N(4)–C(4)	104.9(3)	
O(1)–Na(1)–N(2)	91.0(1)		N(6)–N(5)–C(7)	109.1(4)	
O(1)–Na(1)–N(4)	87.8(1)		N(6)–N(5)–B(1)	124.1(3)	
O(1)–Na(1)–N(4)	99.5(1)		C(7)–N(5)–B(1)	126.8(4)	
N(2)–Na(1)–N(4)	97.1(1)		N(5)–N(6)–C(9)	105.5(4)	
N(2)–Na(1)–N(4)	74.6(1)		N(1)–C(1)–C(2)	108.9(4)	108.5
N(4)–Na(1)–N(4)	168.9(1)		C(1)–C(2)–C(3)	104.2(4)	103.1
Na(1)–O(1)–Na(1)	95.46(10)		N(2)–C(3)–C(2)	112.2(4)	111.4
N(2)–N(1)–C(1)	110.1(3)	110.6	N(4)–C(4)–C(5)	111.8(4)	
N(2)–N(1)–B(1)	123.5(4)	120.3	C(4)–C(5)–C(6)	104.1(4)	
C(1)–N(1)–B(1)	126.0(4)	129.1	N(3)–C(6)–C(5)	109.1(4)	
Na(1)–N(2)–N(1)	121.9(2)		N(5)–C(7)–C(8)	109.0(5)	
Na(1)–N(2)–C(3)	123.8(3)		C(7)–C(8)–C(9)	104.3(4)	
N(1)–N(2)–C(3)	104.6(4)	111.4	N(6)–C(9)–C(8)	112.1(5)	
N(4)–N(3)–C(6)	110.1(3)		N(1)–B(1)–N(3)	109.8(3)	108.2
N(4)–N(3)–B(1)	121.0(3)		N(1)–B(1)–N(5)	112.6(4)	
C(6)–N(3)–B(1)	128.5(3)		N(3)–B(1)–N(5)	108.6(4)	
Na(1)–N(4)–Na(1)	85.97(10)		H(1)–B(1)–N(1)		110.7
Na(1)–N(4)–N(3)	127.6(2)				

[a] The calculated bond lengths and angles are identical for the three methimazolyl rings in NaTm and the three pyrazolyl rings in NaTp. Thus for clarity *ab initio* data are provided for a single representative ring system for each anion only.



Tp anion

NaTp

NaTp·NH_3

Tm anion

NaTm

NaTm·NH_3

Fig. 4 The calculated structures of the Tp and Tm anions, the complexes NaTm and NaTp and their ammonia adducts, NaTm·NH_3 and NaTp·NH_3.

Table 4 Calculated data for Tm, Tp and their metal complexes

	Tm (X-ray)	Tm	Tp	NaTm	NaT(pm_2)	NaT(p_2m)	NaTp	NaTm·NH_3	NaTp·NH_3	CuTm[a]	CuTp[a]
Parameter											
d(B–H)/Å	0.97	1.180	1.196	1.204	1.203	1.201	1.199	1.205	1.201	1.202	1.199
d(B–N)/Å	1.55 (av.)	1.579	1.561	1.563	1.536 1.575 (av.)	1.546 (av.) 1.591	1.556	1.562	1.554	1.565	1.557
d(C=S)/Å	1.70 (av.)	1.704		1.726	1.725 (av.)	1.725		1.724		1.727	
d(M–S)/Å				2.725	2.710 (av.)	2.690		2.780		2.454	
d(M–N)/Å	—				2.353	2.335 (av.)	2.333		2.372		2.155
d(M···B)/Å				3.722	3.439	3.281	3.126	3.863	3.197	3.389	2.908
H–B–N/°		111.3	110.7	105.0	106.0 (av.)	106.2 (av.)	107.4	105.0	107.4	104.8	108.2
N–B–N/°		107.6	108.2	113.5	110.2 (av.) 115.5	112.5	111.4	113.6	111.5	113.7	110.8
S–M–S/°				103.4	110.4			100.1		111.7	
N–M–N/°						87.6	88.6		86.5		95.1
N–M–S/°					90.2 101.4	92.6 105.4					
Complexation energy/kcal mol^{-1}				−146.9	−147.4	−149.0	−153.4	−160.8	−168.7	−174.0	−169.7
Charge on M				+0.59	+0.61	+0.67	+0.76	+0.62	+0.73	+0.81	+0.90
Charge on B		+0.89	+0.83	+0.89	+0.88	+0.87	+0.86	+0.88	+0.87	+0.83	+0.81
Charge on rings		−0.62	−0.57	−0.45	−0.45 (av.)	−0.48 (av.)	−0.50	−0.47	−0.51	−0.50	−0.53

[a] The copper basis set DZ (14,11,5)/[8,6,2] of Ahlrichs and co-workers[26] was used for these calculations.

Lastly, we note that Tp and Tm form the extremes of a potential series of ligands with S_3, S_2N, SN_2 and N_3 donor sets. The S_2N donor with two methimazoles (m) and one pyrazole (p), T(pm$_2$), has recently been prepared by Parkin and co-workers[37] by an alternative synthetic methodology, while the bis(pyrazole) monomethimazole species, T(p$_2$m), remains unknown at this time. However, we have examined the sodium salts of these intermediate ligands by *ab initio* calculations (Table 4). The resulting energies of complexation show a clearly graded change in behaviour on going from Tp through to Tm. We believe this indicates that this series of ligands will modulate the behaviour of metal centres in a controlled fashion by presenting a series of well defined, closely related donor sets with differing electron donor properties.

We have found, in line with the work of Riordan,[38] Parkin[39] and Janiak[40] and their co-workers on related systems, that for the preparation of metal complexes the thallium(I) salt of Tm is more convenient than the sodium salt, particularly when using metal halide precursors. The thallium halide formed during the reaction is insoluble, leaving the clean metal complex in solution. We have repeated the preparation of the previously reported zinc bromide complex, Zn(Tm)Br[18] and find that separation is more straightforward and that the yield is improved. The preparation of the thallium salt is outlined in the Experimental section.

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References

1 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
2 S. Trofimenko, *Inorg. Synth.*, 1970, **12**, 99.
3 S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943.
4 M. I. Bruce and A. P. P. Ostazewski, *J. Chem. Soc., Chem. Commun.*, 1972, 1124.
5 M. I. Bruce and A. P. P. Ostazewski, *J. Chem Soc., Dalton Trans.*, 1973, 2433.
6 N. Kitajima and W. B. Tolman, *Prog. Inorg. Chem.*, 1995, **43**, 419.
7 D. L. Reger, *Coord. Chem. Rev.*, 1996, **147**, 571.
8 M. Etienne, *Coord. Chem. Rev.*, 1996, **156**, 201.
9 K. Yoon and G. Parkin, *J. Am. Chem. Soc.*, 1991, **113**, 8414.
10 S. R. Cooper, *Acc. Chem. Res.*, 1988, **21**, 141.
11 P. Ge, B. S. Haggerty, A. L. Rheingold and C. G. Riordan, *J. Am. Chem. Soc.*, 1994, **116**, 8406.
12 C. Ohrenberg, P. Ge, P. J. Schebler, C. G. Riordan, G. P. A. Yap and A. L. Rheingold, *Inorg. Chem.*, 1996, **35**, 749.
13 C. Ohrenberg, M. M. Saleem, C. G. Riordan, G. P. A. Yap, A. Verma and A. L. Rheingold, *Chem. Commun.*, 1996, 1081.
14 P. J. Schebler, C. G. Riordan, L. Liable-Sands and A. L. Rheingold, *Inorg. Chim. Acta*, 1998, **270**, 543.
15 M. Garner, D. R. Armstrong, J. Reglinski, W. E. Smith, R. Wilson and J. H. McKillop, *Bio-org. Med. Chem. Lett.*, 1994, **4**, 1357.
16 J. Elguero, C. Marzin, A. R. Katritzky and P. Linda, *Adv. Heterocycl. Chem.*, 1976, **1**, Suppl. p. 400.
17 R. S. Balestrero, D. M. Forkey and J. G. Russell, *Magn. Reson. Chem.*, 1986, **24**, 651.
18 M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer and A. R. Kennedy, *Chem. Commun.*, 1996, 1975.
19 SIR 92, A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
20 DIRDIF 92, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, J. M. M. Smits and C. Smykalla, DIRDIF Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.
21 TEXSAN, crystal structure analysis package, Molecular Structure Corporation, Woodlands TX, 1985 and 1992.
22 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.
23 P. C. Harihan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
24 J. D. Dill and J. A. Pople, *J. Chem. Phys.*, 1975, **62**, 2921.
25 GAUSSIAN 94, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. Gill, W. B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Peterssoa, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defress, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian Inc., Pittsburg, PA, 1995.
26 A. Schäfer, H. Horn and J. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571.
27 J. Kister, G. Assef, G. Mille and J. Metzger, *Can. J. Chem.*, 1979, **57**, 813.
28 J. Kister, G. Assef, G. Mille and J. Metzger, *Can. J. Chem.*, 1979, **57**, 822.
29 T. Aoyagi, H. M. M. Shearer, K. Wade and G. Whitehead, *J. Organomet. Chem.*, 1979, **175**, 21.
30 S. Harder, M. H. Prosenc and U. Rief, *Organometallics*, 1996, **15**, 118.
31 H. V. R. Dias, H.-L. Lu, R. E. Ratcliffe and S. G. Bott, *Inorg. Chem.*, 1995, **34**, 1975.
32 H. V. R. Dias and H.-J. Kim. *Organometallics*, 1996, **15**, 5374.
33 H. V. R. Dias, W. Jin, H.-J. Kin and H.-L. Lu, *Inorg. Chem.*, 1996, **35**, 2317.
34 G. G. Lobbia, P. Cecchi, R. Spagna, M. Colapietro, A. Pifferi and C. Pettinari, *J. Organomet. Chem.*, 1995, **485**, 45.
35 C. Janiak, *Chem. Ber.*, 1994, **127**, 1379.
36 C. Lopez, R. M. Claramunt, D. Sanz, C. F. Foces, F. H. Cano, R. Faure, E. Cayon and J. Elguero, *Inorg. Chim. Acta*, 1990, **176**, 195.
37 C. Kimblin, T. Hascall and G. Parkin, *Inorg. Chem.*, 1997, **36**, 5680.
38 P. J. Schebler, C. G. Riordan, I. A. Guzei and A. L. Rheingold, *Inorg. Chem.*, 1998, **37**, 4754.
39 C. M. Dowling, D. Leslie, M. H. Chisholm and G. Parkin, *Main Group Chem.*, 1995, **1**, 29.
40 C. Janiak, S. Temizdemir and T. G. Scharmann, *Z. Anorg. Allg. Chem.*, 1998, **624**, 755.

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