

# Structural and spectroscopic characterisation of bis-ligand complexes of iron(II), nickel(II) and nickel(III) with the hydrotris(methimazolyl)borate anion: soft $S_6$ donor sets generating a weak ligand field

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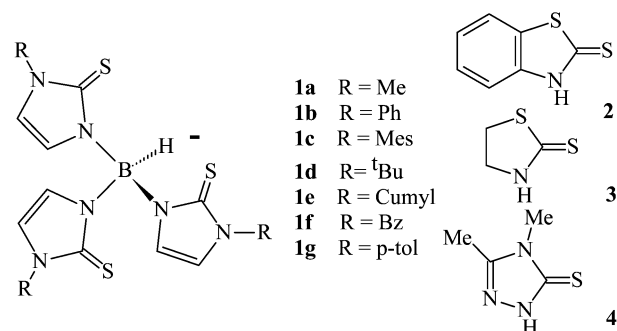
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Reaction of iron(II) and nickel(II) halides with sodium hydrotris(methimazolyl)borate (NaTm) results in the formation of 2 : 1 complexes  $[M(Tm)_2]$ . Crystallographic characterisation reveals in both cases trigonally distorted octahedral geometry in an  $S_6$  donor set. Spectroscopic properties indicate that the Tm ligand generates a weak ligand field, with  $Dq$  between that of  $H_2O$  and  $Cl^-$  and this is confirmed by the high-spin configuration of the iron(II) complex. Both complexes display classical paramagnetic behaviour. Mössbauer spectroscopy of the iron complex is also consistent with a high-spin complex. Reaction of  $NiCl_2 \cdot 6H_2O$  with  $[Ti(Tm)]$  results in a small quantity of a material which is crystallographically demonstrated to be  $[Ni(Tm)_2]Br$ .

## Introduction

Our preparation of the hydrotris(methimazolyl)borate anion (Tm, **1a**),<sup>1</sup> a soft (thione donor) analogue of the now ubiquitous hydrotris(pyrazolyl)borate anion (Tp),<sup>2</sup> has captured the imagination of many workers and has facilitated a significant body of chemistry. Its ready accessibility and adaptability have made it instantly popular. The groups of Parkin,<sup>3</sup> Vahrenkamp<sup>4</sup> and Rabinovich<sup>5</sup> have all prepared analogues in which the N-methyl group is replaced by a more bulky group (e.g. Ph, Mes, <sup>t</sup>Bu etc. **1b–g**), we have investigated the use of alternative heterocyclic thiones (e.g. **2** and **3**),<sup>6</sup> while both Parkin *et al.*<sup>7</sup> and Vahrenkamp and coworkers<sup>8</sup> have prepared hybrid  $S_2N$  donor ligands based on this concept.



Particularly interesting is Bailey's ambidentate ligand based on a 1,2,4-triazole-5-thione heterocycle (**4**), which can make available both nitrogen and sulfur donor atoms giving possible  $N_3$  or  $S_3$  donor sets.<sup>9</sup> Thus a significant body of soft tripodal anionic ligands has become available, although as yet their coordination chemistry is not fully developed and understood.

Many groups<sup>10</sup> have prepared metal complexes with both main group and transition metals, mostly in an effort to meet a particular research need. In the course of our studies we have sought to address the fundamental properties of the ligand system and to make direct comparisons with the broadly analogous Tp and Cp ligands. Thus *ab initio* calculations have been utilised to probe the electronic and structural properties of the ligand<sup>11</sup> the soft nature of the donor set has been demonstrated in the formation of the remarkable ion pair

$[Bi(Tm)_2]^+[Na(Tp)_2]^-$ ,<sup>12</sup> the strong electron donor properties of the ligand relative to Tp and Cp have been elucidated from the relative CO stretching frequencies in the IR spectra of Mo and W carbonyl complexes,<sup>13</sup> and the structural motif has been examined in detail in the context of the group 12 complexes,  $[M(Tm)X]$  (X = halide).<sup>14</sup>

In terms of cyclopentadienyl chemistry, iron holds a central place with both ferrocenes and monocyclopentadienyl "piano-stool" complexes extensively studied. Here we report our studies on the Tm complexes of iron and some related complexes with nickel which have allowed us to further explore the analogy between Tm and its corresponding Cp and Tp complexes.

## Results and discussion

### Iron complexes

Reaction of iron(II) salts with NaTm in polar organic solvents results in the formation of a dark green solution which rapidly deposits a dark green–black solid. Regardless of reaction conditions, counter-ions and co-ligands we have been unable to isolate any other species. Microanalysis and mass spectrometry revealed the complex to be the bis hydrotris(methimazolyl)borate complex,  $[Fe(Tm)_2]$ . Single crystals of the complex as  $[Fe^{II}(Tm)_2] \cdot 4.5H_2O$  were readily obtained and the X-ray crystal structure determined (Fig. 1), which confirmed the stoichiometry of the complex as  $[Fe(Tm)_2]$ . The iron atom lies on a special position and its coordination sphere consists of an  $S_6$  donor set with Fe–S distances of 2.4566(9) Å. These distances are rather longer than most reported Fe<sup>II</sup>–S contacts although relatively few complexes with Fe<sup>II</sup>– $S_6$  coordination spheres are known. Most typical of those in the literature are complexes with thioether macrocycles<sup>15</sup> (e.g.  $[Fe(9aneS_3)_2]^{2+}$  and  $[Fe(10aneS_3)_2]^{2+}$ ) which have Fe–S bond lengths in the range 2.24–2.28 Å and Riordan's tris and tetrakis (methylthio)methyl borates,  $[Fe\{B(CH_2SMe)_4\}_2]^{16}$  and  $[Fe\{PhB(CH_2SMe)_3\}_2]^{17}$  the bond lengths of which are in the range 2.29–2.33 Å. The short bond lengths are commensurate with the low-spin iron(II) ion. High-spin complexes with  $S_6$  donor sets are far less common. A thioxanthate complex,<sup>18</sup>  $[Fe\{S_2C(SEt)\}_3]^-$  with much longer Fe–S distances (between 2.48 and 2.56 Å) is apparently high spin (although it is not explicitly stated), while a  $N,N'$ -

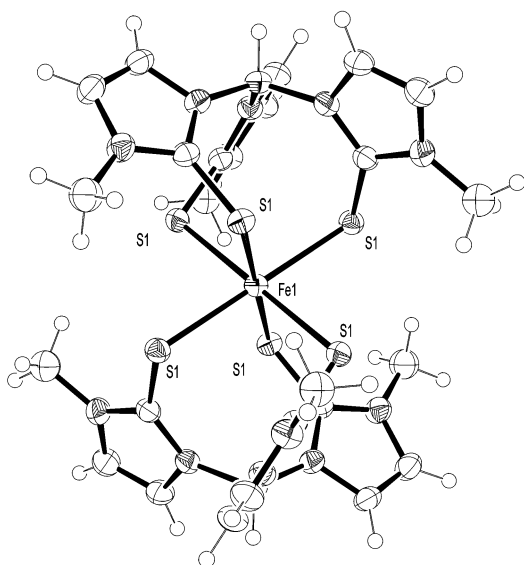


Fig. 1 Crystal structure of  $[\text{Fe}(\text{Tm})_2]$ .

dimethylthiourea complex<sup>19</sup>  $[\text{Fe}(\text{dmtu})_6]^{2+}$  has bond lengths in the range 2.49–2.60 Å. This large range is attributed to Jahn–Teller distortion arising from M–L  $\pi$ -bonding. Thus the bond lengths in our complex are consistent with a high-spin  $\text{Fe}^{\text{II}}$  ion, although slightly shorter than those previously reported. It is noted that the intra-ligand S–Fe–S (bite) angles are greater than  $90^\circ$  ( $94.99(3)^\circ$ ), while the inter-ligand S–Fe–S angles are less than  $90^\circ$  ( $85.01(3)^\circ$ ) resulting in a somewhat compressed  $\text{FeS}_6$  octahedron. The extended structure in the crystal is dominated by a 3D hydrogen bonded network of water molecules as shown in Fig. 2.

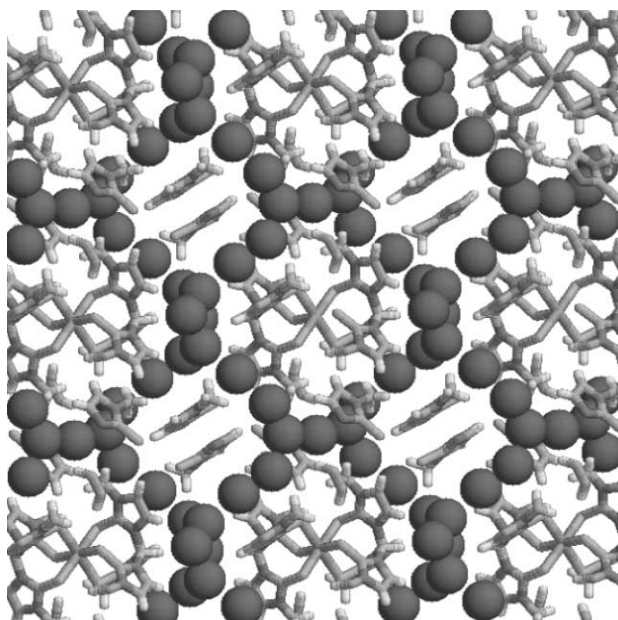


Fig. 2 The extended structure of  $[\text{Fe}(\text{Tm})_2] \cdot 4.5\text{H}_2\text{O}$ . The spheres indicate the positions of the water molecules in the hydrogen bonded network surrounding the  $[\text{Fe}(\text{Tm})_2]$  complexes.

Fig. 3 shows the temperature dependence of the molar susceptibility for  $[\text{Fe}^{\text{II}}(\text{Tm})_2] \cdot 4.5\text{H}_2\text{O}$  obtained from a polycrystalline sample. Variable-temperature magnetic susceptibility measurements in the range 4.6–305 K at constant field (4.998 kOe) can be fitted to the Curie–Weiss equation:

$$\chi_{\text{mol}} = \frac{C}{T - \Theta} - \chi_o \quad (1)$$

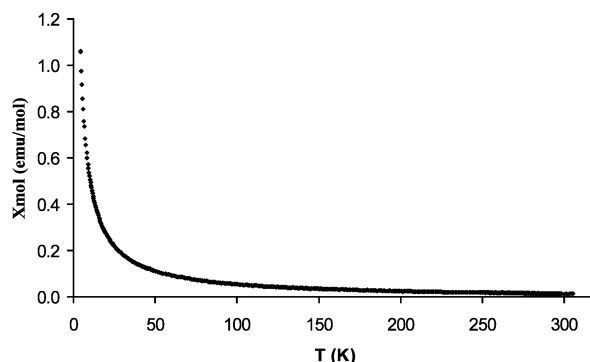


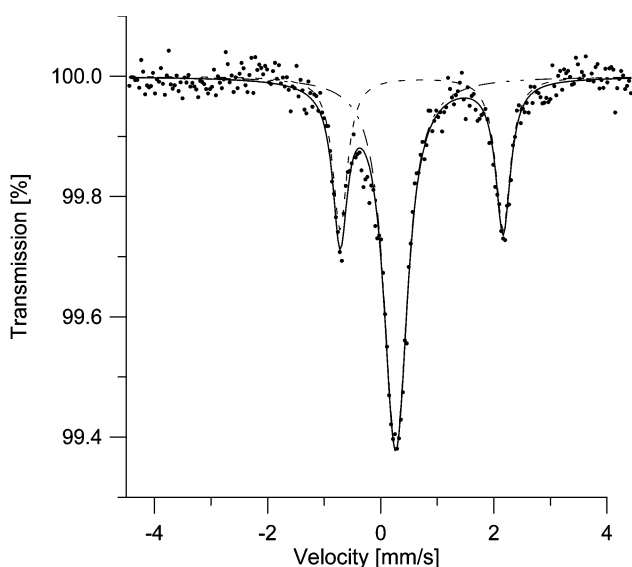
Fig. 3 Temperature variation of molar susceptibility for  $[\text{Fe}(\text{Tm})_2]$ .

with Curie constant  $C = 5.755(7) \text{ emu K mol}^{-1}$ , Weiss temperature  $\Theta = -1.254(9) \text{ K}$  and temperature independent correction, which contains diamagnetic and paramagnetic (TIP) contributions,  $\chi_o = 4.65(9) \times 10^{-3} \text{ emu mol}^{-1}$ . The room-temperature magnetic moment,  $\mu_{\text{eff}} = 6.78 \mu_{\text{B}}$ , is consistent with a high-spin  $d^6$  metal ion with an appreciable orbital angular momentum contribution ( $\mu_{\text{eff}}^{\text{calc}} = 6.71 \mu_{\text{B}}$ ). This magnetic behaviour contrasts with that of the iron complexes of the related ligands, Cp and Tp.  $\text{FeCp}_2$  is diamagnetic (low spin), while  $\text{Fe}(\text{Tp})_2$  exhibits spin cross-over behaviour.<sup>20</sup> This indicates that Tm is a substantially weaker field ligand even than Tp, probably as a result of  $\pi$ -donor interactions from the non-bonded electrons on the sulfur atoms, and thus the relative positions of the three ligands in the spectrochemical series are:  $\text{Cp} > \text{Tp} > \text{Tm}$ .

The electronic spectrum of  $[\text{Fe}^{\text{II}}(\text{Tm})_2]$  is dominated by intense charge transfer bands. We assign bands at  $14180 \text{ cm}^{-1}$  ( $\epsilon = 4200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and  $16290 \text{ cm}^{-1}$  ( $\epsilon = 5800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) as  $\text{S}(\pi) \rightarrow ^5\text{T}_2$ , and bands at  $22300 \text{ cm}^{-1}$  ( $\epsilon = 11100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and  $24450 \text{ cm}^{-1}$  ( $\epsilon = 11300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) as the  $\text{S}(\pi) \rightarrow ^5\text{E}$  transitions, while an absorption at  $32470 \text{ cm}^{-1}$  ( $\epsilon = 16700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) is assigned as the  $\text{S}(\sigma) \rightarrow ^5\text{E}$ . Finally, a high energy band at  $39530 \text{ cm}^{-1}$  is assigned as a  $\pi \rightarrow \pi^*$  intra-ligand transition, corresponding to the only observed band in the spectrum of the free ligand. The difference between two lowest energy bands of ca.  $2100 \text{ cm}^{-1}$  conforms to the expected splitting of the  $^5\text{T}_2$  ground state into  $^5\text{A}_1$  and  $^5\text{E}$  states of trigonally or Jahn–Teller distorted pseudo-octahedral species.<sup>20,21</sup> Attempts to observe the expected d–d transition in the energy range  $10000\text{--}2000 \text{ cm}^{-1}$  both in solution and solid state have been inconclusive.

Room-temperature  $^{57}\text{Fe}$  Mössbauer data were also obtained (Fig. 4). Initial attempts to obtain spectra using  $\text{Al}_2\text{O}_3$  as support resulted in spectra with isomer shifts ( $0.38 \text{ mm s}^{-1}$ ) and small quadrupole splittings more usually associated with low-spin iron(II) or high-spin iron(III) compounds. We now attribute these results to decomposition of the complex on the alumina support. When BN was used as support again a significant level of decomposition was observed, but a component consistent with the high-spin iron(II) state was also present, as a doublet with an isomer shift of  $0.83 \text{ mm s}^{-1}$  and a quadrupole splitting of  $2.88 \text{ mm s}^{-1}$ .<sup>22</sup>

Given the relative ease of oxidation of ferrocene to ferrocenium ion, we wished to try and obtain an analogous complex,  $[\text{Fe}(\text{Tm})_2]^+$ . Initial attempts to prepare this species by direct reaction of  $\text{Fe}^{\text{III}}$  salts with NaTm resulted in the reduction of the  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$  (presumably by the borohydride moiety of the uncomplexed ligand) and isolation of  $[\text{Fe}(\text{Tm})_2]$  in moderate yield. Decomposition of the ligand is evidenced by the recovery of significant quantities of methimazole. Furthermore, attempts to chemically or electrochemically oxidise the complex  $[\text{Fe}(\text{Tm})_2]$  were also unsuccessful. Reaction with  $\text{H}_2\text{O}_2$  resulted in complete decomposition and recovery of substantial amounts of methimazole, indicative of ligand degradation,



**Fig. 4** Mössbauer spectrum of  $[\text{Fe}(\text{Tm})_2]$  in BN showing the best fit. The outer lines constitute the doublet attributable to the complex and the centre line arises from the products of decomposition on the support.

while oxidation with a stoichiometric quantity of  $\text{I}_2$  gives an orange solution which analysis suggests to be the methimazole complex  $[\text{Fe}(\text{mtH})_3\text{I}_3]$ . Cyclic voltammetry in  $\text{CH}_2\text{Cl}_2$ – $\text{NBu}_4\text{BF}_4$  showed ill-defined, irreversible oxidation waves at +380, +560 and +830 mV. It is thought that our inability to prepare the iron(III) complex arises not from an inherent instability of the complex, but from the lack of an oxidation pathway which does not result in oxidation of the B–H functionality and thus to decomposition of the ligand.

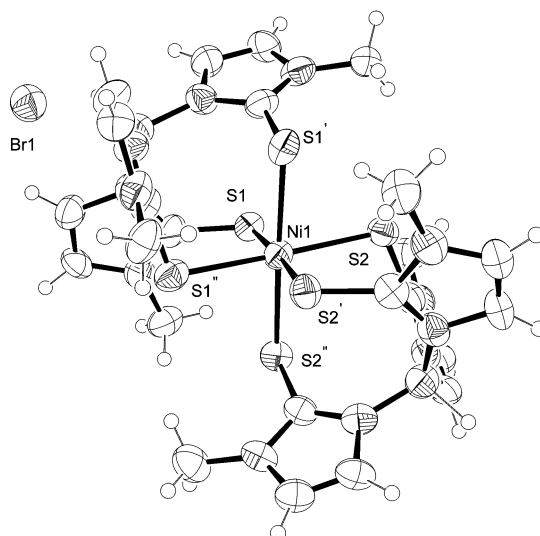
### Nickel complexes

Reaction of nickel(II) halides with NaTm results in the formation of a very insoluble yellow powder which analyses as  $[\text{Ni}(\text{Tm})_2]$ . The compound is paramagnetic, with a room-temperature magnetic moment,  $\mu_{\text{eff}} = 3.60 \mu_{\text{B}}$ , consistent with an  $S = 1$  ground state in an octahedral field. Variable-temperature magnetic measurements may be fitted to the Curie-Weiss equation with Curie constant of  $1.63(2) \text{ emu K mol}^{-1}$ , a Weiss temperature of  $-1.42(7) \text{ K}$  and temperature independent correction, which contains diamagnetic and paramagnetic (TIP) contributions,  $\chi_0 = 9.8 \times 10^{-3} \text{ emu mol}^{-1}$ . The solid state UV-vis spectrum shows absorptions at  $8160 \text{ cm}^{-1}$  ( ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ ) and  $12710 \text{ cm}^{-1}$  ( ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}({}^3\text{F})$ ). The lower energy band appears to be split and this may be explained either by the effects of the trigonal distortion from pure octahedral geometry or by a Jahn–Teller distorted excited state. On the basis of the parameters  $Dq = 816 \text{ cm}^{-1}$  and  $B' = 550 \text{ cm}^{-1}$  estimated from the spectrum, the higher energy transition  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}({}^3\text{P})$  is predicted to fall at *ca.*  $20000 \text{ cm}^{-1}$ . Two weak shoulders are seen on the low energy tail of the charge transfer band at *ca.*  $25000 \text{ cm}^{-1}$  but it is not possible to accurately measure the peak maxima. It is concluded that the field strength of the tris-thione ligand Tm lies between that of chloride ( $Dq = 680 \text{ cm}^{-1}$ ) and  $\text{H}_2\text{O}$  ( $Dq = 850 \text{ cm}^{-1}$ ).

The very poor solubility of the product led us to believe the complex to be polymeric in nature. An alternative preparation, utilising slow diffusion techniques, yielded crystalline material with identical physical and spectroscopic properties to the original powder. To our surprise, the crystal structure revealed the monomeric complex  $[\text{Ni}(\text{Tm})_2]$ . The remarkable difference in solubility between this complex and the highly soluble iron(II) analogue seems to be related to the very tight crystal packing of nickel compound without any inter-lattice solvent molecules.

The structure of  $\text{Ni}(\text{Tm})_2$  is very similar to that of the iron(II) complex, again exhibiting bite angles  $>90^\circ$  ( $93.5$ – $95.1^\circ$ ) and intra-ligand S–Ni–S angles  $<90^\circ$  ( $84.9$ – $86.5^\circ$ ). The Ni–S bond distances are 2.4404(7), 2.4715(7) and 2.4834(8) Å. These are on the whole slightly longer than in Riordan's alkyl methylthio-borate complexes  $[\text{Ni}(\text{FcTt})_2]$  (av. = 2.45 Å),<sup>23</sup>  $[\text{Ni}(\text{PhTt})_2]$  (av. = 2.433 Å)<sup>17</sup> and  $[\text{Ni}(\text{RTt})_2]$  (av. = 2.430 Å)<sup>17</sup> and in thioether macrocycle complexes such as  $[\text{Ni}(\text{9aneS}_3)_2]^{2+}$  (av. = 2.388 Å).<sup>24</sup> However, the more closely analogous thiourea complex,  $[\text{Ni}(\text{tu})_6]^{2+}$ , has Ni–S bond distances in the range 2.498–2.517 Å,<sup>25</sup> much more in accord with our observations. Also notable in this complex is the distortion in the bond angles around the nickel centre, which again parallel those in our chelated complex. It would appear that this distortion arises from the nature of the thione donor rather than the tripodal geometry of the ligand.

In an attempt to obtain a tetrahedral complex of stoichiometry  $[\text{Ni}(\text{Tm})\text{X}]$  (X = halide) a reaction of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with Tm in a 1 : 1 ratio was attempted. Precipitation of white TlCl and yellow  $[\text{Ni}(\text{Tm})_2]$  occurred, but an olive green solution remained. A similar reaction occurred with  $\text{NiBr}_2$ , from which we were able to obtain a few very dark green crystals. The structure obtained from these crystals by X-ray diffraction reveals what is apparently a nickel(III) complex,  $[\text{Ni}(\text{Tm})_2]\text{Br}$  (Fig. 5). The nickel and bromine atoms are situated on three-fold special positions. On the basis of the crystallography it would appear that the stoichiometry of the complex supports the formulation of  $\text{Ni}^{\text{III}}$ . However, the presence of disordered solvent (dichloromethane) in the structure and the resulting uncertainty does not allow us to completely discount the possibility of the Br in fact being HBr, although there is little precedent for this. However, the Ni–S bond distances are significantly shorter (*ca.* 0.1 Å) than those in the  $\text{Ni}^{\text{II}}$  analogue at 2.368(4) and 2.377(4) Å, consistent with the higher oxidation state. The only other crystallographically characterised  $\text{Ni}^{\text{III}}$  complex with an  $\text{S}_6$  donor set is  $[\text{Ni}(\text{9aneS}_3)_2]^{3+}$  which has a Ni–S bond distance of 2.313 Å.<sup>26</sup> Although this is shorter than in our Tm complex, the  $\text{Ni}^{\text{II}}$  analogue also has shorter contacts than in  $[\text{Ni}(\text{Tm})_2]$ . The shortening between analogous  $\text{Ni}^{\text{II}}$  and  $\text{Ni}^{\text{III}}$  complexes is 3.1% in the case of the thioether macrocycle complexes and 3.7% in the Tm complexes.



**Fig. 5** The X-ray structure of  $[\text{Ni}(\text{Tm})_2]\text{Br}$ .

It is not certain how the oxidation has occurred, but we believe that a process similar to that observed for cobalt, where  $[\text{Co}^{\text{II}}(\text{Tm})\text{Br}]$  is air oxidised to  $[\text{Co}^{\text{III}}(\text{Tm})_2]^+$  in coordinating solvents, may be taking place.<sup>27</sup> Aerial oxidation of  $\text{Ni}^{\text{II}}$  to  $\text{Ni}^{\text{III}}$  is not common, although Riordan and coworkers have recently reported oxidation of  $\text{Ni}^{\text{I}}$  complexes of alkylthiomethylborate

**Table 1** Crystal data

	[Fe(Tm) <sub>2</sub> ] $\cdot$ 4.5H <sub>2</sub> O	[Ni(Tm) <sub>2</sub> ]	[Ni(Tm) <sub>2</sub> ] $\cdot$ Br $\cdot$ 4CH <sub>2</sub> Cl <sub>2</sub>
Formula	C <sub>24</sub> H <sub>32</sub> B <sub>2</sub> FeN <sub>12</sub> S <sub>6</sub> $\cdot$ 4.5H <sub>2</sub> O	C <sub>24</sub> H <sub>32</sub> B <sub>2</sub> N <sub>12</sub> NiS <sub>6</sub>	C <sub>24</sub> H <sub>32</sub> B <sub>2</sub> Br <sub>1</sub> N <sub>12</sub> Ni <sub>1</sub> S <sub>6</sub> $\cdot$ 4CH <sub>2</sub> Cl <sub>2</sub>
<i>M</i>	839.52	761.31	1180.92
<i>a</i> /Å	14.8890(6)	10.1690(3)	16.8111(4)
<i>b</i> /Å	14.8890(6)	9.8790(3)	16.8111(4)
<i>c</i> /Å	15.5697(6)	16.8980(6)	16.8111(4)
<i>a</i> <sup>o</sup>	90	90	90
<i>β</i> <sup>o</sup>	90	98.2180(12)	90
<i>γ</i> <sup>o</sup>	120	90	90
<i>V</i> /Å <sup>3</sup>	2989.1(2)	1680.13(9)	4751.0(2)
<i>Z</i>	3	2	4
Crystal system	Trigonal	Monoclinic	Cubic
Space group	<i>R</i> $\bar{3}$ (no. 148)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)	<i>P</i> 2 <sub>1</sub> 3 (no. 198)
<i>T</i> /K	123	293	123
Reflections collected	3074	6498	1771
Unique reflections ( <i>R</i> <sub>int</sub> )	1361 (0.039)	3852 (0.043)	1771
<i>R</i> ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> 1 = 0.0554, <i>wR</i> 2 = 0.1696	<i>R</i> 1 = 0.0427 <i>wR</i> 2 = 0.0793	<i>R</i> 1 = 0.0668, <i>wR</i> 2 = 0.1588
<i>R</i> (all data)	<i>R</i> 1 = 0.0655, <i>wR</i> 2 = 0.1770	<i>R</i> 1 = 0.0815, <i>wR</i> 2 = 0.0919	<i>R</i> 1 = 0.0709, <i>wR</i> 2 = 0.1608
GOF (all data)	1.090	1.027	1.185

ligands by oxygen to give Ni<sup>III</sup> species.<sup>28</sup> Again, attempts to oxidise [Ni(Tm)<sub>2</sub>] electrochemically were thwarted by problems of solubility and decomposition.

## Conclusion

The results of our investigations paint a picture of the Tm anion as a weak field ligand (lying between H<sub>2</sub>O and Cl<sup>-</sup> in the spectrochemical series) which we ascribe to π-donation from the sulfur lone pairs to the metal. The ligand has a strong preference to form 2 : 1 complexes with both iron and nickel, no other species having been observed, despite our concerted efforts. We also note a remarkably facile aerial oxidation of nickel(II) to nickel(III). At the outset we wished to compare the metal complexes of Cp, Tp and Tm. The iron and nickel chemistry reported demonstrates a structural homology between the complexes of the three ligands, in that all form complexes of general formula [M(L)<sub>2</sub>], but significant differences in their stabilities and electronic properties are noted.

## Experimental

### General

NaTm<sup>11</sup> and Tm<sup>6</sup> were prepared by literature methods. All other chemicals and reagents were obtained commercially and used as supplied. NMR spectra were recorded on Bruker AMX400 and Jeol 270 spectrometers with <sup>1</sup>H resonance frequencies of 400 and 270 MHz, respectively. The spectra were referenced to internal solvent peaks. Mössbauer spectra were recorded at room temperature using a <sup>57</sup>Co(Rh) source and a Kr-filled γ-ray proportional counter. The sample was powdered, mixed with Al<sub>2</sub>O<sub>3</sub> or boron nitride and pressed into a pellet (effective thickness *ca.* 10 mg cm<sup>-2</sup>). The spectrum was analysed by a least-squares procedure assuming Lorentzian line shapes and isomer shifts are quoted relative to α-Fe. Variable-temperature magnetic measurements were performed on 7227 Lake Shore AC Susceptometer/DC Magnetometer at the H. Niewodniczański Institute of Nuclear Physics, Kraków.

### Complex preparations

**[Fe<sup>II</sup>(Tm)<sub>2</sub>] $\cdot$ 4.5H<sub>2</sub>O.** A solution of FeCl<sub>2</sub> $\cdot$ 4H<sub>2</sub>O (0.1991 g, 1.0 mmol) in CH<sub>3</sub>OH (20 mL) was degassed under an argon atmosphere and a similarly treated solution of NaTm $\cdot$ 1.5H<sub>2</sub>O (0.8016 g, 2.0 mmol) in CH<sub>3</sub>OH (40 mL) was added. The colour changed immediately from brown to dark green and after stirring for 1 h the resulting dark green precipitate was isolated by filtration, washed with diethyl ether and air dried.

The filtrate could be concentrated to yield a further crop of crude material. Recrystallisation of the combined solids from CH<sub>3</sub>OH–CH<sub>2</sub>Cl<sub>2</sub> yielded crystalline material (0.38 g, 45%) (Found: C, 34.77; H, 4.77; N, 20.05; S, 23.05. Calc. for C<sub>24</sub>H<sub>32</sub>B<sub>2</sub>FeN<sub>12</sub>S<sub>6</sub> $\cdot$ 4.5H<sub>2</sub>O: C, 34.33; H, 4.92; N, 20.02; S, 22.91%). Mp (uncorrected) = 160 °C. *μ*<sub>eff</sub> (291 K) = 5.47 μ<sub>B</sub>.

**[Ni<sup>II</sup>(Tm)<sub>2</sub>].** Solutions of NaTm (0.19 g, 0.48 mmol) and NiCl<sub>2</sub> $\cdot$ 6H<sub>2</sub>O (0.13 g, 0.55 mmol) each in a 1 : 1 mixture of *n*-butanol–methanol (20 mL) were placed, one into each arm, of an H-shaped tube. The two solutions were overlaid with methanol, the apparatus sealed and left for three weeks. During this period amber coloured crystals deposited. These were harvested, washed with diethyl ether and dried (0.17 g, 91% based on NaTm) (Found: C, 37.91; H, 4.39; N, 21.48. Calc. for C<sub>24</sub>H<sub>32</sub>B<sub>2</sub>N<sub>12</sub>NiS<sub>6</sub>: C, 37.86; H, 4.23; N, 22.08%).

**[Ni<sup>III</sup>(Tm)<sub>2</sub>] $\cdot$ Br.** To a solution of NiBr<sub>2</sub> $\cdot$ 6H<sub>2</sub>O (0.1129 g, 0.35 mmol) in acetone (75 mL) was added Tm<sup>6</sup> (0.2195 g, 0.39 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL). After stirring on a warm water bath for 5 min the resulting precipitate was filtered off. The green filtrate was stirred in air for 4 h with a resulting darkening of the colour. Evaporation of the solvent *in vacuo* yielded a dark red–brown powder. This was dissolved in a minimum quantity of dichloromethane and stored in the freezer (–18 °C) for two weeks. A few small crystals were obtained and used for X-ray diffraction studies, but insufficient material could be isolated to permit further characterisation.

### X-Ray crystallography

X-Ray diffraction data were collected on a Nonius Kappa-CCD diffractometer at either 123 K ([Fe<sup>II</sup>(Tm)<sub>2</sub>] $\cdot$ 4.5H<sub>2</sub>O and [Ni<sup>III</sup>(Tm)<sub>2</sub>] $\cdot$ Br) or 293 K ([Ni(Tm)<sub>2</sub>]). The crystals were coated in oil, mounted on glass fibres and data measured using graphite monochromated Mo-Kα radiation. Intensities were corrected for Lorentz-polarisation effects. The structures were solved by direct methods ([Fe(Tm)<sub>2</sub>] and [Ni(Tm)<sub>2</sub>] $\cdot$ Br) and by Patterson methods ([Ni(Tm)<sub>2</sub>]) using SHELXS-97,<sup>29</sup> expanded by Fourier methods and refined on *F*<sup>2</sup> using all data by full-matrix least-squares methods (SHELXL-97<sup>29</sup>). Hydrogen atoms were placed in calculated positions for [Fe(Tm)<sub>2</sub>] and [Ni(Tm)<sub>2</sub>] $\cdot$ Br, and were located and refined for [Ni(Tm)<sub>2</sub>]. They were, however, omitted in the case of the solvent water molecules in [Fe(Tm)<sub>2</sub>] where they could not be meaningfully located and in the case of [Ni(Tm)<sub>2</sub>] $\cdot$ Br where one of the CH<sub>2</sub>Cl<sub>2</sub> solvent molecules was disordered about a three-fold axis. All calculations utilised the WinGX graphical interface.<sup>30</sup> Crystallographic data are collected in Table 1.

CCDC reference numbers 195022–195024.

See <http://www.rsc.org/suppdata/dt/b2/b209877f/> for crystallographic data in CIF or other electronic format.

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