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Note

A comparison of the coordination of two linkage isomers of bis(1-methylthioimidazolyl)methane to zinc salts

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ABSTRACT

A structural comparison of the coordination chemistry of the two linkage isomeric forms of bis(1-methylthioimidazolyl)methane, $[H_2C(N\text{-mt})_2]$ ($\mathbf{L^S}$), and $[H_2C(S\text{-mt})_2]$ ($\mathbf{L^N}$) to a number of zinc complexes has been carried out. The complexes $ZnX_2\mathbf{L^S}$ and $ZnX_2\mathbf{L^N}$ (where X = Cl, Br and I) have all been prepared in good to high yields and have been characterised by spectroscopic and analytical methods. X-ray crystallography studies were also carried out on all of the newly prepared compounds, revealing κ^2-*SS* and κ^2-*NN* coordination modes for $\mathbf{L^S}$ and $\mathbf{L^N}$ containing complexes, respectively.

1. Introduction

The ligand, dihydrobis(1-methylthioimidazolyl)borate (**Bm**), (Fig. 1) has a rich and extensively explored chemistry [1,2b], most notably B–H activation at the boron bridgehead. In contrast the chemistry and reactivity of its carbon analogue, bis(1-methylthioimidazolyl)methane has been much less well studied [2–4], despite the fact that its coordination chemistry is enhanced as a result of tautomerisation of the 1-methylthioimidazole (mt) fragment.

Within the carbon based system, there are two linkage isomers providing one ligand containing sulfur donors, $CH_2(N\text{-mt})_2$ ($\mathbf{L^S}$), and the other based on nitrogen donors, $CH_2(S\text{-mt})_2$ ($\mathbf{L^N}$) (Fig. 2). The sulfur donor ligand, $\mathbf{L^S}$, was first introduced by Williams in 1989 [2a]. Some 10 years later, the second isomer, $\mathbf{L^N}$, was synthesised by Casas et al. [3a]. However, full characterisation of this compound was provided by Silva following a recent reinvestigation of both of these ligands [4].

The coordination chemistry of $\mathbf{L^S}$ and $\mathbf{L^N}$ remains limited [2–4], although there are examples of coordination complexes of silver, rhodium, nickel, cobalt, and rhenium containing these ligands. Other examples also include coordination to tin, lead and bismuth. Fig. 3 highlights the various coordination modes for $\mathbf{L^S}$. This ligand has a more diverse range of coordination modes, compared to $\mathbf{L^N}$, since the second lone pair on sulfur is available to bridge further to other metal centres. The large eight-membered ring size formed upon coordination has been observed over a number of bidentate ligands including those based on heterocyclic carbenes, phosphines and other donor systems [5–8].

In order to further explore the coordination chemistry of these two ligands we set out to prepare and structurally characterise a number of zinc complexes. The coordination chemistry of both sulfur and nitrogen donor ligands to zinc is of interest due to the hard and soft properties of the zinc centre [9]. These donor atoms are found in a wide number of enzymes which feature zinc as an active centre [10]. Herein, we wish to report the synthesis and characterisation of a series of zinc(II) halides coordinated by $\mathbf{L^S}$ and $\mathbf{L^N}$ providing κ^2-*SS* and κ^2-*NN* coordination modes for the two ligands to the zinc centres within an eight-membered ring system.

2. Results and discussion

2.1. Synthesis of zinc complexes containing $\mathbf{L^S}$

The complexes $ZnX_2\mathbf{L^S}$ [where X = Cl (**1**), Br (**2**) and I (**3**)] were prepared by addition of one equivalent of a dichloromethane solution of the ligand ($\mathbf{L^S}$) to a methanol solution of the corresponding zinc halide (Scheme 1). In all cases, within a few minutes, the products started to precipitate from the mixture. After 12 h, the products were isolated, in high yields, by filtration, washing with diethyl ether and drying under reduced pressure.

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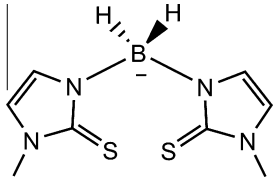


Fig. 1. The structure of dihydrobis(1-methylthioimidazolyl)borate (**Bm**).

Complexes **1**–**3** were obtained as analytically pure white solids in high yields. The three compounds were characterised by spectroscopic and analytical methods. The formation of the three products was confirmed by ^{1}H NMR spectroscopy, IR spectroscopy, ESI mass spectrometry and X-ray crystallography. The ^{1}H data of the isolated solids was consistent with the formation of **1**–**3**. Table 1 shows a comparison of the chemical shifts observed for the ligand and zinc complexes by ^{1}H NMR spectroscopy.

A moderate downfield shift was found for all of the ligand protons upon coordination to the zinc centres. The methylene (CH_2) resonances were located as singlet peaks at 6.34 ppm (**1**), 6.41 ppm (**2**) and 6.45 ppm (**3**) in the ^{1}H NMR spectra (in MeCN-d_3) from 6.19 ppm for the free ligand. The two methylene protons are equivalent in the resulting complexes suggesting some fluxional behaviour within the eight-membered ring of the newly formed complex in solution. The IR spectra of **1**–**3** showed characteristic bands for the ligand shifted relative to the free ligand. The molecular composition and coordination to the metal centres were further confirmed by ESI mass spectrometry and elemental analysis. Single crystals suitable for X-ray diffraction were obtained for the three complexes *via* solvent controlled diffusion experiments (Figs. 4–6).

2.2. Synthesis of zinc complexes containing L^N

The complexes ZnX_2L^N [where X = Cl (**4**), Br (**5**) and I (**6**)] were prepared *via* a similar methodology as described for complexes **1**–**3**. One equivalent of a dichloromethane solution of the ligand was added to a methanol solution of the corresponding zinc halide (Scheme 2).

Complexes **4**–**6** were obtained as analytically pure white solids in high yields. The three compounds were characterised by spectroscopic and analytical methods. The products were characterised by NMR spectroscopy, IR spectroscopy, ESI mass spectrometry and X-ray crystallography. The ^{1}H NMR data of the isolated solids was consistent with the formation of **4**–**6**. Table 2 shows a comparison of the chemical shifts observed for the ligand and zinc complexes by ^{1}H NMR spectroscopy.

As found in the cases of complexes **1**–**3**, a moderate downfield shift was found for all of the ligand protons upon coordination to the zinc centres with the exception of the methylene unit which shows an upfield chemical shift upon coordination. The IR spectra of **4**–**6** showed characteristic bands for the ligand shifted relative to the free ligand. Mass spectrometry of the three complexes revealed high intensity mass/charge peaks corresponding to $[M-X]^+$. Complexes **4**–**6** were further characterised by X-ray crystallography. Single crystals suitable for X-ray diffraction were obtained for the three complexes (Figs. 7–9).

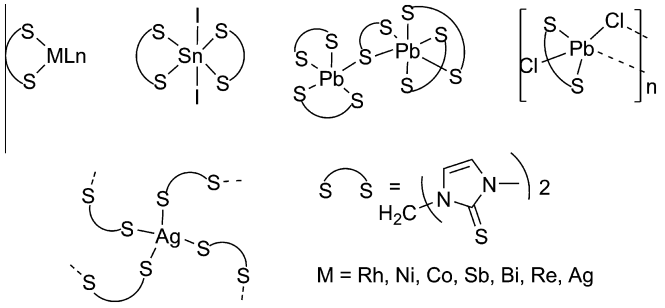
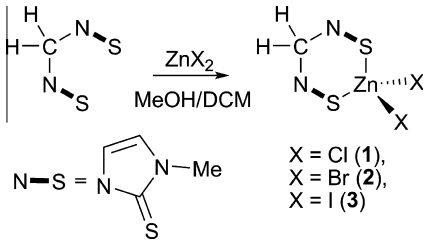


Fig. 3. Various coordination modes for L^S.



Scheme 1. Synthesis of zinc complexes **1**–**3**.

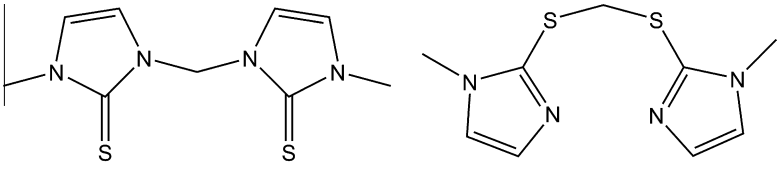
Table 1
^{1}H NMR spectroscopy of ligand and complexes **1**–**3**.

Compound[a]	N–CH_3	N_2CH_2	NC*H*C*H*N
L^S	3.47	6.19	6.79, 7.43
1	3.56	6.34	6.99, 7.43
2	3.60	6.41	7.07, 7.45
3	3.61	6.45	7.15, 7.47

[a] In MeCN-d_3.

2.3. Comparison of the ring conformations in complexes **1**–**6**

Selected bond lengths and angles for complexes **1**–**3** and **4**–**6** are highlighted in Tables 3 and 4, respectively. The crystallographic parameters for these complexes are given in Table 5. The zinc centres are tetracoordinated in all complexes and have distorted tetrahedral geometries due to the ring conformation and halide-halide repulsion. The isoelectronic and isostructural complexes **1**–**3** reveal a κ^2-*SS* coordination mode of the bidentate ligand to the tetrahedral zinc centres. The largest angles about the metal centre are the halide–Zn(1)–halide angles, 117.793(18)° for **1**, 117.24(3)° for **2** and 117.061(13)° for **3**. The corresponding S(1)–Zn(1)–S(1) angles are 109.131(18)°, 109.82(5)° and 109.41(3)°, respectively. The ligand, L^N, binds to the zinc centres with a κ^2-*NN* coordination mode forming the isostructural complexes **4**–**6**. The bidentate



$CH_2(N\text{-mt})_2$, L^S $CH_2(S\text{-mt})_2$, L^N

Fig. 2. The two isomeric forms of bis(1-methylthioimidazolyl)methane, L^S and L^N.