Inorg. Chem. **2004**, *43*, 8212–8214

Bis(pyrazolyl)(thioimidazolyl)borate Ligands: The Missing Member in the $N_3\cdots S_3$ Scorpionate Series

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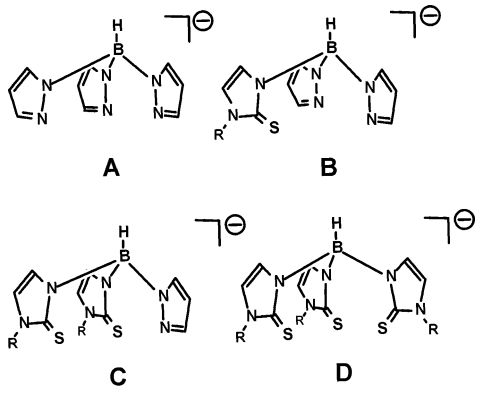
Received September 29, 2004

The anionic bis(pyrazolyl)(thioimidazolyl)borate ligands $BpMt^R$ with R = *tert*-butyl and isopropyl were obtained as their potassium salts by reacting potassium tris(pyrazolyl)borate with the corresponding thioimidazoles in the melt at 150 °C. They were applied to form some tetrahedral zinc complexes and identified by the crystal structures of $(BpMt^{t\text{-}Bu})ZnCl$ and $(BpMt^{i\text{-}Pr})Zn{-}SC_6H_4$-p-Cl.

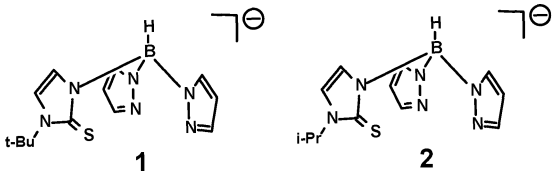
The tripodal scorpionate ligands[1] based on the central anchoring BH unit are unsurpassed in their value as tridentate ligands in coordination chemistry, catalysis, and enzyme modeling. Specifically in our field of research, the bioinorganic chemistry of zinc, they have made possible numerous modeling studies which were inaccessible before.[2,3]

Among the scorpionates, the tris(pyrazolyl)borates **A** are by far the most prominent ones. As a companion to these N_3 donors, the tris(thioimidazolyl)borates **D** as S_3 donors, which were introduced by Reglinski,[4] are gaining ground due to their similarly favorable properties.[5] Having recognized this, it became attractive to make use of the corresponding scorpionates with N_2S and NS_2 donor sets, the bis(pyrazolyl)(thioimidazolyl)borates **B** and the (pyrazolyl)-bis(thioimidazolyl)borates **C**. Until now only the latter have been prepared[6,7] and applied successfully for biomimetic chemistry. It took us some time to learn how to make the last member of the series, the N_2S scorpionates **B**. This Communication reports their synthesis and some zinc complex chemistry of them.

There is still no consistent nomenclature for these ligands and their constituents, whose sulfur-containing units are



alternatively termed mercaptoimidazoles or thioimidazoles. We prefer the latter, as the structure and bonding in all their complexes[5−7] has revealed the ligating sulfur units to be thiourea-like, i.e., derived from thioimidazole. We therefore propose the abbreviation "t" for thioimidazolyl, just like "p" for pyrazolyl. Ligand type **A** is then Tp, as established, with "T" for tris. Accordingly, ligand type **D** is Tt. Using "B" for bis and "M" for mono, ligand type **B** is BpMt and ligand type **C** is MpBt. As established, the substituents in the 3 and 5 positions on the pyrazoles and at N1 of the thioimidazoles are denoted by superscripts. Thus, the ligand (3-phenylpyrazolyl)bis(*N*-methylthioimidazolyl)borate is $Mp^{Ph}Bt^{Me}$, and the two new ligands reported in this paper are $BpMt^{t\text{-}Bu}$ (**1**) and $BpMt^{i\text{-}Pr}$ (**2**). We are aware that this nomenclature is not free from conflicts, as for instance Riordan[8] has used the term Tt for his tris(thioether)borate ligands. It would, however, be favorable if an agreement on the naming of the various scorpionates based on central anchoring BH units could be reached soon.



It has turned out that ligand types **A**, **C**, and **D** can be prepared essentially by the same procedure, which consists

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10.1021/ic048633s CCC: $27.50
Published on Web 11/26/2004

of the high-temperature reaction between KBH_4 and a stoichiometric amount of the pyrazole and/or thioimidazole. This has not worked for type **B**. So far the only way to obtain BpMt ligands has been the reaction between unsubstituted KTp and the corresponding thioimidazole in their own melt at 150 °C.[9] It corresponds to a substitution of the pyrazolyl groups by the thioimidazolyl groups, the driving force for the reaction being the sublimation of pyrazole out of the reaction mixture. The reaction produces mixtures of type **A**, **B**, and **C** complexes. Their separation which is accompanied by serious losses reduces the isolated yields of **1** and **2** to 10−20%. The potassium salts of **1** and **2** are identified by their IR and ^{1}H NMR data;[9] they are soluble only in polar organic solvents. The preparative method did not work in our hands for Tp starting materials with substituted pyrazolyl groups, because the sublimation temperatures of the corresponding pyrazoles are higher than the decomposition temperatures of the resulting type **B** ligands.

Ligands **1** and **2** are not perfect for a biomimetic zinc complex chemistry as they lack the substituents on their pyrazolyl groups which provide the desired encapsulation of the metal ion. Yet it could be shown that they are suitable to form tetrahedral zinc complexes with simple anions occupying the fourth coordination site. Complexes **3a**−**e** and **4a** were obtained by combining the ligands with the appropriate zinc salts in methanol. Some preliminary experiments were made with thiolate coligands in order to test the suitability of the resulting (*N*,*N*,*S*)Zn−SR complexes for the modeling of methionine synthase.[10,11] Complexes **3f** and **4b** resulted from the corresponding nitrate and chloride complexes and the sodium thiolates.[12]

(BpMt$^{t\text{-}Bu}$)Zn-X

X :	Cl	Br	I	NO_3	OAc	SPh
no.:	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**

(BpMt$^{i\text{-}Pr}$)Zn-X

X:	Cl	SC_6H_4-p-Cl
no.:	**4a**	**4b**

The identity of ligands **1** and **2** was confirmed by crystal structure determinations of one of their complexes each. Compounds **3a** and **4b** formed suitable crystals yielding the molecular structures depicted in Figures 1 and 2.[13]

The coordination geometry of both complexes is severely distorted tetrahedral, the distortion being even more pronounced than in the (pyrazolyl)bis(thioimidazolyl)borate zinc complexes.[7] The smallest bond angles are those between the two pyrazole nitrogens (94° in **3a**, 93° in **4b**), and the largest are those between the thioimidazolyl sulfur and the fourth ligand (S−Zn−Cl 119° in **3a**, S−Zn−S 118° in **4b**). The distortions reflect the disparity of the pyrazolyl and thioimidazolyl "arms" with respect to the connecting boron atom and the open space between the two pyrazolyl groups due to the lack of substituents on their 3-positions. All bond lengths involving zinc are normal and compare favorably with those in the related tris(pyrazolyl)borate[10,16] and (pyrazolyl)bis(thioimidazolyl)borate zinc complexes.[7]

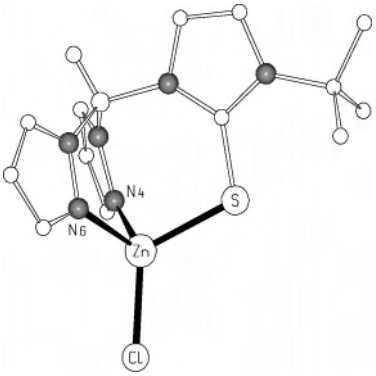

Figure 1. Molecular structure of (BpMt$^{t\text{-}Bu}$)Zn−Cl (**3a**). Bond distances (Å): Zn−N4 2.012(2), Zn−N6 2.007(2), Zn−S 2.323(1), Zn−Cl 2.175-(1).

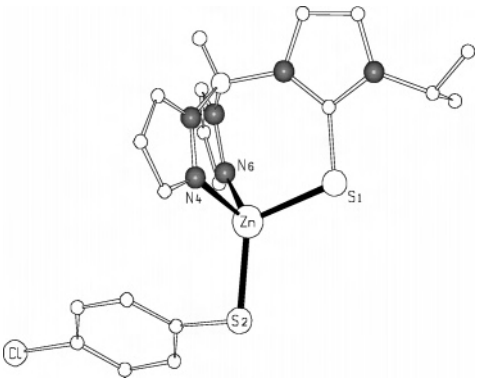

Figure 2. Molecular structure of (BpMt$^{i\text{-}Pr}$)Zn−SC_6H_4-p-Cl (**4b**). Bond distances (Å): Zn−N4 2.025(2), Zn−N6 2.017(2), Zn−S1 2.310(1), Zn−S2 2.240(1).

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(9) Synthetic procedure: ca. 25 mmol each of KTp and of the thioimidazole are finely ground together and then heated to 150 °C in an inert atmosphere, the resulting melt being stirred. Within 6 h, an amount of ca. 30 mmol of pyrazole sublimes. After cooling to room temperature, 40 mL of toluene is added, and the mixture is stirred until a fine powder has formed. After filtration the powder is extracted four times with ca. 15 mL of chloroform each at 65 °C. The final remaining powder is of sufficient purity. For **1**: from 6.23 g (24.7 mmol) of KTp and 3.86 g (24.7 mmol) of 3-*tert*-butyl-2-thioimidazole. Yield 1.32 g (16%). IR (KBr): 2538w (BH), 1388s, 1354vs, 1296s. ^{1}H NMR (acetone-d_6): 1.76 [s, 9H, Me], 6.01 [t, J = 1.84 Hz, 2H, pz], 6.55 [d, J = 2.4 Hz, 1H, im], 6.77 [d, J = 2.4 Hz, 1H, im], 7.37 [d, J = 1.0 Hz, 2H, pz], 7.51 [d, J = 2.0 Hz, 2H, pz]. Anal. Calcd for $C_{13}H_{18}BKN_6S$ (M_r = 340.30): C, 45.88; H, 5.33; N, 24.70; S, 9.42. Found: C, 45.74; H, 5.36; N, 24.60; S, 9.19. For **2**: from 4.76 g (18.9 mmol) of KTp and 2.69 g (18.9 mmol) of 3-isopropyl-2-thioimidazole. Yield 0.67 g (9%). IR (KBr): 2476w (BH), 1388s, 1343vs, 1287s. ^{1}H NMR (DMSO-d_6): 1.22 [d, J = 6.8 Hz, 6H, CH3], 5.00 [sept, J = 6.8 Hz, 1H, CH], 6.00 [t, J = 1.7 Hz, 2H, pz], 6.37 [d, J = 2.2 Hz, 1H, im], 6.84 [d, J = 2.2 Hz, 1H, im], 7.29−7.33 [m, 4H, pz]. Anal. Calcd for $C_{12}H_{16}BKN_6S$ (M_r = 326.27): C, 44.18; H, 4.94; N, 25.76; S, 9.83. Found: C, 43.94; H, 5.12; N, 25.76; S, 9.72.

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(12) The syntheses and characterizations of all complexes **3** and **4** are given in the Supporting Information.

(13) Crystals of **3a** and **4b** were obtained by slow evaporation of methanol solutions. Data sets were obtained on a Bruker Smart CCD diffractometer with Mo Kα radiation. The structures were solved with direct methods and refined to *R* values of 0.033 (**3a**) and 0.035 (**4b**) with SHELX.[14] Drawings were produced with SCHAKAL.[15] All details of the structure determinations are given in the Supporting Information.

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In summary, it can be stated that access to the N_2S scorpionates, the missing link in the series of (pyrazolyl)-(thioimidazolyl)borates, has been found. Although the fact that the pyrazolyl donor units lack substituents on their 3-positions impedes the use of these ligands in biomimetic complex chemistry, they have been shown to form relevant species in the form of tetrahedral and monofunctional zinc complexes. Our aims are to use such species as Zn−OH complexes to model hydrolytic zinc enzymes and as Zn−SR complexes to model zinc enzymes performing thiolate alkylation. The prime value of the new ligands is that they open the possibility for comparative studies employing complete series of N_3, N_2S, NS_2, and S_3 ligated model complex systems.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. We are indebted to Drs. W. Deck and H. Brombacher for technical support.

Supporting Information Available: Experimental details for the preparation of complexes **3** and **4**. X-ray crystallographic files in CIF format for the structure determinations of **3a** and **4b**. Fully labeled ORTEP plots of **3a** and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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