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Solution and solid-state characterization of Zn(II) complexes containing a new tridentate N_2S ligand

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ABSTRACT

A new N_2S ligand bis(pyridyl)(2-mercapto-1-methylimidazolyl)methane (**2**, Py_2MeImS) has been synthesized and characterized. Treatment of this ligand with bromide and triflate salts of Zn(II) results in the complexes $(Py_2MeImS)ZnBr_2$ (**3**) and $[(Py_2MeImS)_2Zn](OTf)_2$ (**4**), respectively. The solid-state structure of $(Py_2MeImS)ZnBr_2$ shows bidentate N,N-coordination of Py_2MeImS to the zinc ion, with the sulfur atom of the 2-mercaptoimidazole moiety uncoordinated. Two conformers of **3** rapidly interconvert in solution at room temperature, and variable temperature NMR studies and DFT calculations were used to help assign the likely identity of these conformers. In contrast, the crystal structure of $[(Py_2MeImS)_2Zn](OTf)_2$ exhibits a zinc ion with a distorted octahedral geometry where the two sulfur atoms of the two ligands are coordinated to the zinc center in a *cis*-configuration. Even though the *cis*-isomer (**4-*cis***) is calculated to be lower in energy than the *trans*-isomer (**4-*trans***), the low temperature ^1H NMR spectrum of **4** reveals a single symmetric species that is inconsistent with the *cis*-isomer observed in the solid-state structure. DFT calculations propose alternative higher energy structures, including a *trans*-configuration of the coordinated S-atoms of the two Py_2MeImS ligands, as well as structures in which the 2-mercaptoimidazole groups are no longer coordinated to the zinc(II) center. These studies provide valuable insight into the potential binding modes of this new ligand and its behavior in solution.

1. Introduction

The coordination chemistry of zinc ions complexed with ligands capable of binding through a sulfur and two nitrogen donors has attracted attention because of its relevance to modeling zinc-containing enzymes with $[N_2S]$ structural binding motifs. For instance, bacteriophage T7 lysozyme [1], peptide deformylase (in plants PDF1A) [2], and bovine 5-aminolevulinate dehydratase [3] all contain active sites consisting of a pseudo-tetrahedral zinc ion bound to a cysteine and two histidine residues with the fourth binding site occupied by a water molecule. The combined nitrogen and sulfur ligation is an important component for tuning the zinc center and activating the water nucleophile. As such, the development of new $[N_2S]$ ancillary ligands to support the synthesis and study of model complexes is crucial to the further understanding of these biological compounds.

Synthetic efforts to prepare zinc complexes with a $[N_2S]$ facial binding motif have primarily used heteroscorpionate-based ligands containing alkyl or aryl thiolates. These ligands have been successfully used to make tetrahedral $[N_2S]ZnX$ complexes, where X = halide, $-CH_3$, —hydroxamate or —SR′ [4]. Alternatively, new heteroscorpionate ligands where mercaptoimidazolyl groups have replaced alkyl and aryl thiolates as the sulfur atom donor(s) have been successfully used to model sulfur-rich active sites [5]. The sulfur atom of the mercaptoimidazolyl moiety is expected to have a significant negative charge similar to thiourea (charge = −0.37 e) [6] and, as such, have been coined by Vahrenkamp [7] as a "tame" thiolate donor. An example of an $[N_2S]$ ligand containing a mercaptoimidazolyl group is the ligand bis(pyrazolyl)(2-mercapto-1-methylimidazolyl)hydroborato ligand ($BpMt^{Me}$, Chart 1) [8].

For the purpose of comparison, we chose to prepare and examine the coordination chemistry of a new tridentate ligand bis(pyridyl)(2-mercapto-1-methylimidazolyl)methane (Py_2MeImS, Chart 1) that is closely related to $BpMt^{Me}$. Py_2MeImS does not contain a central boron atom, which should allow us to explore the influence of the charge of the ligands on the structures and electronic properties of the complexes. Here, we describe the

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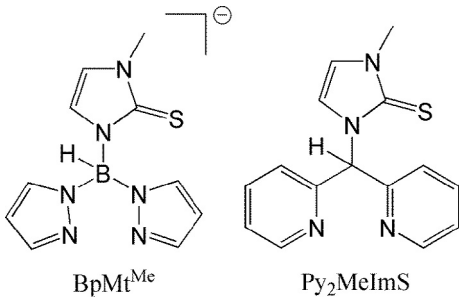

Chart 1.

coordination chemistry of the Py_2MeImS ligand with zinc salts containing coordinating and weakly-coordinating anions. These new complexes provide important insight into both the solid-state and solution-phase behavior of the ligand and its potential binding modes. Computational studies provide further insight into the properties of the Py_2MeImS ligand and how they compare to existing ligand systems.

2. Experimental

2.1. General

All reactions were performed using standard Schlenk techniques under an atmosphere of dry nitrogen gas. Solvents and reagents were obtained from commercial sources in analytical grade quality and used as received unless noted otherwise. The solvents tetrahydrofuran (THF), methanol (MeOH), and dioxane were dried with CaH_2 and distilled prior to use. NMR spectra were recorded on a Bruker AVANCE III 600 MHz NMR or Bruker AVANCE III 300 MHz NMR. Chemical shifts were expressed in parts per million (ppm) and referenced to residual solvent as the internal reference for ^1H ($CDCl_3$: δ = 7.26 ppm or CD_3OD: δ = 3.31 ppm) and ^{13}C ($CDCl_3$: δ = 77.16 ppm and CD_3OD: δ = 49.00 ppm). The NMR probe temperatures were calibrated using the chemical shift separation between the CH_3 and the —OH peaks of a solution of 4% CH_3OH in CD_3OD. IR spectra were measured using a Perkin Elmer Spectrum 100 spectrometer. Elemental analyses were performed by Atlantic Microlabs of Norcross, GA. High resolution mass spectrometry (HRMS) of Py_2MeImS (**2**) was obtained using an ultrahigh resolution Maxis QTOF (Bruker Daltonics) instrument. The compound bis(2-pyridyl)bromomethane was made by a previously reported procedure [9].

2.2. Synthesis and characterization

2.2.1. Preparation of [Py_2MeImH]Br (**1**)

To a solution of bis(2-pyridyl)bromomethane (2.21 g, 8.86 mmol) dissolved in dioxane (50 mL) was added 1-methylimidazole (0.73 g, 8.86 mmol). The solution was refluxed overnight, which resulted in a tan brown precipitate. The precipitate was collected, washed with ether (2 × 10 mL) and then dried under reduced pressure (1.55 g, 53%). ^1H NMR ($CDCl_3$, 300 MHz): δ 10.40 (br dd, 1H), 8.55 (d, J = 4.9 Hz, 2H), 8.20 (s, 1H), 8.19 (dd, J = 1.7, 1.7 Hz, 1H), 7.80–7.68 (m, 4H), 7.35 (dd, J = 1.7, 1.7 Hz, 1H), 7.30–7.22 (m, 2H), 4.05 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) δ 154.7, 149.7, 137.6, 137.4, 124.3, 123.9, 123.7, 122.0, 66.3, 36.9. IR (ATR, cm^{-1}): 3091 (m), 3041 (m), 2994 (m), 1680 (w), 1588 (m), 1571 (m), 1548 (m), 1474 (m), 1446 (w), 1428 (s), 1321 (m), 1210 (w), 1162 (s), 1082 (m), 1052 (m), 994 (m), 950 (w), 883 (w), 848 (m), 770 (s), 752 (s), 738 (s), 689 (m), 670 (s).

2.2.2. Preparation of Py_2MeImS (**2**)

To a solution of [Py_2MeImH]Br (**1**) (1.48 g, 4.49 mmol) dissolved in methanol (50 mL) was added elemental sulfur (0.36 g, 11.22 mmol) and potassium *tert*-butoxide (0.50 g, 4.49 mmol). The solution was refluxed overnight before being cooled to room temperature and water (20 mL) added. The solution was then extracted with dichloromethane (5 × 20 mL), dried with anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure. Crude Py_2MeImS (**2**) was purified by column chromatography (silica gel; DCM followed by EtOAc) to afford Py_2MeImS (**2**) as a yellow oil (0.27 g, 21%). ^1H NMR ($CDCl_3$, 600 MHz): δ 8.59 (d, J = 4.8 Hz, 2H), 7.72 (td, J = 7.7, 7.7, 1.6 Hz, 2H), 7.64 (s, 1H), 7.37 (d, J = 7.7 Hz, 2H), 7.27 (d, J = 2.5 Hz, 1H), 7.24 (dd, J = 7.4, 5.0 Hz, 2H), 6.67 (d, J = 2.5 Hz, 1H), 3.64 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 163.5, 157.0, 149.5, 137.5, 124.2, 123.2, 117.6, 117.2, 65.5, 35.4. IR (ATR, cm^{-1}): 3053 (w), 3005 (w), 1682 (s), 1582 (m), 1568 (m), 1466 (w), 1430 (m), 1315 (s), 1280 (m), 1241 (m), 1227 (m), 1182 (w), 1150 (w), 1090 (w), 1047 (w), 993 (s), 944 (s), 827 (m), 784 (m), 743 (s), 694 (m), 661 (s). HRMS (ESI, Pos) calculated for $[C_{15}H_{14}N_4S_1+Na]^+$: 305.0831, found 305.0844.

2.2.3. Preparation of (Py_2MeImS)$ZnBr_2$ (**3**)

To a solution of Py_2MeImS (**2**) (0.13 g, 0.46 mmol) dissolved in methanol (25 mL) was added anhydrous $ZnBr_2$ (0.105 g, 0.46 mmol). The solution was heated to reflux, resulting in a white precipitate, and stirred overnight. The white solid was collected by filtration, washed with diethyl ether (3 × 5 mL) and dried under reduced pressure to afford (Py_2MeImS)$ZnBr_2$ (**3**) (0.174 g, 74%). Colorless crystals suitable for crystallographic characterization were obtained by diethyl ether diffusion into dichloromethane at room temperature. ^1H NMR (600 MHz, $CDCl_3$, −48 °C), conformer **3a**: δ 8.81 (2H), 8.38 (1H), 8.04 (1H), 7.91 (4H), 7.52 (2H), 6.91 (1H), 3.73 (3H); conformer **3b**: δ 8.92 (2H), 8.23 (1H), 8.11 (4H), 7.83 (1H), 7.75 (2H), 6.68 (1H), 3.62 (3H). IR (ATR, cm^{-1}): 3528 (w), 3173 (w), 3133 (w), 3104 (w), 2810 (w), 1602 (s), 1575 (m), 1467 (s), 1455 (s), 1436 (s), 1390 (s), 1359 (m), 1337 (w), 1298 (w), 1232 (s), 1162 (w), 1136 (m), 1100 (m), 1062 (m), 1026 (s), 914 (w), 868 (m), 828 (s), 767 (m), 766 (s), 716 (s), 681 (s). *Anal.* Calc. for $C_{15}H_{14}Br_2N_4SZn$: C, 35.49; H, 2.78; N, 11.04. Found: C, 35.34; H, 2.95; N, 10.50%.

2.2.4. Preparation of [(Py_2MeImS)$_2$Zn](OTf)$_2$ (**4**)

To a solution of Py_2MeImS (**2**) (0.10 g, 0.35 mmol) dissolved in methanol (14 mL) was added $Zn(OTf)_2$ (0.064 g, 0.18 mmol). The solution was stirred for 18 h before the volume was reduced to 5 mL under reduced pressure. The addition of diethyl ether (15 mL) resulted in the formation of a white solid, which was collected, washed with diethyl ether (3 × 10 mL) and dried under reduced pressure to afford [(Py_2MeImS)$_2$Zn](OTf)$_2$ (**3**) (0.089 g, 54%). Colorless crystals suitable for crystallographic characterization were obtained by diethyl ether diffusion into dichloromethane at room temperature. ^1H NMR (CD_3OD, 10 mM, −35 °C): δ 8.55 (d, J = 4.4 Hz, 2H), 7.90 (t, J = 7.7 Hz, 2H), 7.48 (s, 1H), 7.44 (dd, J = 7.0, 5.2 Hz, 2H), 7.29 (dd, J = 7.7, 4.8 Hz, 2H), 7.12 (d, J = 2.2 Hz, 1H), 7.09–7.06 (m, 1H), 3.61 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3OD, 10 mM, −35 °C): δ 163.7, 158.2, 150.5, 139.3, 125.2, 124.8, 120.0, 117.4, 67.0, 35.4. IR (ATR, cm^{-1}): 3170 (w), 3115 (w), 1602 (m), 1578 (w), 1487 (w), 1466 (w), 1436 (m), 1400 (w), 1367 (w), 1252 (s), 1224 (s), 1153 (s), 1100 (w), 1065 (w), 1029 (s), 910 (w), 898 (w), 833 (w), 762 (m), 678 (m). *Anal.* Calc. for $C_{32}H_{28}ZnN_8O_6S_4F_6$: C, 41.40; H, 3.04; N, 12.07. Found: C, 41.14; H, 3.03; N, 11.83%.

2.3. X-ray crystallography

Crystals suitable for X-ray diffraction were obtained from slow vapor diffusion and mounted on a glass fiber using hydrocarbon oil