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Examining the impact of steric and electronic variation in N_2S scorpionate ligands on the properties of zinc(II) and cadmium(II) complexes

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ABSTRACT

A series of LZn(II)Br (**1–4**) and LCd(II)Cl complexes (**9–11**) has been prepared by the reaction of metal halide precursors with the lithium salts of the N_2S^- ligands bis(3,5-diisopropylpyrazol-1-yl)dithioacetate (L^1), bis(3,5-di-*tert*-butylpyrazol-1-yl)dithioacetate (L^2), *N*-phenyl-2,2-bis(3,5-diisopropylpyrazol-1-yl)thioacetamide (L^3) and *N*-phenyl-2,2-bis(3,5-di-*tert*-butylpyrazol-1-yl)thioacetamide (L^4). Characterization by X-ray crystallography and DOSY NMR studies indicate that LZnBr complexes **1–4** are mononuclear both in the solid state and in solution. Steric differences between ligands L^1–L^4 result in distortion from an ideal tetrahedral geometry for each complex, with the degree of distortion depending on the bulk of the ligand substituents. In contrast, the related complex L^3CdCl was shown by X-ray crystallography to dimerize in the solid state to form the chloride-bridged five-coordinate complex $[L^3CdCl]_2$ (**10**). Despite **10** having a dinuclear structure in the solid state, DOSY NMR studies indicate **9–11** exist as mononuclear LCdCl species in solution. In addition, Zn(II) cyanide complexes of the form LZnCN [L = L^1 (**5**), L^3 (**7**), L^4 (**8**)] have been characterized and the X-ray structure of **8** determined. Moreover, density functional theory calculations have been conducted which yield important insight into the bonding in **1–4** and **5–8** and the electronic impact of ligands L^1–L^4 on the zinc(II) ion and its ability to function as a Lewis acid catalyst.

1. Introduction

The electronic and steric properties of an ancillary ligand can dramatically influence the reactivity of a metal ion to which it is bound. As such, extensive efforts have focused on the development of ligand systems whose steric environment and donor atom types (e.g. N, O, and S) can be easily modified, with the ultimate goal being the ability to “fine-tune” a metal complex to produce a desired type of chemical reactivity. One important example of a modifiable ligand system is the carbon-bridged heteroscorpionate ligands derived from bis(pyrazol-1-yl)methanes. These tridentate ligands are similar to tris(pyrazolyl)methanes with one pyrazolyl group replaced by an anionic coordinating group, such as a carboxylate, dithiocarboxylate, acetamidate or thioacetamidate. Ligands of this type provide facially coordinating N_2O^- and N_2S^- donor environments, which are particularly relevant to the study of metalloproteins in which this type of coordination environment is common. As such, they have been used to prepare numerous transition metal complexes [1,2].

Given the potential usefulness of these ligands in studying biomimetic systems, the coordination chemistry of bis(pyrazol-1-yl)dithioacetate and bis(pyrazol-1-yl)thioacetamide ligands with zinc(II) and cadmium(II) remain surprisingly unexplored. In particular, zinc(II)-containing metalloproteins bacteriophage T7 lysozyme and peptide deformylase (in plants PDF1A) both consist of a zinc ion bound through a cysteine and two histidine residues [3,4]. While other examples of N_2S^- ligands have been explored for this type of system, these particular ligands present unique electronic and steric properties that could potentially affect the properties and reactivity of the zinc(II) center. Thus, we wanted to explore potential impacts of variation in these two ligand types (dithioacetate versus thioacetamide) on the geometry and electronic structure of zinc(II) complexes. Moreover, because cadmium substitution of zinc-containing enzymes is often used as a spectroscopic probe (via NMR) to study protein active sites, we expanded the study to also include cadmium [5].

Herein, we report the synthesis and characterization of a series of sterically bulky bis(pyrazol-1-yl)dithioacetate and bis(pyrazol-1-yl)thioacetamide ligands (L^1–L^4) and their lithium salts, which were subsequently used to prepare L^nM-X where n = 1–4, M = Zn, Cd and X = Br, Cl (Scheme 1). Extensive efforts were used to identify the structures and nuclearity of these halide complexes both in the solid state (X-ray crystallography) and in solution (NMR, diffusion ordered spectroscopy (DOSY)). In addition, we describe a synthetic and computation investigation examining the electronic properties of ligands L^1–L^4 and their effect on polarizing cyanide substrates in LZnCN complexes (where L = L^1–L^4).

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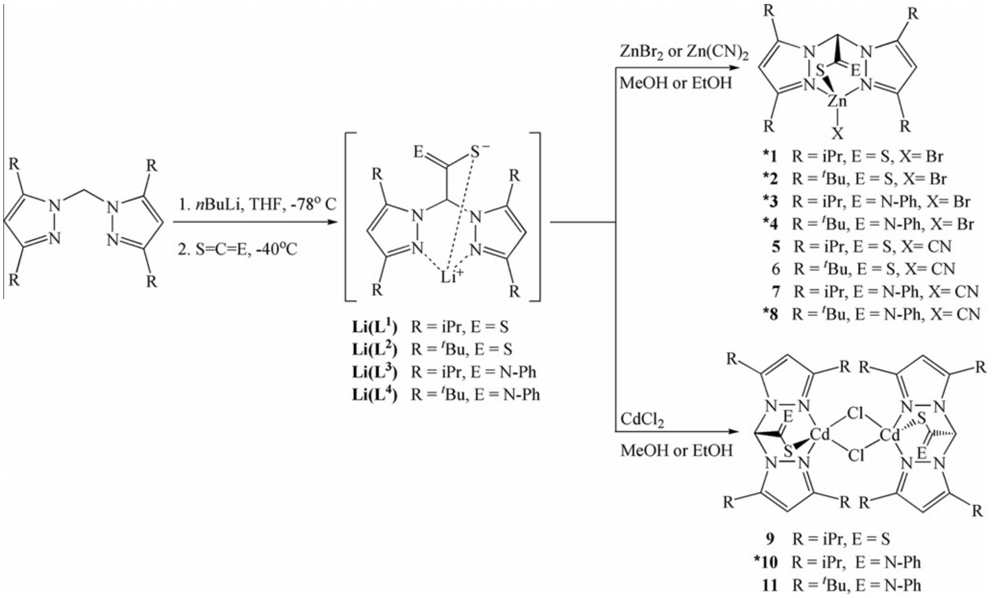

Scheme 1. Zinc(II) and cadmium(II) complexes **1–11**. Asterisks indicate those complexes characterized by X-ray diffraction.

2. Experimental

2.1. General

All reactions were performed using standard Schlenk-tube techniques under a nitrogen atmosphere. Solvents and reagents were obtained from commercial sources and used without further purification. The solvents tetrahydrofuran (THF), methanol and ethanol were dried with CaH_2 and distilled prior to use. NMR spectra were recorded on a Bruker AVANCE III 600 NMR. Chemical shifts for ^{1}H or ^{13}C NMR spectra were referenced to residual solvent peaks. Infrared spectra were measured using a Perkin–Elmer Spectrum 100 spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc. of Norcross, GA. High resolution electrospray mass spectra were recorded on an Applied Biosystems Qstar Elite Quadrupole Time of Flight Instrument. 3,5-Diisopropylpyrazole, 3,5-di-*tert*-butylpryazole and bis(3,5-di-*tert*-butylpyrazol-1-yl)methane were prepared by previously reported procedures [6,7].

2.2. Synthesis and characterization

2.2.1. Preparation of bis(3,5-diisopropylpyrazol-1-yl)methane

Bis(3,5-diisopropylpyrazol-1-yl)methane was prepared using 3,5-diisopropylpyrazole as described for bis(3,5-dimethylpyrazol-1-yl)methane [8]. Yield: 96%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.22 (s, 2H), 5.84 (s, 2H), 3.39 (m, 2H), 2.82 (m, 2H), 1.21 (d, 12H), 1.03 (d, 12H).

2.2.2. Preparation of lithium bis(3,5-diisopropylpyrazol-1-yl)dithioacetate, Li(L^1)

To a solution of bis(3,5-diisopropylpyrazol-1-yl)methane (1.0 g, 3.2 mmol) dissolved in dry THF (40 mL) was added *n*BuLi (1.6 M, 2.94 mL, 4.7 mmol) in hexane at −78 °C. After 1 h of stirring, carbon disulfide (0.28 mL, 4.7 mmol) was added slowly to the reaction at −40 °C. The solution was allowed to reach ambient temperature before the volume was reduced to 5 mL under reduced pressure. Addition of hexane (20 mL) resulted in the formation of an orange solid, which was filtered, washed with hexane (2 × 10 mL) and dried under reduced pressure (0.98 g, 77%). ^{1}H NMR (DMSO, 600 MHz): δ 7.08 (s, 1H), 5.81 (s, 2H), 3.29 (m, 2H), 2.75 (m, 2H), 1.13 (d, 6H), 1.12 (d, 6H), 1.02 (d, 6H), 0.98 (d, 6H). ^{13}C NMR (DMSO, 150 MHz): δ 243.2, 155.4, 151.4, 98.3, 87.5, 27.3, 25.1, 23.5, 23.1, 22.8, 22.8. IR (ATR, cm^{-1}): 2965 (m), 1554 (m), 1457 (m), 1381 (m), 1362 (w), 1299 (s), 1247 (w), 1227 (m), 1178 (m), 1153 (w), 1098 (m), 1076 (m), 1050 (m), 1005 (s), 902 (m), 844 (s), 821 (s), 787 (s), 749 (s), 721 (m), 672 (m). HRMS (ESI, Neg) calculated for $[C_{20}H_{31}N_4S_2{-}Li]^-$: 391.1990, found 391.1996.

2.2.3. Preparation of lithium bis(3,5-di-tert-butylpyrazol-1-yl)dithioacetate·THF, Li(L^2)·THF

To a solution of bis(3,5-di-*tert*-butylpyrazol-1-yl)methane (1.0 g, 2.7 mmol) dissolved in dry THF (40 mL) was added *n*BuLi (1.6 M, 2.56 mL, 4.1 mmol) in hexane at −78 °C. After 1 h of stirring, carbon disulfide (0.25 mL, 4.1 mmol) was added to the reaction at −40 °C, resulting in a red colored solution. The solution was allowed to reach ambient temperature before the volume was reduced to 5 mL under reduced pressure. Addition of hexane (20 mL) resulted in the formation of a orange solid, which was filtered, washed with hexane (2 × 10 mL) and dried under reduced pressure (1.15 g, 81%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.68 (s, 1H), 5.96 (s, 2H), 3.86 (THF), 1.89 (THF), 1.44 (s, 18H), 1.23 (s, 18H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 248.1, 161.3, 154.1, 101.9, 83.6, 68.7, 32.2, 31.9, 31.1, 30.4, 25.5. IR (ATR, cm^{-1}): 2965 (m), 2871 (w), 1644 (w), 1537 (m), 1460 (m), 1397 (w), 1362 (m), 1318 (m), 1252 (m), 1224 (s), 1126 (w), 1084 (s), 1058 (s), 1035 (m), 1006 (s), 900 (w), 878 (m), 853 (m), 828 (w), 816 (m), 800 (s), 743 (s), 727 (m), 691 (m). HRMS (ESI, Neg) calculated for $[C_{24}H_{39}N_4S_2{-}Li{-}THF]^-$: 447.2616, found 447.2634.

2.2.4. Preparation of lithium N-phenyl-2,2-bis(3,5-diisopropylpyrazol-1-yl)thioacetamide·THF, Li(L^3)·THF

To a solution of bis(3,5-diisopropylpyrazol-1-yl)methane (1.0 g, 3.2 mmol) dissolved in dry THF (30 mL) was added *n*BuLi (1.6 M, 2.94 mL, 4.7 mmol) in hexane at −78 °C. After 1 h of stirring, phenyl isothiocyanate (0.56 mL, 4.7 mmol) was added slowly to the reaction at −40 °C. The solution was allowed to reach ambient temperature before the volume was reduced to 5 mL under reduced pressure. Addition of hexane (20 mL) resulted in the formation of a white solid, which was filtered, washed with hexane (2 × 10 mL) and dried under reduced pressure (1.16 mg, 68%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.53 (s, 1H), 7.19 (t, 2H), 6.91 (t, 1H), 6.83 (d, 2H), 5.88 (s, 2H), 3.71 (THF), 3.32 (m, 2H), 2.86 (m, 2H),