# Inorganica Chimica Acta 376 (2011) 562-573

Contents lists available at SciVerse ScienceDirect

# Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# Examining the impact of steric and electronic variation in N<sub>2</sub>S scorpionate ligands on the properties of zinc(II) and cadmium(II) complexes

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# ARTICLE INFO

Article history: Received 25 April 2011 Received in revised form 11 July 2011 Accepted 20 July 2011 Available online 28 July 2011

Keywords: Heteroscorpionate ligands Zinc Cadmium DOSY NMR X-ray crystal structures DFT calculations

# 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<sub>2</sub>S<sup>-</sup> ligands bis(3,5-diisopropylpyrazol-1-yl)dithioacetate (L<sup>1</sup>), bis(3,5-di-*tert*-butylpyrazol-1-yl)dithioacetate (L<sup>2</sup>), *N*-phenyl-2,2-bis(3,5-diisopropylpyrazol-1-yl)thioacetamide (L<sup>3</sup>) and *N*-phenyl-2,2-bis(3,5-di-*tert*-butylpyrazol-1-yl)thioacetamide (L<sup>4</sup>). 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<sup>1</sup>–L<sup>4</sup> 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<sup>3</sup>CdCl was shown by X-ray crystallography to dimerize in the solid state to form the chloride-bridged five-coordinate complex [L<sup>3</sup>CdCl]<sub>2</sub> (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<sup>1</sup>(5), L<sup>3</sup>(7), L<sup>4</sup>(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<sup>1</sup>–L<sup>4</sup> 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-1yl)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  $L^n$ M-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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<sup>0020-1693/\$ -</sup> see front matter  $\odot$  2011 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2011.07.033



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<sub>2</sub> and distilled prior to use. NMR spectra were recorded on a Bruker AVANCE III 600 NMR. Chemical shifts for <sup>1</sup>H or <sup>13</sup>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%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  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)dithio-acetate, $Li(L^1)$

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%). <sup>1</sup>H NMR (DMSO, 600 MHz):  $\delta$  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). <sup>13</sup>C NMR

# 2.2.3. Preparation of lithium bis(3,5-di-tert-butylpyrazol-1-yl)dithio-acetate 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  $(2 \times 10 \text{ mL})$  and dried under reduced pressure (1.15 g, 81%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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<sup>-1</sup>): 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<sub>24</sub>H<sub>39</sub>N<sub>4</sub>S<sub>2</sub>-Li-THF]<sup>-</sup>: 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<sup>3</sup>).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%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  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),

1.78 (THF), 1.51 (d, 6H), 1.28 (d, 6H), 1.21 (d, 6H), 1.19 (d, 6H).  $^{13}$ C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  181.9, 158.5, 153.0, 151.9, 128.5, 122.6, 122.5, 99.0, 77.0, 68.4, 31.1, 28.0, 26.0, 25.6, 24.2, 23.0, 22.8. IR (ATR, cm<sup>-1</sup>): 2964 (m), 2871 (w), 1594 (w), 1543 (s), 1517 (s), 1456 (s), 1384 (m), 1366 (m), 1287 (m), 1222 (m), 1180 (m), 1062 (m), 1046 (s), 1015 (m), 923 (m), 896 (m), 879 (m), 838 (s), 819 (s), 797 (s), 756 (s), 726 (m), 695 (s), 677 (m). HRMS (ESI, Neg) calculated for  $[C_{26}H_{36}N_5S-Li-THF]^-$ : 450.2691, found 450.2679.

# 2.2.5. Preparation of lithium N-phenyl-2,2-bis(3,5-di-tert-butylpyrazol-1-yl)thioacetamide-THF, Li(L<sup>4</sup>)-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 nBuLi (1.6 M, 2.56 mL, 4.1 mmol) in hexane at -78 °C. After 1 h of stirring, phenyl isothiocyanate (0.49 mL, 4.1 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  $(2 \times 10 \text{ mL})$  and dried under reduced pressure (1.15 mg, 73%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.82 (s, 1H), 7.20 (t, 2H), 6.92 (t, 1H), 6.75 (d, 2H), 5.97 (s, 2H), 3.54 (THF), 1.55 (THF), 1.51 (s, 18H), 1.23 (s, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  186.5, 160.5, 154.1, 152.8, 128.7, 122.6, 122.3, 101.6, 80.7, 68.5, 32.2, 32.1, 31.0, 30.5, 25.1. IR (ATR,  $cm^{-1}$ ): 2958 (m), 1594 (w), 1538 (m), 1513 (s), 1486 (m), 1462 (m), 1363 (m), 1344 (w), 1317 (w), 1255 (m), 1228 (m), 1202 (m), 1071 (m), 1040 (m), 1004 (m), 920 (m), 887 (m), 869 (m), 851 (w), 826 (w), 816 (m), 800 (s), 753 (m), 693 (s). HRMS (ESI, Neg) calculated for [C<sub>30</sub>H<sub>44</sub>N<sub>5</sub>S-Li-THF]<sup>-</sup>: 506.3318, found 506.3334.

#### 2.2.6. Preparation of $L^1$ ZnBr (1)

 $ZnBr_2$  (0.225 g, 1.0 mmol) was added to  $Li(L^1)$  (0.400 g, 1.0 mmol) in dry MeOH (20 mL). The reaction was stirred for 24 h, during which time a pink solid formed. The pink solid was collected and dried under reduced pressure (0.408 g, 76%). Orange crystals suitable for crystallographic characterization were obtained by Et<sub>2</sub>O diffusion into THF at room temperature. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 600 MHz):  $\delta$  7.75 (s, 1H), 6.40 (s, 2H), 3.44 (m, 2H), 3.24 (m, 2H), 1.36 (d, 6H), 1.33 (d, 6H), 1.30 (d, 6H), 1.26 (d, 6H). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  7.68 (s, 1H), 6.11 (s, 2H), 3.50 (m, 2H), 3.16 (m, 2H), 1.39 (d, 6H), 1.34 (d, 6H), 1.29 (d, 6H), 1.25 (d, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 235.1, 162.3, 153.8, 100.7, 78.8, 27.2, 26.1, 23.1, 23.0, 22.91, 22.88. IR (ATR, cm<sup>-1</sup>): 2964 (m), 2930 (w), 1550 (m), 1469 (m), 1395 (w), 1383 (m), 1367 (w), 1297 (m), 1283 (m), 1239 (w), 1222 (m), 1181 (m), 1159 (w), 1089 (m), 1078 (m), 1060 (m), 1040 (s), 1027 (s), 963 (w), 932 (w), 907 (w), 880 (w), 847 (m), 805 (s), 730 (s), 716 (m), 686 (m), 669 (m). Anal. Calc. for C<sub>20</sub>H<sub>31</sub>BrN<sub>4</sub>S<sub>2</sub>Zn: C, 44.74; H, 5.82; N, 10.43. Found: C, 44.80; H, 5.27; N, 10.01%.

# 2.2.7. Preparation of $L^2$ ZnBr (2)

ZnBr<sub>2</sub> (0.171 g, 0.76 mmol) was added to Li(L<sup>2</sup>) THF (0.400 g, 0.76 mmol) in dry MeOH (20 mL). The reaction was stirred for 24 h, during which time a pink solid formed. The pink solid was collected and dried under reduced pressure (0.425 g, 94%). Orange crystals suitable for crystallographic characterization were obtained by hexane diffusion into THF at room temperature. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 600 MHz):  $\delta$  8.11 (s, 1H), 6.46 (s, 2H), 1.50 (s, 18H), 1.46 (s, 18H). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  8.06 (s, 1H), 6.18 (s, 2H), 1.50 (s, 18H), 1.46 (s, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  238.4, 165.2, 156.7, 104.4, 81.1, 32.8, 32.5, 31.1, 30.5. IR (ATR, cm<sup>-1</sup>): 2963 (m), 1597 (w), 1544 (s), 1459 (s), 1383 (m), 1366 (m), 1338 (w), 1308 (m), 1289 (m), 1252 (s), 1235 (m), 1182 (m), 1154 (w), 1109 (w), 1081 (s), 1058 (s), 1014

(m), 971 (w), 934 (w), 894 (w), 878 (m), 827 (s), 814 (m), 799 (s), 766 (m), 737 (m), 728 (m), 719 (s), 670 (s). Anal. Calc. for  $C_{24}H_{39}BrN_4S_2Zn$ : C, 48.61; H, 6.63; N, 9.45. Found: C, 48.51; H, 6.87; N, 9.54%.

# 2.2.8. Preparation of $L^3ZnBr(3)$

ZnBr<sub>2</sub> (0.171 g, 0.76 mmol) was added to  $Li(L^3)$ -THF (0.400 g, 0.76 mmol) in dry EtOH (20 mL). The reaction was stirred for 24 h, during which time a white solid formed. The white solid was collected and dried under reduced pressure (0.390 g, 86%). Clear crystals suitable for crystallographic characterization were obtained by Et<sub>2</sub>O diffusion into THF at room temperature. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 600 MHz):  $\delta$  7.32 (t, 2H), 7.09 (t, 1H), 6.77 (d, 2H), 6.37 (s, 2H), 3.45 (m, 2H), 3.29 (m, 2H), 1.42 (d, 6H), 1.39 (d, 6H), 1.30 (d, 6H), 1.26 (d, 6H). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  7.30 (t, 2H), 7.26 (s, 1H), 7.06 (t, 1H), 6.85 (d, 2H), 6.10 (s, 2H), 3.52 (m, 2H), 3.18 (m, 2H), 1.45 (d, 6H), 1.39 (d, 6H), 1.31 (d, 6H), 1.25 (d, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 168.9, 161.7, 153.0, 150.4, 128.8, 124.0, 120.3, 100.2, 73.1, 27.1, 26.0, 23.3, 23.3, 22.6, 22.2. IR (ATR, cm<sup>-1</sup>): 2970 (m), 2935 (w), 2884 (w), 1550 (s), 1480 (m), 1465 (s), 1450 (m), 1395 (m), 1386 (m), 1372 (w), 1342 (w), 1301 (m), 1289 (m), 1230 (m), 1183 (m), 1096 (m), 1082 (m), 1058 (m), 1026 (m), 973 (w), 918 (w), 878 (m), 824 (s), 814 (s), 801 (s), 776 (s), 733 (s), 722 (m), 694 (s), 669 (m). Anal. Calc. for C<sub>26</sub>H<sub>36</sub>BrN<sub>5</sub>SZn: C, 52.40; H, 6.09; N, 11.75. Found: C, 52.27; H, 6.03; N, 11.69%.

### 2.2.9. Preparation of $L^4$ ZnBr (**4**)

 $ZnBr_2$  (0.153 g, 0.68 mmol) was added to  $Li(L^4)$ -THF (0.400 g, 0.68 mmol) in dry EtOH (20 mL). The reaction was stirred for 24 h, during which time a white solid formed. The white solid was collected and dried under reduced pressure (0.376 g, 85%). Clear crystals suitable for crystallographic characterization were obtained by hexane diffusion into THF at room temperature. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 600 MHz):  $\delta$  7.90 (s, 1H), 7.32 (t, 2H), 7.09 (t, 1H), 6.80 (d, 2H), 6.46 (s, 2H), 1.55 (s, 18H), 1.47 (s, 18H). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  7.85 (s, 1H), 7.29 (t, 2H), 7.04 (t, 1H), 6.89 (d, 2H), 6.19 (s, 2H), 1.56 (s, 18H), 1.49 (s, 18H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 169.7, 164.5, 156.1, 150.4, 128.7, 124.0, 120.7, 104.0, 76.7, 32.8, 32.5, 31.3, 30.6. IR (ATR, cm<sup>-1</sup>): 2966 (m), 1582 (s), 1541 (m), 1533 (m), 1514 (w), 1463 (m), 1442 (m), 1365 (s), 1352 (m), 1306 (w), 1250 (m), 1218 (s), 1133 (w), 1108 (m), 1063 (m), 1022 (m), 933 (w), 902 (w), 856 (w), 835 (m), 824 (m), 809 (s), 801 (s), 770 (m), 735 (m), 721 (m), 695 (s). Anal. Calc. for C<sub>30</sub>H<sub>44</sub>BrN<sub>5</sub>SZn: C, 55.26; H, 6.80; N, 10.74. Found: C, 55.19; H, 6.87; N, 10.46%.

### 2.2.10. Preparation of $L^1$ ZnCN (**5**)

Zn(CN)<sub>2</sub> (0.117 g, 1.0 mmol) was added to Li(L<sup>1</sup>) (0.400 g, 1.0 mmol) in dry MeOH (20 mL). The reaction was stirred for 48 h, during which time a pink solid formed. The pink solid was collected and dried under reduced pressure (0.180 g, 36%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  7.64(s, 1H), 6.12 (s, 2H), 3.30 (m, 2H), 3.14 (m, 2H), 1.34 (m, 24H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  234.5, 161.9, 154.1, 134.0 (–CN), 100.8, 78.8, 27.7, 26.1, 23.1, 22.8, 22.74, 22.72. IR (KBr, cm<sup>-1</sup>): 2969 (s), 2931 (m), 2870 (m), 2079 (w), 1551 (s), 1471 (s), 1384 (m), 1301 (s), 1221 (m), 1182 (m), 1080 (m), 1060 (s), 1044 (s), 1028 (s), 933 (w), 906 (w), 879 (w), 846 (m), 807 (s), 730 (m), 717 (m), 688 (m), 669 (m). *Anal.* Calc. for C<sub>21</sub>H<sub>31</sub>N<sub>5</sub>S<sub>2</sub>·0.5CH<sub>3</sub>OH: C, 51.74; H, 6.66; N, 14.03. Found: C, 51.53; H, 6.52; N, 14.11%.

#### 2.2.11. Preparation of $L^3$ ZnCN (**7**)

 $Zn(CN)_2$  (0.090 g, 0.76 mmol) was added to Li(L<sup>3</sup>) THF (0.400 g, 0.76 mmol) in dry EtOH (20 mL). The reaction was stirred for 48 h, during which time a white solid formed. The white solid

was collected and dried under reduced pressure (0.236 g, 57%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 600 MHz):  $\delta$  7.30 (t, 3H), 7.06 (t, 1H), 6.73 (m, 2H), 6.34 (s, 2H), 3.25 (m, 4H), 1.39 (d, 6H), 1.35 (d, 6H), 1.31 (d, 6H) 1.27 (d, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  168.4, 161.4, 153.2, 150.3, 134.8 (–CN), 128.9, 124.2, 120.2, 100.3, 73.1, 27.5, 26.0, 23.3, 23.2, 22.7, 22.1. <sup>13</sup>C NMR (CD<sub>3</sub>CN, 150 MHz):  $\delta$  168.1, 161.2, 154.3, 150.6, 133.7 (–CN), 128.8, 123.8, 119.9, 100.6, 72.8, 27.4, 25.7, 22.5, 22.1, 21.9, 20.9. IR (KBr, cm<sup>-1</sup>): 2967 (m), 2932 (m), 2871 (m), 1549 (s), 1471 (s), 1368 (m), 1300 (m), 1230 (m), 1184 (m), 1082 (m), 1060 (m), 1044 (m), 1028 (s), 933 (w), 906 (w), 878 (w), 846 (m), 804 (s), 769 (m), 731 (m), 716 (m), 690 (s), 669 (m). Anal. Calc. for C<sub>27</sub>H<sub>36</sub>N<sub>6</sub>S: C, 59.82; H, 6.69; N, 15.5. Found: C, 59.55; H, 6.73; N, 15.4%.

#### 2.2.12. Preparation of $L^4$ ZnCN (8)

 $Zn(CN)_2$  (0.080 g, 0.68 mmol) was added to Li(L<sup>4</sup>) THF (0.400 g, 0.68 mmol) in dry EtOH (20 mL). The reaction was stirred for 48 h, during which time a white solid formed. The white solid was collected and dried under reduced pressure (0.236 g, 54%). Clear colorless crystals were isolated from slow vapor diffusion of hexanes into THF at room temperature. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.85 (s, 1H), 7.30 (t, 3H), 7.05 (t, 1H), 6.84 (d, 2H), 6.19 (s, 2H), 3.72 (EtOH), 1.57 (s, 18H), 1.49 (s, 18H), 1.24 (EtOH).  $^{13}\mathrm{C}$  NMR (CDCl\_3, 150 MHz):  $\delta$  169.0, 164.1, 156.4, 150.4, 137.8 (– CN), 128.8, 124.1, 120.4, 104.1, 76.7, 58.6, 32.8, 32.5, 31.4, 30.6, 18.6. IR (KBr, cm<sup>-1</sup>): 3144 (w), 3056 (w), 2971 (s), 2874 (m), 1581 (s), 1541 (s), 1464 (s), 1442 (s), 1366 (s), 1306 (m), 1250 (s), 1218 (s), 1133 (m), 1108 (m), 1066 (s), 1025 (s), 934 (w), 902 (m), 856 (m), 835 (m), 809 (s), 793 (s), 755 (s), 736 (m), 720 (m), 696 (s), 664 (w), 643 (m), 605 (w), 563 (m), 507 (w). Anal. Calc. for C31H44N6S·C2H5OH: C, 61.52; H, 7.82; N, 13.04. Found: C, 61.23; H, 7.51; N, 13.31%.

# 2.2.13. Preparation of $L^1$ CdCl (**9**)

CdCl<sub>2</sub> (0.183 g, 1.0 mmol) was added to Li(L<sup>1</sup>) (0.400 g, 1.0 mmol) in dry MeOH (20 mL). The reaction was stirred for 24 h, during which time an orange solid formed. The orange solid was collected and dried under reduced pressure (0.380 g, 71%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 600 MHz):  $\delta$  7.73 (s, 1H), 6.26 (s, 2H), 3.31 (m, 4H), 1.30 (m, 24H). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  7.00 (s, 1H), 6.03 (s, 2H), 3.51 (m, 2H), 3.03 (m, 2H), 1.40 (d, 6H), 1.34 (d, 6H), 1.27 (d, 6H), 1.09 (d, 6H). <sup>13</sup>C NMR (solid, 150 MHz):  $\delta$  244.5, 161.7, 155.7, 98.8, 76.2, 28.6, 26.6, 24.5, 24.5, 24.1, 22.1. IR (ATR, cm<sup>-1</sup>): 2967 (m), 2930 (w), 2868 (w), 1552 (m), 1470 (s), 1400 (m), 1382 (m), 1365 (m), 1306 (s), 1293 (s), 1242 (m), 1224 (w), 1182 (m), 1153 (w), 1080 (s), 1055 (s), 1019 (m), 962 (w), 930 (w), 909 (w), 881 (w), 849 (m), 831 (s), 804 (m), 796 (s), 761 (s), 722 (m), 692 (m), 683 (m) 668 (m). *Anal.* Calc. for C<sub>20</sub>H<sub>31</sub>ClN<sub>4</sub>S<sub>2</sub>Cd: C, 44.53; H, 5.79; N, 10.39. Found: C, 44.15; H, 5.91; N, 10.31%.

#### 2.2.14. Preparation of $L^3$ CdCl (**10**)

CdCl<sub>2</sub> (0.139 g, 0.76 mmol) was added to  $[\text{Li}(\text{L}^3)]$ -THF (0.400 g, 0.76 mmol) in dry EtOH (20 mL). The reaction was stirred for 24 h, during which time a white solid formed. The white solid was collected and dried under reduced pressure (0.390 g, 86%). Clear crystals suitable for crystallographic characterization were obtained by hexane diffusion into CHCl<sub>3</sub> at room temperature. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 600 MHz):  $\delta$  7.30 (t, 3H), 7.06 (t, 1H), 6.73 (d, 2H), 6.31 (s, 2H), 3.41 (m, 2H), 3.22 (m, 2H), 1.39 (d, 6H), 1.33 (d, 6H), 1.28 (d, 6H), 1.21 (d, 6H). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  7.33 (s, 1H), 7.28 (t, 2H), 7.05 (t, 1H), 6.80 (d, 2H), 6.08 (s, 2H), 3.28 (m, 2H), 3.16 (m, 2H), 1.42 (d, 6H), 1.35 (d, 6H), 1.30 (d, 6H), 1.26 (d, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  169.0, 161.0, 153.4, 150.6, 128.9, 124.0, 120.1, 100.1, 73.5, 27.9, 26.2, 23.51, 23.47, 22.7, 22.4. IR (ATR, cm<sup>-1</sup>): 2963 (m), 2929 (w), 2870 (w), 1597 (w), 1559 (s), 1548 (s), 1485 (w), 1458 (m), 1383 (m), 1365 (w), 1342

(w), 1306 (m), 1252 (m), 1235 (m), 1204 (w), 1181 (m), 1154 (w), 1110 (w), 1068 (m), 1057 (m), 1014 (m), 971 (w), 933 (w), 894 (w), 877 (w), 829 (m), 800 (s), 766 (m), 726 (m), 690 (s), 670 (m). Anal. Calc. for  $C_{26}H_{36}CIN_5SCd$ : C, 52.17; H, 6.06; N, 11.70. Found: C, 51.93; H, 6.06; N, 11.68%.

# 2.2.15. Preparation of L<sup>4</sup>CdCl (**11**)

CdCl<sub>2</sub> (0.124 g, 0.68 mmol) was added to [Li(L<sup>4</sup>)] THF (0.400 g, 0.68 mmol) in dry EtOH (20 mL). The reaction was stirred for 24 h, during which time a white solid formed. The white solid was collected and dried under reduced pressure (0.307 g, 69%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 600 MHz):  $\delta$  7.72 (s, 1H), 7.30 (t, 2H), 7.06 (t, 1H), 6.74 (d, 2H), 6.42 (s, 2H), 1.46 (s, 18H), 1.46 (s, 18H). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 150 MHz):  $\delta$  171.1, 165.1, 157.0, 151.0, 128.7, 123.7, 120.1, 104.0, 77.0, 32.3, 32.0, 29.9, 29.6. IR (ATR, cm<sup>-1</sup>): 2967 (m), 1579 (s), 1542 (m), 1463 (m), 1443 (m), 1366 (s), 1308 (w), 1251 (m), 1225 (s), 1132 (w), 1103 (m), 1063 (m), 1022 (m), 933 (w), 903 (w), 858 (w), 835 (m), 825 (m), 810 (s), 792 (s), 770 (s), 735 (m), 721 (m), 692 (s). Anal. Calc. for C<sub>30</sub>H<sub>44</sub>ClN<sub>5</sub>SCd: C, 55.04; H, 6.77; N, 10.70. Found: C, 55.13; H, 6.85; N, 10.53%.

### 2.3. X-ray crystallography

Suitable crystals of L<sup>1</sup>ZnBr (1), L<sup>2</sup>ZnBr (2), L<sup>3</sup>ZnBr (3), L<sup>4</sup>ZnBr (4),  $L^4$ ZnCN (8) and  $[L^3$ CdCl]<sub>2</sub> (10) were mounted on a glass fiber using hydrocarbon oil and cooled under a nitrogen stream to 150(1) K. A Nonius Kappa CCD diffractometer (Mo K $\alpha$  radiation;  $\lambda$  = 0.71073 Å) was used for data collection. Unit cell parameters were determined from 10 data frames with an oscillation range of 1 deg/frame and an exposure time of 20 s/frame. Indexing and unit cell refinement based on the reflections from the initial set of frames were consistent with monoclinic P lattices for 2, 3 and 10, and triclinic P lattices for 1, 4 and 8. The intensity data for each compound was then collected. These reflections were then indexed, integrated and corrected for Lorentz, polarization and absorption effects using DENZO-SMN and SCALEPAC [9]. The space group for each compound was determined from the systematic absences in the diffraction data. The structures were solved by a combination of direct and heavy atom methods using SIR 97 [10]. Compound 1 crystallized with two crystallographically independent molecules per unit cell and the carbon atoms of one isopropyl group were disordered over two positions with a 74:26 occupancy ratio. Compounds 4 and 8 each contain a molecule of disordered cyclohexane that rests on an inversion center within the asymmetric unit. Compound 10 contains two molecules of disordered CHCl<sub>3</sub>. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and assigned isotropic displacement coefficients U(H) = 1.2U(C)or 1.5U(C<sub>methyl</sub>) using SHELXL-97 [11]. X-ray crystallographic data and collection parameters are listed in Table 1 and selected interatomic distances and angles are provided in Tables 2 and 3.

#### 2.4. Diffusion ordered spectroscopy (DOSY)

Spectra were collected on a Bruker Avance III spectrometer operating at 600 MHz running Topspin 2.1.6. The instrument was equipped with a 5 mm HCN inverse probe (TXI) having a *z*-axis gradient coil, having a specified gradient strength of  $3.57 \text{ G cm}^{-1} \text{ A}^{-1}$ . Samples (~5 mg) were dissolved in deuterated acetonitrile (~0.6 mL) and run at 293 K without sample spinning.

The DOSY analysis followed Bruker's documented procedure [12]. Diffusion data were obtained using the stebpgp1s Bruker pulse sequence, a variation of the variable-gradient Stejskal-Tanner experiment [13]. The reported diffusion coefficients were calculated from the NMR data using the T1/T2 Relaxation Module software provided in the Topspin analysis menu. This program

Та	b	le	1

Summary	of V ray	cructallog	raphic data	and	naramotore <sup>a</sup>
Summerv	Vb1-A 10	Crystallog	Tadille Gala	i and	Darameters.

	1	2	3	$4 \cdot \frac{1}{2} (C_6 H_{12})$	$8 \cdot \frac{1}{2}(C_6H_{12})$	10-2CHCl <sub>3</sub>
Empirical formula	C <sub>20</sub> H <sub>31</sub> BrN <sub>4</sub> S <sub>2</sub> Zn	C24H39BrN4S2Zn	C <sub>26</sub> H <sub>36</sub> BrN <sub>5</sub> SZn	C33H50BrN5SZn	C34H50N6SZn	$C_{54}H_{74}Cd_2Cl_8N_{10}S_2$
Formula weight	536.89	592.99	595.94	694.12	640.23	1435.76
Crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	ΡĪ	$P2_1/n$	$P2_1/m$	ΡĪ	ΡĪ	$P2_1/n$
a (Å)	10.02770(10)	14.3410(2)	8.4632(2)	9.44230(10)	9.5212(2)	11.8790(3)
b (Å)	13.0702(2)	11.9119(2)	13.8637(2)	11.26220(10)	11.1733(2)	15.0492(2)
<i>c</i> (Å)	18.9911(3)	16.8844(3)	11.7280(2)	17.1048(3)	17.0612(3)	18.8828(4)
α (°)	109.5399(6)	90	90	92.6532(8)	91.8074(10)	90
β (°)	93.3334(9)	105.3060(11)	98.1392	91.3042(7)	92.8982(11)	103.8016(7)
γ (°)	90.6329(8)	90	90	108.7771(8)	110.1479(9)	90
V (Å <sup>3</sup> )	2340.50(6)	2782.03(8)	1362.20(4)	1718.92(4)	1699.46(6)	3278.20(12)
Ζ	4	4	2	2	2	2
$D_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.524	1.416	1.453	1.341	1.251	1.455
T (K)	150(1)	150(1)	150(2)	150(1)	150(1)	150(1)
Color	orange	orange	colorless	colorless	colorless	colorless
Crystal size (mm)	$0.30 \times 0.23 \times 0.18$	$0.25 \times 0.20 \times 0.18$	$0.28 \times 0.23 \times 0.08$	$0.30 \times 0.30 \times 0.10$	$0.23\times0.18\times0.15$	$0.33 \times 0.30 \times 0.10$
Abs coefficient (mm <sup>-1</sup> )	2.948	2.488	2.468	1.966	0.816	1.081
$\theta$ Range (°)	1.14-27.47	2.12-25.34	2.29-27.48	2.20-27.48	2.39-27.47	2.29-27.53
Completeness to $\theta$ (%)	99.3	99.7	99.7	99.7	99.6	97.1
Reflections collected	19 885	9331	6054	14 948	14 670	13 608
Independent reflections	10 630	5084	3231	7854	7753	7349
Parameters	543	301	250	366	380	380
$R_1/wR_2$ (all data) <sup>b</sup>	0.0496/0.0914	0.0754/0.2039	0.0367/0.0679	0.0445 /0.0869	0.0602/0.1058	0.0501/0.0834
Goodness-of-fit (GOF)	1.018	1.158	1.044	1.050	1.029	1.057
Difference in peak/hole (e Å <sup>-3</sup> )	0.495/-0.593	2.325/-0.732	0.378/-0.463	0.639/-0.618	0.432/-0.655	0.749 / -0.822

<sup>a</sup> Radiation used: Mo K $\alpha$  ( $\lambda$  = 0.71073 Å).

<sup>b</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ ;  $wR_2 = [\sum [w(F_0^2 - F_c^2)^2] / [\sum (F_0^2)^2]]^{1/2}$ , where  $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ .

provided the diffusion coefficients by directly fitting the data to a gaussian profile, in contrast to the alternative linearized Stejskal–Tanner attenuation plots.

#### Table 2

Selected interatomic distances (A	Å)	) and ang	les (	(°)	) for Zr	(II	) comj	plexes	5
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12 0 (1)			
$L^{2}$ <i>I L</i> <sup>2</sup> <i>I L</i> <sup>2</sup> <i>L</i> <sup>1</sup>			
Zn(1)-N(2)	2.0413(19)	N(2) - Zn(1) - N(3)	90.78(7)
Zn(1) - N(3)	2.0491(19)	N(2)-Zn(1)-S(1)	95.00(6)
Zn(1)-Br(1)	2.3031(4)	N(3)-Zn(1)-S(1)	93.92(6)
Zn(1)-S(1)	2.3207(7)	N(2)-Zn(1)-Br(1)	116.83(5)
S(1)-C(1)	1.717(2)	N(3)-Zn(1)-Br(1)	118.86(5)
S(2)-C(1)	1.634(2)	Br(1)-Zn(1)-S(1)	131.95(2)
$L^2$ ZnBr ( <b>2</b> )			
Zn(1) - N(1)	2.054(7)	N(1) - Zn(1) - N(3)	86.8(3)
Zn(1) - N(3)	2.138(7)	N(1) - Zn(1) - S(1)	93 1(2)
Zn(1) - Br(1)	2.3188(12)	N(3) - Zn(1) - S(1)	100.0(2)
Zn(1) - S(1)	2.334(2)	N(1) - Zn(1) - Br(1)	128 97(19)
S(1) - C(4)	1 714(9)	N(3) - Zn(1) - Br(1)	122 16(18)
S(2) - C(4)	1.633(8)	Br(1) - 7n(1) - S(1)	117 93(7)
3(2) C(1)	1.055(0)		117.55(7)
L <sup>3</sup> ZnBr ( <b>3</b> )			
Zn(1) - N(2)	2.0583(14)	N(2) - Zn(1) - N(2A)	88.95(8)
Zn(1)-N(2A)	2.0584(14)	N(2)-Zn(1)-S(1)	97.01(4)
Zn(1)-Br(1)	2.3093(4)	N(2A)-Zn(1)-S(1)	97.01(4)
Zn(1)-S(1)	2.3031(7)	N(2)-Zn(1)-Br(1)	120.21(4)
S(1) - C(1)	1.751(2)	N(2A)-Zn(1)-Br(1)	120.21(4)
N(3)-C(1)	1.291(3)	Br(1)-Zn(1)-S(1)	125.31(2)
$L^4$ ZnBr ( <b>4</b> )			
$Z_{n(1)-N(4)}$	2 0714(18)	N(4) = 7n(1) = N(1)	85 61(7)
Zn(1) - N(1)	2.0711(10) 2.1080(18)	N(4) = 7n(1) = S(1)	99.05(5)
Zn(1) - Br(1)	2 3172(3)	N(1) = 7n(1) = S(1)	98 26(5)
2n(1) - S(1)	2.3172(3)	N(4) = 7n(1) = Br(1)	12440(5)
S(1) = C(8)	1.741(2)	N(1) = 7n(1) = Br(1)	125.91(5)
N(5) - C(8)	1.741(2) 1.275(3)	R(1) - 2n(1) - S(1)	125.51(5) 116.470(18)
N(J)-C(8)	1.275(5)	DI(1) - ZII(1) - J(1)	110.470(10)
L <sup>4</sup> ZnCN ( <b>8</b> )			
Zn(1)-N(4)	2.0855(17)	N(4) - Zn(1) - N(1)	85.53(7)
Zn(1) - N(1)	2.0527(17)	N(4)-Zn(1)-S(1)	98.59(5)
Zn(1)-C(8)	1.961(2)	N(1)-Zn(1)-S(1)	98.37(5)
Zn(1)-S(1)	2.3056(6)	N(4)-Zn(1)-C(8)	125.93(8)
S(1)-C(9)	1.739(2)	N(1)-Zn(1)-C(8)	123.98(8)
C(8)-N(5)	1.139(3)	C(8)-Zn(1)-S(1)	117.10(7)

<sup>a</sup> Estimated standard deviations in parentheses and "A" refers to symmetryrelated atoms. Experiments were performed with identical experimental parameters: 8 µs 1H 90° pulse, 1 ms gradient pulse duration, and 96.8 ms diffusion time; pulsed field-gradients were varied from 2% to 95% over 16 steps. The residual solvent signal for CD<sub>3</sub>CN was used as the internal reference and its diffusion coefficient ( $D_{CD3CN}$ ) was determined to be  $4.12 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  (±0.19). The  $D_{CD3CN}$  obtained in this study is similar to the value obtained by Kato et al. ( $4.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) [14]. The Stokes–Einstein equation [15] was used to calculate the hydrodynamic radii (r) for the halide complexes **1–4** and **9–11** from their diffusion coefficients (D), using a literature value of  $0.39 \times 10^{-3} \text{ kg s}^{-1} \text{ m}^{-1}$  (293 K) for the acetonitrile viscosity [16]. The calculated radii (r') from the solid state structures were determined by approximating the shape of the molecules as prolate ellipsoids [17].

#### 2.5. DFT calculations

All DFT calculations were performed with the GAUSSIAN 03W [18] suite of programs (Revision E.01) using the restricted B3LYP functional [19]. Geometry optimizations were performed without symmetry constraints using atomic coordinates from experimental X-ray crystal structures as input geometries, when available. For all optimizations, the Stuttgart/Dresden (SDD) effective core potential and basis set [20] was used for zinc and the 6-31g(d,p) basis set

Table 3	
Selected interatomic distances (Å) and angles (°) for $[L^3CdCl]_2$ ( <b>10</b> ). <sup>a</sup>	
$[L^3CdCl]_2$ ( <b>10</b> )	

$[L \operatorname{Cuci}]_2(\mathbf{I0})$			
Cd(1)-N(1)	2.3778(19)	N(4)-Cd(1)-S(1)	92.26(5)
Cd(1)-N(4)	2.294(2)	N(1)-Cd(1)-S(1)	89.61(5)
Cd(1)-S(1)	2.4859(6)	Cl(1)-Cd(1)-S(1)	136.89(2)
Cd(1)-Cl(1)	2.4541(6)	N(4)-Cd(1)-Cl(1A)	93.78(5)
Cd(1)-Cl(1A)	2.7174(6)	N(1)-Cd(1)-Cl(1A)	172.16(5)
N(4)-Cd(1)-N(1)	78.50(7)	Cl(1)-Cd(1)-Cl(1A)	84.30(2)
N(4)-Cd(1)-Cl(1)	130.82(5)	S(1)-Cd(1)-Cl(1)	92.09(2)
N(1)-Cd(1)-Cl(1)	99.65(5)	Cd(1)-Cl(1)-Cd(1A)	95.70(2)

<sup>a</sup> Estimated standard deviations in parentheses and "A" refers to symmetryrelated atoms. [21] was used for all other atoms. All optimized structures were verified as energetic minima by the absence of imaginary frequencies in subsequent frequency calculations using this same basis set combination. Natural population analysis using the methods of Weinhold and co-workers [22] was performed on optimized geometries during single point energy calculations using the SDD effective core potential and basis set [21] for zinc and the TZVP basis set of Ahlrichs and co-workers [23] for all other atoms. Compositions of molecular orbitals and overlap populations between molecular fragments were calculated using the AOMIX program with this same basis set combination [24]. Analysis of molecular orbitals using fragment orbital compositions, charge decomposition analyses (CDA), and the construction of orbital interaction diagrams were performed using AOMIX-CDA [24].

#### 3. Results and discussion

# 3.1. Ligand synthesis

The synthetic procedure for the new heteroscorpionate ligands having dithioacetate or thioacetamide functional groups and bulky pyrazole substituents is shown in Scheme 1. Deprotonation of the methylene group of either bis(3,5-diisopropylpyrazol-1-yl)methane or bis(3,5-di-*tert*-butylpyrazol-1-yl)methane with *n*BuLi in THF at  $-78 \,^{\circ}$ C followed by reaction with carbon disulfide or phenyl isothiocyanate at  $-40 \,^{\circ}$ C gave the lithium dithioacetate or thioacetamide compounds Li(L<sup>1</sup>) [L<sup>1</sup> = bis(3,5-diisopropylpyrazol-1-yl)dithioacetate], Li(L<sup>2</sup>) [L<sup>2</sup> = bis(3,5-di-*tert*-butylpyrazol-1-yl)dithioacetate], Li(L<sup>3</sup>) [L<sup>3</sup> = *N*-phenyl-2,2-bis(3,5-diisopropylpyrazol-1-yl)thioacetamide], and Li(L<sup>4</sup>) [L<sup>4</sup> = *N*-phenyl-2,2-bis(3,5-di-*tert*-butylpyrazol-1-yl)thioacetamide]. The compounds were isolated as air-stable white or orange colored solids in good yields (ca. 78%). The synthetic procedure is similar to the strategy reported by Otero et al. [1a,2b].

The lithium salts were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR and electrospray mass spectrometry (ESI-MS). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of each compound show magnetically equivalent pyrazole rings indicative of complexes having C<sub>s</sub>-symmetry in solution. With the exception of  $Li(L^1)$ , each complex contains a THF solvent molecule, as observed by <sup>1</sup>H and <sup>13</sup>C NMR. One possible explanation for the absence of a THF molecule in  $Li(L^1)$  is loss due to drying under vacuum. For  $Li(L^1)$  and  $Li(L^2)$ , the <sup>13</sup>C NMR signal for the thiocarbonyl of the dithioacetate group is observed at 243.2 and 248.1 ppm, while, for  $Li(L^3)$  and  $Li(L^4)$ , the <sup>13</sup>C NMR signal for the imine of the thioacetamide group is observed at 181.9 and 186.5 ppm. The high resolution ESI-MS (negative mode) spectra of each compound in a chloroform/methanol solution contained only peaks with m/z values consistent with the molecular ion  $[L^n]^-$ , indicating loss of the lithium ion and THF. Recently, the solid state structure of Li(L<sup>2</sup>) was reported by Marchiò et al. to have the trinuclear composition [Li(L<sup>2</sup>)]<sub>3</sub>.(2.25)THF [1j].

# 3.2. Synthesis of metal complexes 1-11

The N<sub>2</sub>S<sup>-</sup> ligands  $L^1-L^4$  contain steric and electronic variations that could potentially have an important impact on the properties of a bound metal ion. Such variations could be potentially manifested as differences in the electronic properties of the complexes or in the coordination environment of the metal ions. As noted previously, this ligand set is particularly relevant to the study of metalloproteins containing zinc(II) ions. Complexes of Zn(II) were therefore chosen as ideal candidates for studying the effects of these ligands. Moreover, because of the larger ionic radius of cadmium(II) ions and their ability to substitute for zinc(II) ions in enzymes and other coordination complexes, we chose to explore the analogous chemistry with Cd(II). Zn(II) and Cd(II) halide complexes **1–4** and **9–11** were prepared in 69–94% yield by treatment of the lithium compounds of  $L^1-L^4$ with either ZnBr<sub>2</sub> or CdCl<sub>2</sub> in alcoholic solvent (Scheme 1). Each of the metal products were precipitated from the reaction mixture as pure solids, with the choice of alcohol solvent (MeOH or EtOH) dependent on the insolubility of the specific products. An attempt to make the cadmium chloride complex using  $L^2$  resulted in an inseparable mixture of products and was not further pursued. Compounds **1–4** and **9–11** were characterized using <sup>1</sup>H and <sup>13</sup>C NMR, IR, elemental analysis (CHN) and, in the case of compounds **1–4** and **10**, by single-crystal X-ray crystallography.

Synthetic studies were also undertaken to determine the electronic properties of ligands  $L^1 - L^4$  by preparing zinc cyanide complexes 5-8 (Scheme 1). The stretching frequencies and <sup>13</sup>C NMR chemical shifts of metal-bound cyanides are known to be sensitive to the Lewis acidity of a metal center, which is influenced by the electron-donating properties of the supporting auxillary ligands. Attempts to prepare complex 6 were unsuccessful and led only to an inseparable mixture of products. Even though 6 could not be isolated synthetically, it was studied computationally. Complexes 5, 7 and 8 were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR, elemental analysis and X-ray crystallography. <sup>13</sup>C NMR spectroscopy and X-ray crystallography confirmed that complexes 5, 7 and 8 each contain a coordinated CN<sup>-</sup> ligand. The <sup>13</sup>C NMR spectra of 5-8 show slight differences in chemical shift for the carbon resonance of the bound cyanide anion ( $\delta \approx 134$  ppm for **5** and **7**;  $\delta \approx 138$  ppm for **8**), suggesting L<sup>1</sup>–L<sup>4</sup> have similar electron-donating properties. Surprisingly, the FT-IR spectra of 5-8 display extremely weak v<sub>CN</sub> stretching vibrations, which prevented their assignment.

#### 3.3. X-ray structures of zinc bromide complexes 1-4

The solid state structures of  $L^1$ ZnBr (1) and  $L^2$ ZnBr (2) with supporting ligands containing the dithioacetate functional group are shown in Fig. 1. A summary of the X-ray crystallographic data and selected bond distances and angles are given in Tables 1 and 2. Each compound is monomeric and contains a monoanionic N<sub>2</sub>S ligand coordinated to a zinc center through two pyrazolyl nitrogen atoms and one dithioacetate sulfur atom. In addition, each zinc atom is coordinated to one bromide ligand in a distorted tetrahedral geometry. Deviation from an idealized tetrahedral geometry (109.5°) is most noticeable in 2. The extent of the structural deviation in **2** is evident by the differences in the bond angles, with bond angles varying from 86.8(3)° for the N3–Zn1–N1 angle to 128.97(19)° for the N1–Zn1–Br1 angle. Another measure for determining the degree of distortion is made by measuring the angle between the N3–Zn1–N1 and S1–Zn1–Br1 planes. An angle of 90° is observed in an idealized tetrahedral geometry, while an angle of 0° is observed in a square planar geometry. The angle in 1 and 2 are 89.1° and 84.7°, respectively, illustrating the greater structural deviation from an idealized tetrahedral geometry in 2 compared to **1**. Indeed, the bulky *tert*-butyl groups on L<sup>2</sup> cause the two pyrazole rings to twist, as evidenced by the angle between the two rings (41.64°) and the Zn–S–C–C torsion angle of the thioacetate bridge (24.6(6)°). This twisting also results in two inequivalent Zn-N bond lengths (2.054(7) and 2.138(7)Å) and a bromide ligand bent towards N3. In contrast the less bulky iPr groups of L<sup>1</sup> result in significantly less structural distortion, with the observed twist angle of the two pyrazoles at only 3.93° and nearly identical Zn-N bond lengths (2.0413(19) and 2.0491(19) Å).

The solid state structures of  $L^3$ ZnBr (**3**) and  $L^4$ ZnBr (**4**) having the thioacetamide S-donor groups were also determined crystallographically. Their ORTEP diagrams are shown in Fig. 2 and Table 2 gives selected bond distances and angles. Complexes **3** and **4**, also exhibit facial coordination of their respective ligands and adopt



Fig. 1. ORTEP diagrams of complexes (a) L<sup>1</sup>ZnBr (1) and (b) L<sup>2</sup>ZnBr (2). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.



Fig. 2. ORTEP diagrams of complexes (a) L<sup>3</sup>ZnBr (3) and (b) L<sup>4</sup>ZnBr (4). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. "A" refers to symmetry-related atoms.

distorted tetrahedral geometries. The smallest bond angle in both complexes is the N–Zn–N angle ( $88.95^{\circ}$  in **3**,  $85.61^{\circ}$  in **4**), while the largest angles are the Br–Zn–S angle ( $125.31^{\circ}$ ) in **3** and the N1–Zn1–Br1 angle ( $125.91^{\circ}$ ) in **4**. The Zn–Br distance (2.3093(4) Å in **3**, 2.3172(3) Å in **4**) is similar to the Zn–Br distance



**Fig. 3.** ORTEP diagram of complex L<sup>4</sup>ZnCN (8). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

in **1** (2.3031(4) Å) and **2** (2.3188(12) Å) and other tetrahedral Zn(II) complexes containing a terminal bromide [25]. The average Zn–S bond length in **3** and **4** (2.3043 Å) is slightly shorter than that in **1** and **2** (2.3274 Å). However these values are all in the range of analogous four-coordinate Zn(II) complexes (2.25–2.36 Å) with nonbridging thiolate or thiophenolate ligands [25a,26].

# 3.4. X-ray structure of zinc cyanide complex 8

The molecular structure of **8** is shown in Fig. 3 and Table 2 gives selected bond angles and distances. The zinc center adopts a four-coordinate distorted tetrahedral geometry. The smallest bond angle is the N4–Zn1–N1 angle ( $85.53(7)^\circ$ ) and the largest is the N4–Zn1–C8 angle ( $125.93(8)^\circ$ ). Compared with **4**, which is also supported by L<sup>4</sup>, the Zn–N distances in **8** are slightly shorter ( $\sim$ 0.02 Å) but the Zn–S distances are statistically identical (**8**, 2.3056(6) Å; **4**, 2.3055(6) Å). The C–N bond length of 1.139(3) Å for the cyanide ligand is slightly longer than that reported for the related complex {HB(3-Bu<sup>t</sup>pz)<sub>3</sub>}ZnCN (C–N, 1.117(9) Å; Zn–C, 1.962(6) Å), but the Zn–C bond length of 1.961(2) Å in **8** is identical [25c].

# 3.5. X-ray structure of $[L^3Cd(II)Cl]_2$ (10)

The structure of the representative complex  $L^3Cd(II)Cl$  was structurally characterized by X-ray crystallography, with the structure shown in Fig. 4 and selected crystallographic data listed



Fig. 4. ORTEP diagram of complex [L<sup>3</sup>CdCl]<sub>2</sub> (10). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. "A" refers to symmetryrelated atoms.

in Table 3. In contrast to zinc complexes 1-8, the structure of the cadmium(II) chloride analogue 10 is dimeric. Each cadmium ion is in a distorted trigonal bipyramidal environment consisting of two nitrogen atoms and a sulfur atom from the L<sup>3</sup> ligand and two chlorine atoms from the bridging chloride ligands. The equatorial plane is defined by the sulfur atom S1, the bridging chlorine atom Cl1 and the nitrogen atom N4. The equatorial S1-Cd1-N4 angle of 92.26(5)° is smaller than the S1-Cd1-Cl1 and N4-Cd1-Cl1 angles of 136.89(2)° and 130.82(5)°, respectively. The axial positions consist of the nitrogen atom N1 and the other bridging chlorine atom Cl1A. The N1-Cd1-Cl1A angle is almost linear at 172.16(5)°. The Cd<sub>2</sub>( $\mu$ -Cl)<sub>2</sub> core is asymmetric, with each cadmium ion having a long Cd-Cl distance (2.7174(6)Å) and a short Cd-Cl distance (2.4541(6)Å). The two cadmium centers are separated by an intramolecular Cd1...Cd1A distance of 3.838 Å, which is similar to values reported for other 5-coordinate, dimeric Cd(II) complexes with bridging chlorides [27]. The Cd1-S1 distance (2.4859(6)Å) in **10** is similar to Cd–S distances observed in cadmium(II) complexes with aliphatic thiolates (2.47–2.55 Å) [28] but shorter than cadmium(II) complexes with thioethers (2.58-2.76 Å) [27b,29].

### 3.6. Solution state behavior of zinc and cadmium halide complexes

Diffusion ordered spectroscopy (DOSY) in CD<sub>3</sub>CN was used to examine possible differences between the solution and solid state structures of complexes 1-4 and 9-11. DOSY NMR allows for the determination of the diffusion coefficient (D) of a molecule in solution, which is inversely related to the hydrodynamic radius (r) of the molecule [15]. For **1–4**, diffusion coefficients of  $1.35 \times$  $10^{-9} \text{ m}^2 \text{ s}^{-1}$  for **1**,  $1.30 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for **2**,  $1.17 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for **3** and  $1.28 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup> for **4** were obtained. These diffusion coefficients afforded hydrodynamic radii of r = 4.08 Å for 1, 4.23 Å for 2, 4.70 Å for **3** and 4.30 Å for **4**. The radii (*r*) obtained from the DOSY experiments do not differ significantly from the calculated radii (*r*'), which were determined from the X-ray crystal structures of 1-4 (r' = 4.3 Å for 1, 4.5 Å for 2, 4.7 Å for 3 and 4.8 Å for 4). The results of the DOSY and X-ray studies are therefore consistent with complexes 1-4 having a mononuclear structure both in solution and in the solid state.

Analogous DOSY experiments were conducted for cadmium complexes **9–11**, and surprisingly, the diffusion coefficients

 $(1.25 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ for } 9, 1.16 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ for } 10 \text{ and } 1.14 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ for } 11)$  and hydrodynamic radii (r = 4.40 Å for 9, 4.74 Å for 10, and 4.83 Å for 11) obtained are similar to the values obtained for complexes 1-4. Indeed, the calculated hydrodynamic radius of 10 determined from the X-ray crystal structure is 7.7 Å, ~38% larger than that obtained from the DOSY experiment (4.74 Å). These data suggest that, like 1-4, the cadmium complexes 9-11 are also monomeric species in solution, despite the dimeric solid state structure obtained for 10.

# 3.7. Computational studies

Zinc(II) complexes, like other Lewis acids, facilitate reactions by accepting electron density from substrate molecules and by polarizing the electronic distribution within these molecules [30-32]. Because the ability of the zinc ion to perform these tasks is directly related to the charge density of the ion [31], the nature of the supporting auxiliary ligand on the zinc center and its ability to donate charge to the metal center can have an important impact. To help elucidate the potential impact of the structural and electronic differences in the N<sub>2</sub>S<sup>-</sup> ligands on the electronic nature of the zinc center, complexes 1-8 were investigated using density functional theory. DFT-optimized geometries were obtained for all complexes using the restricted B3LYP functional [19], the SDD basis set and effective core potential [20] for zinc, and the 6-31g(d,p) basis set [21] for all other atoms. As shown from the overlay in Fig. 5, the geometry-optimized structures of the LZnBr complexes 1-4 are in good agreement with the experimental X-ray crystal structures (selected geometric parameters are listed in Table S1). Generally, only minor deviations of ligand alkyl substituents are observed. One notable exception is the phenyl ring of the thioacetamide ligand  $L^3$ , which is rotated ~56° in the calculated structure of **3** relative to the crystal structure. The calculated Zn-N bond lengths are slightly elongated relative to the X-ray structures (elongation of 0.025–0.072 Å; average = 0.059 Å). All calculated Zn–S and Zn–Br bond lengths are in excellent agreement with the experimental structures, with all deviations from the experimental structures of less than 0.02 Å.

Natural atomic orbital populations and related natural atomic charges [22] were subsequently computed for the optimized geometries of **1–4** at the B3LYP level of theory [20] using the SDD basis set and effective core potential [21] for zinc and the



**Fig. 5.** Structural overlay of X-ray crystal structures (blue) with geometry optimized structures (red) for LZnBr complexes **1–4**. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

TZVP basis set [23] for all other atoms. Natural atomic orbitals and natural atomic charges are useful for quantifying the charge distribution within a metal complex. Thus, comparison of the results within this series of complexes can provide a means of comparing the electronic impact of the dithioacetate and thioacetamide ligands on the charge on the zinc center. Indeed, the use of natural population and Mulliken charge analysis on related zinc(II) complexes of N<sub>2</sub>S<sup>-</sup> ligands has been recently shown to yield excellent insight into the nature of zinc(II)-catalyzed reactions [33]. The calculated natural atomic charges for the zinc ions in **1–4** range from 0.85 to 0.89, consistent with a net delocalization of electron density (~1.1 electrons) onto the zinc center from the bromide ion and the supporting N<sub>2</sub>S<sup>-</sup> ligands. These values are consistent with the anticipated Lewis acidic role of the zinc(II) ion and the electron donating natures of the two coordinated anions.

The calculated natural atomic charges for the zinc ions in 1-4 are very similar to one another, suggesting that the variations within the N<sub>2</sub>S<sup>-</sup> ligands have relatively little impact on the zinc center. The charge donation to the zinc center in these complexes is the combined amount from both the  $Br^-$  and the  $N_2S^-$  ligands, however, which complicates the individual quantification of the N<sub>2</sub>S<sup>-</sup> ligand component. To help quantify the relative electron donation from ligands L<sup>1</sup>–L<sup>4</sup> without the influence of the bromide ion, natural atomic charges were similarly computed for the [LZn]<sup>+</sup> fragments after removal of the bromide ion from complexes 1-4.<sup>1</sup> As shown in Table 4, the natural atomic charges for the "bare" zinc center in the [LZn]<sup>+</sup> fragments are virtually unchanged across the series (1.11-1.16), again suggesting a similar magnitude of electron donation from  $L^1-L^4$  to the zinc ion (0.84–0.89 electrons) despite the changes in both the electronic and structural nature of the N<sub>2</sub>S<sup>-</sup> ligands. Fig. 6 shows the calculated natural atomic charges for selected atoms in the [L<sup>1</sup>Zn]<sup>+</sup> and [L<sup>3</sup>Zn]<sup>+</sup> fragments for comparison. While slight variations in the zinc natural atomic charges are observed between the dithioacetate ligands and the thioacetamide ligands, as well as with changes in alkyl group substitution, the effects are relatively minor.

To further understand the charge localization onto the Zn(II) ion in the bare  $[LZn]^+$  complexes, the electron occupancies of the Zn(4s) and Zn(4p) orbitals were investigated by natural population

#### Table 4

Calculated natural atomic charges for selected atoms in LZnBr complexes 1-4 and related "bare" [LZn]<sup>+</sup> fragments.<sup>a</sup>

	1	2	3	4	1-bare <sup>a</sup>	2-bare <sup>a</sup>	3-bare <sup>a</sup>	4-bare <sup>a</sup>
Zn	0.85	0.88	0.87	0.89	1.12	1.11	1.16	1.13
Ν	-0.35	-0.37	-0.34	-0.36	-0.42	-0.43	-0.41	-0.42
N′	-0.35	-0.37	-0.34	-0.36	-0.42	-0.43	-0.41	-0.43
S	-0.08	-0.10	-0.25	-0.27	-0.07	-0.08	-0.24	-0.24
Br	-0.53	-0.53	-0.54	-0.54	N/A	N/A	N/A	N/A

<sup>a</sup> Geometries of [LZn]<sup>+</sup> fragments used were those obtained from the optimization of the full LZnBr complexes.



**Fig. 6.** Natural atomic charge distribution for selected atoms within  $[LZn]^+$  fragments for dithioacetate and thioacetamide ligands  $L^1$  and  $L^3$  (hydrogens and isopropyl groups omitted for clarity).

analysis. Analysis of the natural atomic orbital populations of the [LZn]<sup>+</sup> fragments in **1–4** reveals significant population of the zinc orbitals resulting from interaction with the N<sub>2</sub>S<sup>-</sup> ligands (Table S3). The average Zn(4s) orbital population in this series of complexes is approximately 0.58 electrons, and the total Zn(4p) orbital population is approximately 0.29 electrons. These values are similar within all four complexes, leading to comparable natural atomic charges for the zinc centers. These results suggest that, in the bare [LZn]<sup>+</sup> complexes, the Zn(4s) orbital plays the dominant role in accepting electrons from the N<sub>2</sub>S<sup>-</sup> ligands, while the Zn(4p) orbitals play a lesser role.

Because the strength of a Lewis acid is related not only to the charge of the metal center, but also to its ability to induce charge polarization within substrate molecules, the binding of the polarizable cyanide (CN<sup>-</sup>) ligand with the [LZn]<sup>+</sup> fragments was also investigated. Cyanide is a strong  $\sigma$ -donor and a poor  $\pi$ -acceptor, and comparison of the charge distribution within the CN<sup>-</sup> ligand among the series of complexes **5–8** could help quantify the relative Lewis acidity of the different [LZn]<sup>+</sup> fragments. The geometry optimized structures of the analogous LZnCN complexes were computed and are shown in Fig. S1, with selected structural parameters given in Table S2. The DFT calculated geometric parameters for complex 8 are in good agreement with the X-ray structure of this complex, which is the only one for which a crystal structure was obtained. As in complexes 1-4, the calculated Zn-N bond lengths in 8 are lengthened by an average of 0.06 Å relative to the crystal structure, while the calculated Zn-S and Zn-C bond lengths deviate from the experimental values by less than 0.015 Å.

The calculated  $v_{CN}$  values for LZnCN range from ~2191 to 2196 cm<sup>-1</sup>, which is within the range typically observed for other metal–cyanide complexes [30,34].<sup>2</sup> Surprisingly, no CN vibrations were observed in the experimental FT-IR spectra of complexes **5–8**, despite the conformation of a coordinated CN<sup>-</sup> ligand by X-ray crystallography and <sup>13</sup>C NMR spectroscopy. The simulated IR spectra of these complexes were obtained, however, and that

<sup>&</sup>lt;sup>1</sup> Note: Geometries of the [LZn]<sup>+</sup> fragments were not optimized in the absence of the bromide ion prior to natural population analysis.

 $<sup>^2</sup>$  Calculated using the B3LYP functional, the SDD basis set and effective core potential for Zn, and the 6-31g(d,p) basis set for all other atoms. These vibrational frequency values have been scaled by a factor of 0.961 as recommended for this functional and basis set combination.

of the representative complex **8** is shown in Fig. S2. Indeed, the CN vibration is predicted to give rise to a very low intensity IR absorption that is consistent with the lack of an observable CN stretch in the experimental spectrum of these complexes [34].

Natural atomic orbital populations and related natural atomic charges [22] were computed for the optimized geometries of 5-8 at the B3LYP level of theory [20] using the SDD basis set and effective core potential [21] for zinc and the TZVP basis set [23] for all other atoms. As seen in Table 5, the calculated natural atomic charges of the zinc centers in the LZnCN complexes range from 0.85–0.89, while the calculated charges of the zinc centers in the related "bare" [LZn]<sup>+</sup> fragments range from 1.11-1.16. These charges on the zinc centers of the LZnCN complexes are the same as those computed for the LZnBr complexes 1-4 (0.85-0.89), suggesting a comparable amount of charge delocalization onto the zinc centers. Indeed, the occupancy of the Zn(4s) orbital is calculated to range from 0.52-0.54 electrons in both series of complexes, despite the coordination of the different anions. Moreover, the sum of the orbital occupancies of the Zn(4p) orbitals for all complexes is calculated to be between 0.57-0.65 electrons. Thus, the Zn(4s) and Zn(4p) orbitals accept similar amounts of electron density from the combination of the Br<sup>-</sup>, CN<sup>-</sup> and N<sub>2</sub>S<sup>-</sup> ligands in all complexes 1-8.

In addition to quantification of charge on the zinc center of the [LZn]<sup>+</sup> fragments as an indicator of Lewis acidity, analysis of the charge polarization within the cyanide anion is also informative. Natural atomic charge calculations for the free cyanide anion at the B3LYP level of theory using the TZVP basis set predict the negative charge to be localized mainly on the nitrogen atom (-0.75)and less on the carbon atom (-0.25), as expected based on the greater electronegativity of the nitrogen atom. Using the bare [Zn(CN)]<sup>+</sup> cation as a baseline for comparison, the binding of the cvanide anion to the Zn(II) cation results in the net delocalization of  $\sim$ 0.57 electrons to the Lewis acidic zinc ion. Moreover, the remaining charge distributed within the bound cyanide anion is now significantly polarized towards the carbon atom (-0.32) relative to the nitrogen atom (-0.11). Thus, binding to the zinc center results in both significant transfer of electron density to the metal and away from the bound cyanide anion as well as a redistribution of charge density within the cyanide molecule itself.

Upon binding to the  $[LZn]^+$  fragments in **5–8**, average charge delocalization from the bound cyanide anion to the  $[LZn]^+$  fragment is calculated to be less than that observed for the bare zinc(II) cation (~0.40 electrons versus 0.57 electrons), likely due to the influence of the bound N<sub>2</sub>S<sup>-</sup> ligands which also donate electron density into the zinc acceptor orbitals. The polarization of the remaining charge on the CN<sup>-</sup> anion is significantly less pronounced than observed with the bare zinc(II) cation, with the natural atomic charge of the carbon atom in **5–8** ranging from –0.17 to –0.21, and the nitrogen charge calculated to be approximately –0.4 (Table 5). While the relative charge distribution within the CN<sup>-</sup> anion in complexes **5** and **7** are roughly the same as that observed in free

Table 5

Calculated natural atomic charges for selected atoms in LZnCN complexes  ${\bf 5-8},$  L^2ZnCN and related "bare" [LZn]\* fragments.<sup>a</sup>

	5	6	7	8	5-bare	6-bare	7-bare	8-bare
Zn	0.85	0.88	0.86	0.89	1.13	1.11	1.16	1.13
Ν	-0.34	-0.36	-0.33	-0.35	-0.42	-0.43	-0.41	-0.42
N′	-0.34	-0.36	-0.33	-0.35	-0.42	-0.43	-0.41	-0.43
S	-0.07	-0.09	-0.24	-0.26	-0.07	-0.08	-0.24	-0.25
С	-0.17	-0.21	-0.17	-0.20	N/A	N/A	N/A	N/A
Ν	-0.41	-0.40	-0.41	-0.40	N/A	N/A	N/A	N/A
<sup>13</sup> C	133.9	N/A	134.8	137.7	N/A	N/A	N/A	N/A

<sup>a</sup> Geometries of [LZn]<sup>\*</sup> fragments used were those obtained from the optimization of the full LZnCN complexes. CN<sup>−</sup> (29% on C; 71% on N), the charge distribution within the CN<sup>−</sup> anion is slightly more polarized towards the carbon atom in compounds **6** and **8** (34% on C; 66% on N). While these differences are small, consistent shifts in the <sup>13</sup>C NMR resonance for the bound cyanide ligand in these complexes ( $\delta \approx 134$ –135 ppm for **5** and **7**;  $\delta \approx 138$  ppm for **8**) do suggest the possibility of electronic differences in the zinc centers imposed by variations in the N<sub>2</sub>S<sup>−</sup> ligands. Such differences and their potential use in probing the Lewis acidity of zinc(II) complexes are currently being explored further.

To gain further insight into the similarities and differences imparted upon the  $[LZn]^+$  fragments by the different classes of  $N_2S^-$  ligands, important orbital interactions between the  $[LZn]^+$  fragments and the  $CN^-$  anion for dithioacetate and thioacetamide ligands  $L^1$  and  $L^3$  were investigated using AOMIX-CDA [24]. Fig. 7 gives the orbital interaction diagram between the two fragments in the representative complex **5**. The main orbitals involved in bonding between the two fragments are the filled  $\sigma$ -donating HOFO (highest occupied fragment orbital) of the  $CN^-$  anion, and the empty LUFO (lowest unoccupied fragment orbital) of the



**Fig. 7.** Orbital interaction diagram for L<sup>1</sup>ZnCN (only selected interfragment donor/acceptor orbital interactions are shown for clarity).



**Fig. 8.** LUFO of  $[L^1Zn]^+$  and  $[L^3Zn]^+$  fragments (isovalue = 0.035).

 $[LZn]^+$  fragment, which is predominantly composed of the Zn(4s) and Zn(4p) orbitals. This interaction very closely resembles the "classic" Lewis acid/base interaction that is expected for the zinc(II) center. Other filled frontier orbitals on the  $[LZn]^+$  fragment are predominantly ligand based and are not significantly involved in bonding with the cyanide ligand. The filled  $[LZn]^+$  fragment orbitals having predominantly Zn(3d) character are low energy (E = -18.3 to -19.9 eV) when compared to the energy of the empty  $\pi^+$ -orbitals of the CN<sup>-</sup> fragment (E = 7.94 eV), resulting in no observable Zn(3d)  $\rightarrow$  CN( $\pi^*$ ) backbonding interaction.

Comparison of the Lewis acidic LUFO of the  $[L^1Zn]^+$  and  $[L^3Zn]^+$ fragments for the dithioacetate and thioacetamide ligands reveals them to be quite similar, both in energy and in composition. Fig. 8 shows a representation of these two orbitals. Indeed, both orbitals are predicted to have similar energies (E = -7.02 eV for  $[L^1Zn]^+$ ; E = -6.85 eV for  $[L^3Zn]^+$ ) Moreover, the LUFO for  $[L^1Zn]^+$ has 78% Zn character (42% Zn(4s) and 36% Zn(4p) character), while the LUFO for  $[L^3Zn]^+$  has 79% Zn character (42% Zn(4s) and 37% Zn(4p) character). The remaining composition of both LUFOs results mostly from contributions from the sulfur atoms of the ligands. Because the orbital that dominates the Lewis acidic behavior of these  $[LZn]^+$  fragments is the LUFO, the similar energies and compositions of this orbital within the series of compounds likely helps to explain their very similar Lewis acidities, despite apparent differences in the two classes of ligands.

# 4. Conclusion

The present study has examined the coordination chemistry of sterically bulky bis(pyrazol-1-yl)dithioacetate and bis(pyrazol-1yl)thioacetamide ligands  $(L^1-L^4)$  with Zn(II) and Cd(II). For the LZnBr complexes 1-4, the solid state structures are mononuclear and the overall geometries of the complexes are distorted tetrahedral. DOSY NMR studies confirm the solution structures of 1-4 are mononuclear and correspond to the solid state structures. In contrast, the LCdCl complex 10, was determined to be a chloridebridged five-coordinate dimer. Despite the dinuclear structure of **10** in the solid state, cadmium chloride complexes **9–11** were each shown to be mononuclear in solution by DOSY NMR. In an effort to determine the electronic impact of the bis(pyrazol-1-yl)dithioacetate and bis(pyrazol-1-yl)thioacetamide ligands, computational studies were performed on LZnX complexes 1-4 (X = Br<sup>-</sup>) and 5-**8** ( $X = CN^{-}$ ). Based on natural population analysis, the amount of charge localization onto the zinc(II) center from ligands  $L^1-L^4$  are roughly equal, indicating a similar electronic impact from each of these ligands despite their structural and electronic differences. Moreover, examination of the LUFO of zinc fragments  $[L^1Zn]^+$  and [L<sup>3</sup>Zn]<sup>+</sup> revealed similar energies and compositions, consistent with zinc(II) centers having similar Lewis acidic properties despite differences in supporting ligand.

# Acknowledgements

This work was funded by a Mountain State Tumor Institute Small Project Grant and startup funds from Boise State University. J.T.Y. thanks Stetson University for partial financial support of this project. N.G.S. and M.S. were supported by a summer fellowship by NIH Grant #P20 RR0116454 from the INBRE Program of the National Center for Research Resources. We thank Dr. Atta M. Arif (University of Utah X-ray Crystallographic Facility) for assistance with X-ray crystallography and Dr. Greg Khitrov (University of California, Los Angeles Molecular Instrumentation Center) for assistance with mass spectrometry. NMR and FT-IR instrumentation was purchased through funds from NSF (CRIF/MU #0639251 and CCLI #0737128).

#### Appendix A. Supplementary material

CCDC 818529, 818530, 818531, 818532, 818533 and 818534 contain the supplementary crystallographic data for complexes **1**, **2**, **3**, **4**, **8** and **10**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.07.033.

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