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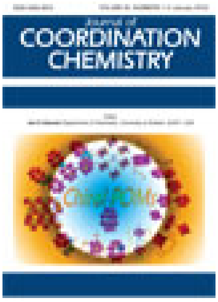

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Multidentate bis(pyrazolylmethyl)pyridine ligands: coordination chemistry and binding properties with zinc(II) and cadmium(II) cations

Stephen O. Ojwach [a] [b], George S. Nyamato [a], Benard Omondi [b], James Darkwa [b] & Alexander O. Okoth [a]

[a] Department of Chemistry, Maseno University, P.O. Box 333, Maseno 40105, Kenya

[b] Department of Chemistry, University of Johannesburg, Auckland Park Kingsway Campus, Auckland Park 2006, South Africa

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Multidentate bis(pyrazolylmethyl)pyridine ligands: coordination chemistry and binding properties with zinc(II) and cadmium(II) cations

STEPHEN O. OJWACH*†‡, GEORGE S. NYAMATO†, BENARD OMONDI**‡,
JAMES DARKWA‡ and ALEXANDER O. OKOTH†

†Department of Chemistry, Maseno University, P.O. Box 333, Maseno 40105, Kenya
‡Department of Chemistry, University of Johannesburg, Auckland Park Kingsway Campus,
Auckland Park 2006, South Africa

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The coordination chemistry and cationic binding properties of 2,6-bis(pyrazol-1-ylmethyl)pyridine (**L1**), 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L2**), and 2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (**L3**) with zinc(II) and cadmium(II) have been investigated. Reactions of **L2** with zinc(II) and cadmium(II) nitrate or chloride salts produced monometallic complexes $[Zn(NO_3)_2(\mathbf{L2})]$ (**1**), $[ZnCl_2(\mathbf{L2})]$ (**2**), $[Cd(NO_3)_2(\mathbf{L2})]$ (**3**), and $[CdCl_2(\mathbf{L2})]$ (**4**). Solid state structures of **1** and **3** confirmed that **L2** binds in a tridentate mode. While the nitrates in the zinc complex (**1**) adopt monodentate binding fashion, in cadmium complex (**3**), they exhibit bidentate mode. **L1**–**L3** show binding efficiencies of 99% for zinc(II), 60% for lead(II), and 30% for cadmium(II) cations from aqueous solutions of the metal ions. Theoretical studies using Density Functional Theory were consistent with the observed extraction results.

Keywords: Pyrazolyl ligands; Zinc and cadmium; Structures; Metal extractions; DFT calculations

1. Introduction

The diverse nature of transition metal coordination chemistry has led to interesting avenues for the design and development of novel ligands with unique structures and functional characteristics [1–4]. Significant efforts are being directed towards the design of specific ligand architecture in synthetic and applied chemistry [5]. One such area is study of the coordination chemistry of zinc, cadmium, mercury, and lead in attempts to design specific ligands that can selectively bind these metals [6–8].

Recently, coordination chemistry of zinc(II) and cadmium(II) has received attention due to their significance and impact on the environment and human body [9, 10]. The coordination chemistry of cadmium is very similar to that of zinc, since both have

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*Corresponding author. Email: sojwach@gmail.com
**Current address: Department of Chemistry, University of KwaZulu Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa.

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similar electronic configuration; the toxicity of cadmium(II) is associated with its competition with zinc for a variety of important binding sites in cells [11]. Therefore, comparative investigation of the coordination chemistry of zinc(II) and cadmium(II) with various ligands is crucial to handle cadmium toxicity and zinc availability in living systems. In this article, we discuss the coordination chemistry of 2,6-bis(pyrazol-1-ylmethyl)pyridine zinc(II) and cadmium(II) complexes. These pyrazolyl ligands have also been used as model chelating agents to remove zinc(II), cadmium(II), and lead(II) from water. Theoretical calculations using Density Functional Theory in addition to structural studies have been used to probe the metal–ligand interactions.

2. Experimental

2.1. *General materials and methods*

2,6-Bis(pyrazol-1-ylmethyl)pyridine (**L1**), 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L2**), and 2,6-bis(3,5-di-tertbutylpyrazol-1-ylmethyl)pyridine (**L3**) were prepared following the literature methods [12, 13]. All solvents and chemicals were obtained from Sigma-Aldrich and used as received. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker instrument at room temperature in $CDCl_3$ at the University of Johannesburg (^1H at 400 MHz) and on a Varian instrument at the University of Nairobi (^1H at 200 MHz). Chemical shifts are reported in δ (ppm) and coupling constants are measured in Hertz (Hz). Elemental analyses were performed on a Vario Elementar III microbe CHN analyzer at the Department of Chemistry, Rhodes University, South Africa. Metal concentrations were measured using Atomic Absorption Spectrophotometry on a Shimadzu AAS 6200 at the Department of Chemistry, Maseno University, Kenya.

2.2. *Synthesis of zinc(II) and cadmium(II) complexes*

2.2.1. Dinitro{2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine}zinc(II) (1). To a solution of 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L2**) (0.10 g, 0.34 m mol) in methanol (10 mL), a solution of $Zn(NO_3)_2 \cdot 4H_2O$ (0.10 g, 0.34 m mol) in methanol (10 mL) was added. The clear solution was stirred for 16 h and the solvent was removed under vacuum to afford an off-white solid. Recrystallization from CH_2Cl_2 afforded single-crystals suitable for X-ray analysis. Yield: 0.10 g (60%). ^1H NMR: (400 MHz, $CDCl_3$): δ 2.31 (s, 6H, CH_3, pz); 2.35 (s, 6H, CH_3, pz); 5.51 (s, 4H, CH_2); 5.84 (s, 2H, pz); 7.45 (d, 2H, py, $^3J_{HH} = 7.6$ Hz); 7.86 (t, 2H, py, $^3J_{HH} = 8.0$ Hz). Anal. Calcd for $C_{17}H_{21}ZnN_7O_6$: C, 42.12; H, 4.30; N, 20.22. Found: C, 42.50; H, 4.12; N, 20.10.

2.2.2. Dichloro{2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine}zinc(II) (2). To a solution of 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (0.10 g, 0.34 m mol) in methanol (10 mL), a solution of $ZnCl_2$ (0.05 g, 0.34 m mol) in methanol (10 mL) was added to form a white precipitate. The mixture was stirred for 18 h and filtered to give a white compound. The crude product was recrystallized from CH_2Cl_2 to give **2** as an analytically pure compound. Yield: 0.09 g (59%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.31 (s, 6H, CH_3, pz); 2.44 (s, 6H, CH_3, pz); 5.52 (s, 4H, CH_2); 5.78 (s, 2H, pz); 7.44 (d, 2H, py, $^3J_{HH} = 7.6$ Hz); 7.96 (t, 2H, py, $^3J_{HH} = 7.6$ Hz). Anal. Calcd for $C_{17}H_{21}ZnN_5Cl_2$: C, 47.30; H, 4.90; N, 16.22. Found: C, 47.65; H, 5.15; N, 16.55.

2.2.3. Dinitro{2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine}cadmium(II) (3). To a solution of 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (0.20 g, 0.68 mmol) in methanol (10 mL), a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.21 g, 0.68 m mol) in methanol (10 mL) was added. The resultant white suspension was stirred for 6 h to give a white precipitate. The precipitate was filtered, washed with methanol (10 mL), and dried. Recrystallization from CH_2Cl_2 at room temperature afforded single-crystals suitable for X-ray analysis. Yield: 0.21 g (58%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.33 (s, 6H, CH_3, pz); 2.39 (s, 6H, CH_3, pz); 5.41 (s, 4H, CH_2); 5.94 (s, 2H, pz); 7.47 (d, 2H, py, $^3J_{HH} = 7.6$ Hz); 7.96 (t, 2 H, py, $^3J_{HH} = 8.0$ Hz). Anal. Calcd for $C_{17}H_{21}CdN_7O_6$: C, 38.39; H, 3.98; N, 18.44. Found: C, 38.73; H, 3.88; N, 18.13.

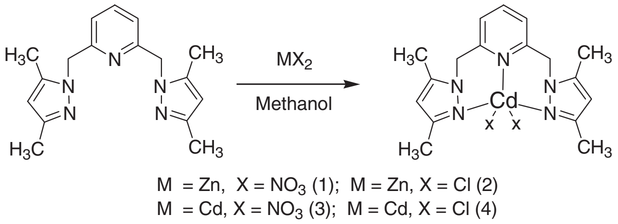
2.2.4. Dichloro{2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine}cadmium(II) (4). To a solution of 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (0.10 g, 0.34 m mol) in methanol (10 mL), a solution of $CdCl_2$ (0.07 g, 0.34 m mol) in methanol (10 mL) was added. The resultant mixture was stirred for 18 h to give a white precipitate, which was filtered and washed with methanol to give **4** as a pure white solid. Yield: 0.10 g (61%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.30 (s, 6H, CH_3, pz); 2.54 (s, 6H, CH_3, pz); 5.62 (s, 4H, CH_2); 5.85 (s, 2H, pz); 7.44 (d, 2H, py, $^3J_{HH} = 7.6$ Hz); 7.91 (t, 2H, py, $^3J_{HH} = 8.0$ Hz). Anal. Calcd for $C_{17}H_{21}CdN_5Cl_2$: C, 42.65; H, 4.42; N, 14.63. Found: C, 42.25; H, 4.15; N, 14.95.

2.3. *X-ray crystallography*

Crystal evaluation and data collection were performed on a Bruker APEXII diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) radiation and a diffractometer to a crystal distance of 4.00 cm at 100(1)K. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite [14]. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. A successful solution by the direct methods of SHELXS-97 [15] provided all non-hydrogen atoms from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement coefficients.

2.4. *Extraction of metal ions*

Extractions of metal ions were performed using metal nitrate salts dissolved in distilled water to give concentrations of 1000 ppm. The organic phase was prepared by dissolving an equivalent amount of the appropriate ligand in dichloromethane. Solvent extractions were carried out by shaking equal volumes of the aqueous metal solution and the organic ligand in dichloromethane for 2 h. Temperature was maintained constant at 25°C in all experiments and at pH of 7.00. The aqueous phase was then separated, appropriately diluted and extraction efficiency of each ligand determined



Scheme 1. Synthesis of the pyrazolyl zinc(II) and cadmium(II) metal complexes.

from the decrease of metal ion concentration in the aqueous phase by atomic absorption spectrometry.

2.5. *Molecular modeling*

Molecular modeling experiments were performed using Gaussian03 [16]. Geometry and energies of the reactants and products were computed using hybrid density functional theory at the B3LYP/LANL2DZ level of theory. All calculations were performed using restricted Hartree–Fock approximations and all structures were optimized without symmetry constraints. The basis set LANL2DZ was used as a standard basis set and was not augmented. The enthalpies of formation of the complexes were computed by calculating the enthalpies of formation of the respective metal chloride salts and **L1**. The smaller metal chloride salts and **L1** were chosen for better accuracy and shorter calculation times.

3. Results and discussion

3.1. *Synthesis and molecular structures of zinc(II) and cadmium(II) complexes*

Reactions of **L2** with either $Zn(NO_3)_2$ or $Cd(NO_3)_2$ in a 1 : 1 mole ratio resulted in formation of the corresponding **1**–**4** (scheme 1). The complexes were isolated as white solids in moderate to good yields (50–75%).

^{1}H NMR spectra of all the complexes were used as evidence of ligand coordination by comparing the signature peaks in the free ligands and the respective metal complexes. For instance, in **1**, the CH_2 linker protons were observed as a singlet at 5.41 ppm compared to 5.30 ppm in **L2**. Similarly, methyl peaks at 2.33 and 2.39 ppm in **1** were downfield relative to 2.16 and 2.24 ppm in **L2**. The cadmium complexes, **3** and **4**, also displayed similar downfield shifts of the signals in comparison to **L2**. Microanalyses data of all the complexes were consistent with the proposed structural formulae in scheme 1.

The structures of **1**–**4** were confirmed from single-crystal X-ray analyses of **1** and **3**. Crystallographic data and structure refinement parameters of **1** and **3** are given in table 1, while selected bond lengths and angles are listed in table 2. Molecular structures

Table 1. Crystal data and structure refinement for **1** and **3**.

Parameter	**1**	**3**
Empirical formula	$C_{17}H_{21}N_7O_6Zn$	$C_{17}H_{21}CdN_7O_6$
Formula weight	484.78	531.81
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*P2₁/c*
Unit cell dimensions (Å, °)		
a	17.215(3)	14.967(5)
b	10.3340(17)	8.803(5)
c	11.5280(19)	17.490(4)
α	90	90
β	106.607(4)	115.37(2)
γ	90	90
Volume (Å^3), *Z*	1965.3(6), 4	2082.1(15), 4
Calculated density (Mg m^{-3})	1.638	1.696
Absorption coefficient (mm^{-1})	1.303	1.099
F(000)	1000	1072
Reflections collected	20,309	51,226
Completeness to θ (%)	99.6	99.8
Goodness-of-fit on F^2	1.081	1.126
Largest difference peak and hole (e Å^{-3})	0.393 and −0.235	1.482 and −1.147

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **3**.

1			
N(1)–Zn(1)	2.0837(12)	N(1)–Zn(1)–O(1)	90.05(5)
N(3)–Zn(1)	2.1795(16)	N(3)–Zn(1)–O(1)	91.33(3)
O(1)–Zn(1)	2.2072(12)	N(1)–Zn(1)–O(1)#1	89.96(5)
		N(3)–Zn(1)–O(1)#1	91.33(3)
		O(1)–Zn(1)–O(1)#1	177.35(7)
3			
Cd(1)–N(5)	2.2789(18)	N(5)–Cd(1)–N(1)	160.26(6)
Cd(1)–N(1)	2.2815(18)	N(5)–Cd(1)–O(2)	90.58(6)
Cd(1)–O(2)	2.3346(17)	N(1)–Cd(1)–O(2)	103.75(6)
Cd(1)–N(3)	2.4100(16)	N(5)–Cd(1)–N(3)	79.20(6)
Cd(1)–O(4)	2.4413(16)	O(4)–Cd(1)–O(5)	52.58(5)
Cd(1)–O(5)	2.4463(14)	O(2)–Cd(1)–N(3)	141.02(5)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, y, $-z+1/2$.

of **1** and **3** are shown in figures 1 and 2, respectively. The solid state structures of **1** and **3** are monometallic containing one metal per one ligand. The ligand **L2** coordinates tridentate to both zinc and cadmium in **1** and **3**. In addition, **L2** exhibits meridional coordination to both zinc(II) and cadmium(II), attributed to the symmetrical nature of **L2**. In **1**, both nitrates are monodentate giving a distorted square pyramidal geometry around zinc (figure 1). The two pyrazolyl nitrogen atoms and two coordinated oxygen atoms of the nitrate ligand occupy the basal plane with the pyridine nitrogen atom residing on the axial position. Complex **1** is symmetrical with C9, N_{py}, and Zn constituting the mirror plane. The N(3)–Zn–O(1) and O(1)–Zn–O(1)#1 bond angles of 91.33(13)° and 177.35(7)° , respectively, slightly deviate from 90° or 180° presumably due to restrictions imposed by **L2**. The flexibility of the monodentate nitrates could be

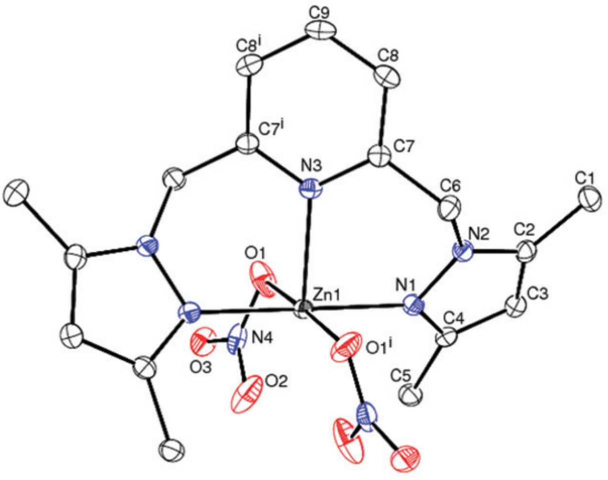


Figure 1. Molecular structure of **1** shown with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

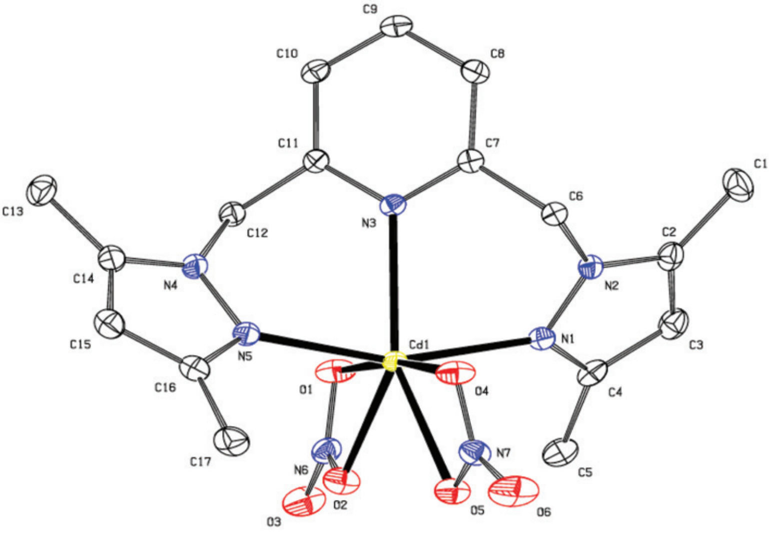


Figure 2. Molecular structure of **3** shown with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

responsible for the near perfect square base (N(1)–Zn–O(1) bond angle of 90.05(5)°). The Zn–N_{pz} bond distance of 2.0837(12) Å and Zn–$O_{nitrate}$ average bond lengths of 2.2072(12) Å are close to those found in the literature [16–18]. In **3**, both nitrates are bidentate. The geometry around cadmium in **3** can thus be described as distorted capped octahedral (figure 2). The pyridine nitrogen is directly above the cadmium. The bond angles of 79.20(6)° to 160.26(6)° around the cadmium atom in **3** appreciably

Table 3. Liquid–liquid extraction of zinc(II), lead(II), and cadmium(II) by **L1**–**L3**.[a]

Entry	Ligand	Metal ion	Final conc. (ppm)[b]	% Extraction
1	**L1**	Zn	10	99
2	**L2**	Zn	20	98
3	**L3**	Zn	400	60
4	**L1**	Pb	340	66
5	**L2**	Pb	390	61
6	**L3**	Pb	800	20
7	**L1**	Cd	690	31
8	**L2**	Cd	730	27
9	**L3**	Cd	850	15

[a](M : L = 1 : 1), time of mixing, 2 h, original concentration of metal solution, 1000 ppm. Solvent system, dichloromethane (20 mL) and water (20 mL).
[b]Determined by AAS.

deviate from 72° and 180° expected for a seven-coordinate geometry, a result induced by steric restrictions from tridentate **L2**. The bite angle between the cadmium and the coordinated nitrate oxygen atoms of 52.58(6)° for O(4)–Zn–O(5) is slightly smaller than the range of 56.57(6)° to 57.05(13)° reported for the related complexes [17–19]. The average Cd–N_{pz} bond distances of 2.2802(16) Å in **3** compares well with Cd–N_{pz} distances of 2.3111(19) Å reported for $[CdCl_2(L)]$ (L = 1,8-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-3,6-dioxaoctane) [18]. Similarly, the Cd–N_{py} bond distance of 2.4100(16) Å in **3** is consistent with the Cd–N_{py} of 2.363(4) Å obtained for $[Cd(NO_3)_2(C_5H_4NCOOEt)_2]$ [11]. The average Cd–$O_{nitrate}$ bond distance of 2.4074(16) Å in **3** correlates well with those found in the literature [11, 16–18]. The five-coordinate and seven-coordinate geometries in **1** and **3**, respectively, demonstrate cadmium's preference to higher coordination numbers than zinc, attributed to the larger size of cadmium(II) (1.71 Å) compared to zinc(II) (1.38 Å) [20].

3.2. *Extraction of zinc(II), cadmium(II), and lead(II) metals*

The isolation of stable zinc(II) and cadmium(II) complexes of 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L2**) was utilized to investigate the capacity of the pyrazolyl compounds (**L1**–**L3**) to remove zinc(II), lead(II), and cadmium(II) cations from water by liquid–liquid extraction using dichloromethane as the organic solvent (table 3). All the ligands showed highest affinity towards zinc(II), moderate binding capacities for lead(II) but low extraction efficiencies for cadmium(II). For example, extraction efficiencies of 98%, 66%, and 31% were observed for zinc(II), lead(II), and cadmium(II) by **L1**, respectively. This trend can be explained using the Hard–Soft Acid–Base (HASB) theory [21–23]. Zinc(II) is a moderately hard acid compared to lead, while cadmium is a soft acid. The preference to zinc(II) by **L1**–**L3** thus indicated that **L1**–**L3** are moderately hard bases. It is thus conceivable that the soft-base pyridine linker in these pyrazolyl ligands results in moderation of the donor abilities of the ligands. In a similar work using tripodal N-donor pyrazole ligands, extraction capacities of 64% and 5% for lead(II) and cadmium(II), respectively, were observed [24], consistent with the binding capacities for **L1** of 66% for lead(II) and 31% for cadmium(II).

Table 4. Enthalpies and Gibbs free energies of coordination by **L1**.

Metal ion	$\Delta H^{a}_{\text{coordination}}$	$\Delta G^{a}_{\text{coordination}}$	% Extraction[b]
Zn	−116.75	−101.23	99
Cd	−107.24	−92.89	31
Pb	−109.25	−97.72	66

[a]Determined by calculation of the respective energies of **L1**, metal dichloride salts, and the complexes using DFT at the B3LYP/LANL2DZ level of theory (kcal mol^{-1}). [b]Determined by liquid–liquid extraction of metal ions using **L1** : M ratio of 1 : 1; water/CH_2Cl_2 system, time, 2 h of mixing.

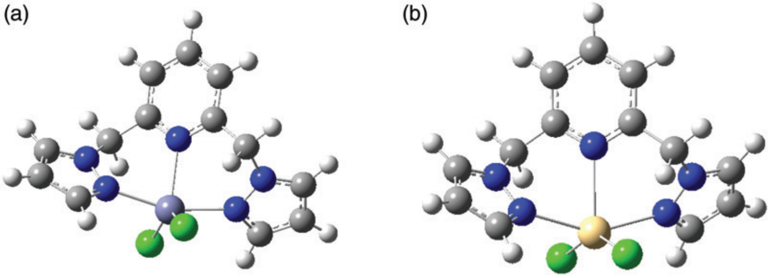


Figure 3. Optimized structures from DFT calculations of [Zn(**L1**)Cl_2)] (a) and [Cd(**L1**)Cl_2] (b).

The influence of the alkyl substituent on the pyrazolyl unit was investigated by comparing the binding affinities of **L1** (R = H), **L2** (R = Me), and **L3** (R = ^{t}Bu). While **L1** and **L2** gave extraction efficiencies of 99% and 98%, respectively, for zinc(II), **L3** gave a relatively lower percentage of 60% (table 3, entries 1–3). A similar trend was observed for lead(II) and cadmium(II). This behavior can be ascribed to two reasons; steric effect and aqueous solubility of **L1–L3**. **L1** and **L2** are sterically less demanding than **L3**, making it easier for metal ions to access **L1** and **L2** than **L3**. The ease of coordination of **L1** and **L2** enhances their binding affinities and thus greater extraction efficiencies are observed. We recently demonstrated that increased steric hindrance lowers the stability of the resultant metal complexes [12]. It is therefore conceivable that the lower extraction ability of **L3** could result from reduced formation constant of its metal complexes. In addition, reduced solubility of **L3** in aqueous media could lower its diffusion into the aqueous phase prior to the formation of the metal complexes.

3.3. *Density functional theory studies*

Theoretical calculations were used to corroborate the varied binding capacities towards zinc(II), cadmium(II), and lead(II) by **L1**–**L3**. Metal chloride salts and **L1** were used in the Density Functional Theory calculations due to their small sizes, hence shorter calculation times and better accuracy. Table 4 gives the energies of coordination of the complexes, while figure 3 shows the optimized structures of [Zn(**L1**)Cl_2] and [Cd(**L1**)Cl_2]. The negative values of ΔG clearly indicate that the reactions are spontaneous (table 4) and therefore support the formation of stable complexes between **L1** and **L2** with zinc(II) and cadmium(II) metals. The reaction between $ZnCl_2$ and **L1** gave the lowest coordination barriers ($\Delta H = -87\,\text{kcal mol}^{-1}$ and $\Delta G = -75.03\,\text{kcal mol}^{-1}$) while the reaction of $CdCl_2$ with **L1** gave the highest coordination energy barriers ($\Delta H = -76.02\,\text{kcal mol}^{-1}$ and $\Delta G = -64.02\,\text{kcal mol}^{-1}$). This trend is consistent with the observed extraction results where **L1** showed highest affinity for zinc(II) of 99% and lowest extraction efficiency of cadmium(II) of 31%. The DFT results further supported the significance of the soft–hard acid–base interactions during the extraction process.

4. Conclusions

We have demonstrated that bis(pyrazolylmethyl)pyridine ligands form stable complexes with zinc(II) and cadmium(II). **L2** is tridentate in both zinc(II) and cadmium(II); nitrate displays monodentate binding to zinc in **1**, but coordinates bidentately to cadmium in **3**. The bis(pyrazolylmethyl)pyridine ligands show potential as chelating agents for removal of zinc(II), lead(II), and cadmium(II) from water with high preference to zinc(II). Density Functional Theoretical calculations can be used to study the ligand–metal interactions and development of selective chelating agents.

Supplementary material

CCDC numbers; 828072 and 828070, contain the supplementary crystallographic data for **1** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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