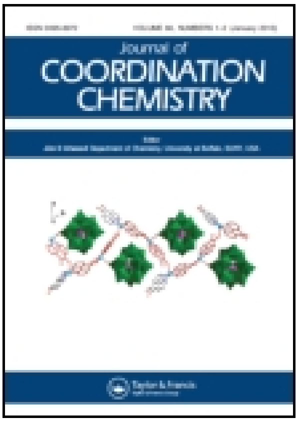
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:53
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Coordination behavior and binding properties of (3,5-dimethyl-1H-pyrazol-1-yl)ethanol with Cu(II), Zn(II), Cd(II), and Pb(II) metals

Martha W. Njoroge [a] , Stephen O. Ojwach [b] , George S. Nyamato [b] , Bernard Omondi [c] & James Darkwa [d]
[a] Department of Chemistry , Maseno University , Maseno , Kenya
[b] School of Chemistry and Physics, University of KwaZulu-Natal , Scottsville , South Africa
[c] School of Chemistry and Physics, University of KwaZulu-Natal , Durban , South Africa
[d] Department of Chemistry , University of Johannesburg , Auckland Park , South Africa

Accepted author version posted online: 18 Mar 2013.Published online: 29 Apr 2013.

To cite this article: Martha W. Njoroge , Stephen O. Ojwach , George S. Nyamato , Bernard Omondi & James Darkwa (2013) Coordination behavior and binding properties of (3,5-dimethyl-1H-pyrazol-1-yl)ethanol with Cu(II), Zn(II), Cd(II), and Pb(II) metals, Journal of Coordination Chemistry, 66:9, 1626-1634, DOI: 10.1080/00958972.2013.784904

To link to this article: http://dx.doi.org/10.1080/00958972.2013.784904

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

Journal of Coordination Chemistry, 2013
Vol. 66, No. 9, 1626–1634, http://dx.doi.org/10.1080/00958972.2013.784904

Coordination behavior and binding properties of (3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol with Cu(II), Zn(II), Cd(II), and Pb(II) metals

MARTHA W. NJOROGE†, STEPHEN O. OJWACH*‡, GEORGE S. NYAMATO‡,
BERNARD OMONDI§ and JAMES DARKWA¶

†Department of Chemistry, Maseno University, Maseno, Kenya
‡School of Chemistry and Physics, University of KwaZulu-Natal, Scottsville, South Africa
§School of Chemistry and Physics, University of KwaZulu-Natal, Durban, South Africa
¶Department of Chemistry, University of Johannesburg, Auckland Park, South Africa

(*Received 22 November 2012; in final form 22 January 2013*)

The coordination chemistry and binding properties of (3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol (**L1**) with Cu(II), Zn(II), Cd(II), and Pb(II) have been investigated. Reactions of **L1** with Zn(II) and Cd (II) nitrate or chloride salts produced the corresponding monometallic and bimetallic complexes [Zn(NO_3)$_2$(**L1**)] (**1**), [ZnCl_2(**L1**)] (**2**), [Cd(NO_3)$_2$(**L1**)$_2$] (**3**) and [Cd_2Cl_2(μ-Cl_2)(**L1**)$_2$] (**4**). Solid-state structures of **3** and **4** confirmed the bidentate coordination mode of **L1**. The extraction efficiency of the metals by **L1** is dependent upon the size and electronic properties of the metal. Binding affinities of 92% for Cu(II), 90% for Zn(II), 70% for Pb(II), and 61% for Cd(II) were observed.

Keywords: Pyrazolyl ligands; Transition metals; Structures; Extractions

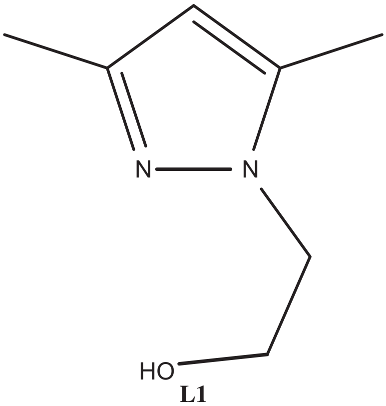
1. Introduction

The interaction between metal cations and biological systems is dependent upon interrelationships encompassing physical, chemical, biological, and pharmacological factors [1–5]. One or more of these factors may influence the outcome of the metal–biological interaction. For example, while Zn(II) is an essential element for living organisms [6], Cd(II) is highly toxic [7]. To understand these diverse interactions between metals and biological systems, the study of coordination chemistry of metals and biologically relevant ligands is important. This has led to the design of ligands with unique structures and functional characteristics [8–10]. Coordination chemistry of heavy metals, such as Zn(II), Cd(II), Hg(II), and Pb(II), is important for the design of ligands that can selectively bind these metals to mimic biological enzymes or avert their toxicity [10–12].

In particular, coordination chemistry of Zn(II) and Cd(II) has received considerable attention due to their significance and impact on the environment and human body [13]. The coordination chemistry of Cd(II) is very similar to that of Zn(II) and the toxic effect of Cd(II) is associated with its competition with Zn(II) for a variety of important binding sites in cells

---

*Corresponding author. Email: ojwach@ukzn.ac.za such as gene regulation [14]. Therefore, comparative investigation of the coordination chemistry of Zn(II) and Cd(II) with various ligands is significant in order to regulate cadmium toxicity and zinc availability in living systems. We recently reported the coordination chemistry of (pyrazol-1-ylmethyl)pyridine ligands and their ability to selectively bind Zn(II) and Cd(II) from aqueous solutions [15, 16]. As a continuation of our contribution to this research, we now report coordination chemistry of Zn(II) and Cd(II) with (3,5-dimethyl-*1H*-pyrazol-1-yl) ethanol (**L1**). **L1** has been shown to efficiently remove Cu(II), Zn(II), Cd(II), and Pb(II) from aqueous solutions.



L1

2. Materials and methods

The ligand (3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol (**L1**) was prepared according to the literature procedures [17]. 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). 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 Atomic Absorption Spectrometry (AAS) 6200 at the Department of Chemistry, Maseno University, Kenya.

2.1. *Synthesis of Zn(II) and Cd(II) complexes*

2.1.1. Synthesis of dinitro[2-(3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol]zinc(II) (1). To a solution of (3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol, **L1** (0.10 g, 0.71 mmol), in methanol (10 mL), a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (0.21 g, 0.71 mmol) in methanol (10 mL) was added. The clear solution was stirred for 4 h, filtered after the reaction period and solvent removed under reduced pressure. Recrystallization of the crude product from dichloromethane-hexane mixture afforded **1** as an analytically pure white solid. Yield = 0.24 g (72%). ^1H NMR: (400 MHz, $CDCl_3$): δ, 2.11 (s, 3H, CH_3, pz); 2.30 (s, 3H, CH_3, pz); 4.11 (t, 2H, CH_2, $^2J_{HH} = 4.8$ Hz); 4.35 (t, 2H, CH_2, $^2J_{HH} = 4.4$ Hz); 5.98 (s, 1H, pz). Anal. Calcd for $C_7H_{12}N_4O_7Zn$: C, 25.51; H, 3.67; N, 17.00. Found: C, 25.01; H, 3.87; N, 17.32.

2.1.2. Synthesis of dichloro[2-(3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol]zinc(II) (2). To a solution of **L1** (0.10 g, 0.71 mmol) in methanol (10 mL), a solution of $ZnCl_2$ (0.10 g, 0.71 mmol) in methanol (10 mL) was added. The resultant clear solution was stirred for 2 h to give a clear solution. Slow evaporation of methanol solution gave the crude product which was recrystallized from hexane/CH_2Cl_2 to give **2** as an analytically pure white compound. Yield = 0.16 g (57%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ, 2.28 (s, 3H, CH_3, pz); 2.39 (s, 3H, CH_3, pz); 4.35 (t, 4H, CH_2, $^2J_{HH} = 4.8$ Hz); 5.99 (s, 1H, pz). Anal. Calcd for $C_7H_{12}Cl_2N_4OZn$: C, 30.41; H, 4.37; N, 10.13. Found: C, 30.65; H, 4.69; N, 10.12.

2.1.3. Synthesis of dinitro[2-(3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol]cadmium(II) (3). To a solution of **L1** (0.10 g, 0.71 mmol) in methanol (10 mL), a solution of Cd$(NO_3)_2 \cdot 4H_2O$ (0.22 g, 0.71 mmol) in methanol (10 mL) was added and the mixture was stirred for 6 h. Slow evaporation of the solution at room temperature afforded white single crystals suitable for X-ray analysis. Yield = 0.30 g (80%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.04 (s, 3H, CH_3, pz); 2.22 (s, 3H, CH_3, pz); 4.03 (t, 2H, CH_2, $^2J_{HH} = 5.2$ Hz); 4.24 (t, 2H, CH_2, $^2J_{HH} = 4.0$ Hz); 5.87 (s, 1H, pz). Anal. Calcd for $C_{14}H_{24}N_6O_8Cd$: C, 32.54; H, 4.68; N, 16.24. Found: C, 32.66; H, 4.41; N, 16.19.

2.1.4. Synthesis of dichloro-μ-dichlorobis[2-(3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol]dicadmium (II) (4). To a solution of **L1** (0.10 g, 0.71 mmol) in methanol (10 mL), a solution of $CdCl_2 \cdot H_2O$ (0.14 g, 0.71 mmol) in methanol (10 mL) was added. The resultant mixture was stirred for 2 h to give a clear solution and then stored to allow slow evaporation of the methanol affording white single crystals suitable for X-ray analysis. Yield: 0.21 g (68%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.01 (s, 3H, CH_3, pz); 2.12 (s, 3H, CH_3, pz); 3.98 (t, 2H, CH_2, $^2J_{HH} = 4.8$ Hz); 4.25 (t, 2H, CH_2, $^2J_{HH} = 4.4$ Hz); 5.84 (s, 1H, pz). Anal. Calcd. for $C_{14}H_{24}Cl_4N_4O_2Cd_2$: C, 25.99; H, 3.74; N, 8.66. Found: C, 26.18; H, 3.92; N, 8.42.

2.2. *X-ray crystallography*

The crystal evaluation and data collection were performed on a Bruker APEXII diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation and diffractometer to crystal distance of 4.00 cm [18a] at 100(1) K. The reflections were indexed by an automated indexing routine built in the APEXII program suite [18b]. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [19a]. A successful solution by direct methods of SHELXS97 [19b] provided all non-hydrogen atoms from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement coefficients.

2.3. *Extraction of metal ions*

Extractions of metal ions were performed using metal nitrate salts dissolved in distilled water at 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 ligand in dichloromethane for 2 h. Temperature was maintained constant at 25 °C in all experiments at pH of 7. The aqueous phase was then separated, appropriately diluted and extraction efficiency of each ligand determined from the decrease of metal ion concentration in the aqueous phase by AAS.

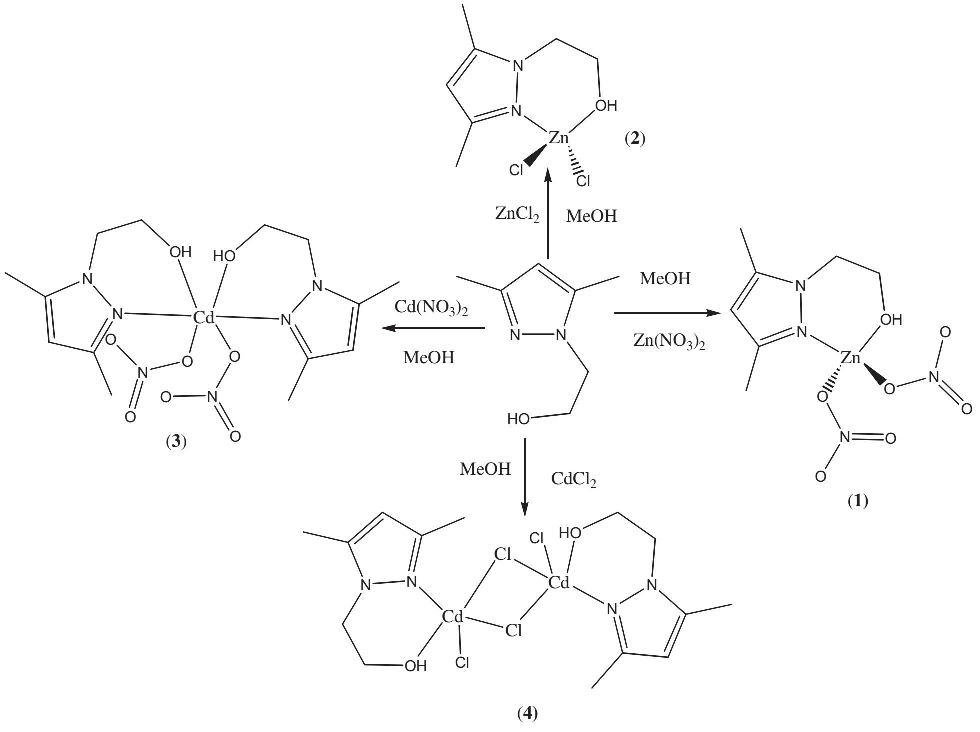
3. Results and discussion

3.1. *Synthesis and molecular structures of (3,5-dimethyl-1H*-pyrazol-1-yl)*ethanol zinc (II) and Cadmium(II)*

Reactions of (3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol (**L1**) with Zn(II) or Cd(II) salts in a 1 : 1 mol ratio resulted in formation of [Zn(NO_3)$_2$(**L1**)] (**1**), [ZnCl_2(**L1**)] (**2**), [Cd (NO_3)$_2$(**L1**)$_2$] (**3**) and [Cd_2Cl_2(μ-Cl_2)(**L1**)$_2$] (**4**).

^{1}H NMR spectra of the complexes were used as preliminary evidence of ligand coordination, by comparing signature peaks in the free ligands and the corresponding complexes. For example, while the ^{1}H NMR spectrum of **L1** gave signature peaks of the two methyl groups of the pyrazolyl ring close to each other at 2.20 and 2.22 ppm, the spectrum of **1** showed a larger separation of these two signals at 2.11 and 2.30 ppm. Most notable was the appearance of the ethylene linker protons as a triplet at 4.35 ppm in **3** as opposed to two triplets at 3.97 and 4.04 ppm in **L1**. Microanalyses of all the complexes were consistent with the proposed structures shown in Scheme 1.

Single crystals suitable for X-ray analysis of **3** and **4** were grown by slow evaporation of methanol solutions and were used to determine their solid-state structures. Crystallographic data and structural refinement parameters of **3** and **4** are given in table 1 while



Scheme 1. The complexes were isolated as white solids in moderate to high yields (57–80%).

Table 1. Crystal data and structure refinement for **3** and **4**.

Parameters	**3**	**4**
Empirical formula	$C_{14}H_{24}CdN_6O_8$	$C_{14}H_{24}Cd_2Cl_4N_4O_2$
Formula weight	516.79	646.97
Temperature (*K*)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
a/Å	9.094(5)	8.3816(7)
b/Å	15.783(5)	8.4192(7)
c/Å	13.731(5)	8.8866(8)
α/°	90	73.070(2)
β/°	102.693(5)	81.910(2)
γ/°	90	65.564(1)
Volume (Å^3)	1922.7(14)	546.03(8)
Z	4	1
Density calcd. (mg/m^3)	1.785	1.968
Absorption coefficient (mm^{-1})	1.193	2.452
F(0 0 0)	1048	316
Reflections collected	21,921	13,350
Completeness to theta	99.4%	99.9%
Goodness-of-fit on F^2	1.051	1.030
Largest diff. peak and hole (e Å^{-3})	0.426 and −0.586	0.629 and −0.592

selected bond lengths and angles are listed in table 2. The solid state structures of **3** and **4** are shown in figures 1 and 2, respectively. Attempts to grow single crystals of **1** and **2** were unsuccessful, hence, their structures were deduced by comparison with the zinc dichloride structure obtained for a similar ligand, (3,5-diphenyl-*1H*-pyrazol-1-yl)ethanol, reported by Pons *et al.* [20].

The solid-state structure of **3** is monometallic with two **L1** units acting as N^O chelates, while the two nitrates are monodentate to give six-coordinate cadmium. Complex **4** is bimetallic, containing an N^O chelate **L1**, one terminal and one bridging chloride per cadmium to give five-coordination. The solid structure of a related zinc dichloride complex of (3,5-diphenyl-*1H*-pyrazolyl)ethanol is tetrahedral containing one bidentate ligand and two terminal chlorides [20]. The five-coordinate **4** could be attributed to the larger ionic radius of Cd(II) compared with Zn(II), thus bridging chlorides are necessary to stabilize the Cd(II) complex. We recently reported that **L1** adopts monodentate and bidentate coordination to palladium and nickel, respectively [21]. Similar structures have been reported

Table 2. Selected bond lengths (Å) and angles (°) for **3** and **4**.

Bond lengths (Å)		Angles (°)	
3			
Cd(1)–N(1)	2.2836(14)	N(1)–Cd(1)–O(1)	76.59(3)
Cd(1)–O(3)	2.3510(10)	N(1)–Cd(1)–O(3)	92.69(4)
Cd(1)–O(1)	2.4115(10)	O(1)–Cd(1)–O(3)	167.62(3)
N(5)–O(3)	1.2712(13)	N(1)–Cd(1)–N(1a)	172.10(5)
4			
Cd(1)–N(2)	2.2311(12)	N(2)–Cd(1)–Cl(1)	125.90(3)
Cd(1)–O(1)	2.4101(11)	O(1)–Cd(1)–Cl(1)	89.31(3)
Cd(1)–Cl(1)	2.4356(4)	Cl(1)–Cd(1)–Cl(2)	94.554(13)
Cd(1)–Cl(2)	2.6329(4)	O(1)–Cd(1)–Cl(2)	175.14(3)

for the Pd(II) and Ni(II) complexes of a related (3,5-diphenyl-*1H*-pyrazolyl)ethanol ligand [20]. This behavior was assigned to the soft palladium which does not favor bonding to oxygen. Ni(II) is a harder metal and favors coordination to the harder oxygen [22]. **L1** was thus expected to coordinate in a monodentate mode to Cd(II) via the pyrazolyl nitrogen; the structures of **3** and **4** contradict this hypothesis. This could be attributed to the larger ionic size of Cd(II), which prefers higher coordination numbers, hence the bidentate nature of **L1** in **3** and **4**. Another interesting feature observed in the solid-state structure of **3** is the monodentate coordination of the two nitrates. Nitrate exhibits variable coordination to transition metals of monodentate, bidentate, or anisodentate [23]. We recently reported variable coordination behavior of NO_3^- in 2-(pyrazolylmethyl)pyridine Zn(II) and Cd(II) complexes [16]. The unidentate NO_3^- in **3** could thus be ascribed to stronger coordination ability of the O–H in **L1** compared with oxygen donors in nitrate.

The bond angles around Cd(II) in **3** of 72.62° for O(3)–Cd1–O(3a) and 172.10° for N(1)–Cd1–N(1a) significantly deviate from the expected 90° and 180° for octahedral geometry. The geometry around Cd(II) in **3** could thus be described as distorted octahedral, imposed by steric interactions from chelating **L1** and flexibility of the ethylene bridges (figure 1). The geometry around Cd(II) in **4** may be described as a distorted square pyramid, where N2, O1, Cl2, and Cl2 occupy the basal plane, while the terminal Cl1 occupies the axial position. The bond angles in 4 of 89.31(3)° for O(1)–Cd1–Cl(1) and 94.554(13)° for Cl(1)–Cd1–Cl2 deviate from 90° expected for square pyramidal geometry. This slight distortion in **4** could be assigned to reduced steric restrictions around cadmium in **4** compared with **3**, which contains two **L1** units and two nitrates per Cd(II).

The Cd–N$_{\mathbf{(L1)}}$ and Cd–O$_{\mathbf{(L1)}}$ bond distances of 2.2836(14) Å and 2.4115(10) Å in **3** are similar to bond distances of 2.2311(12) Å and 2.4101(2) Å in 4. This similarity attests to the lack of significant *trans*-effect of nitrate, **L1** and chloride. The average Cd–N$_{\mathbf{(L1)}}$ bond distances of 2.319(14) Å in **3** and **4** compares well with the average Cd–N$_{pz}$ bond distance of 2.290(19) Å obtained for five related pyrazolyl Cd(II) complexes [15, 16, 24]. The

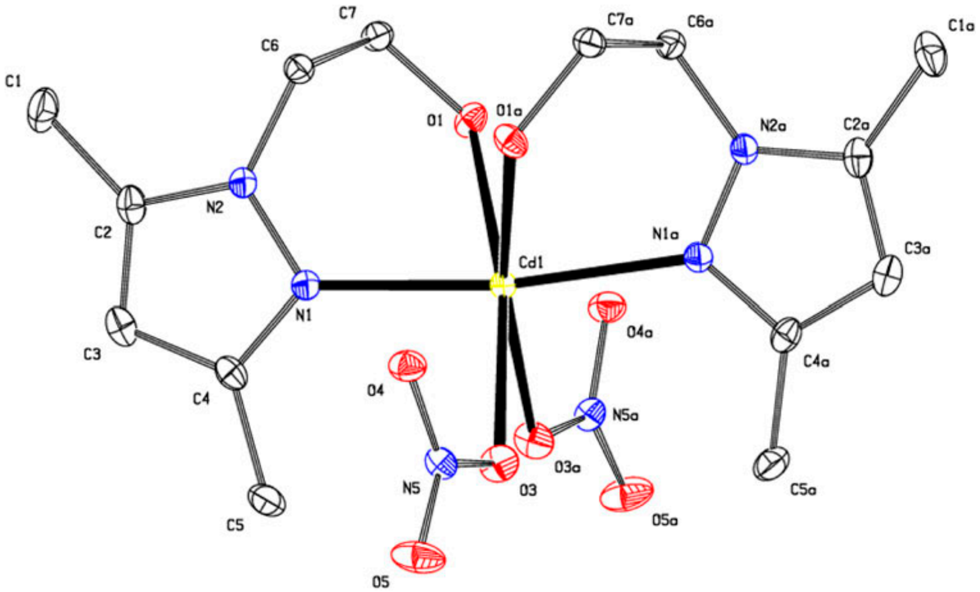


Figure 1. Molecular structure of **3** drawn with 50% probability. Hydrogens are omitted for clarity.

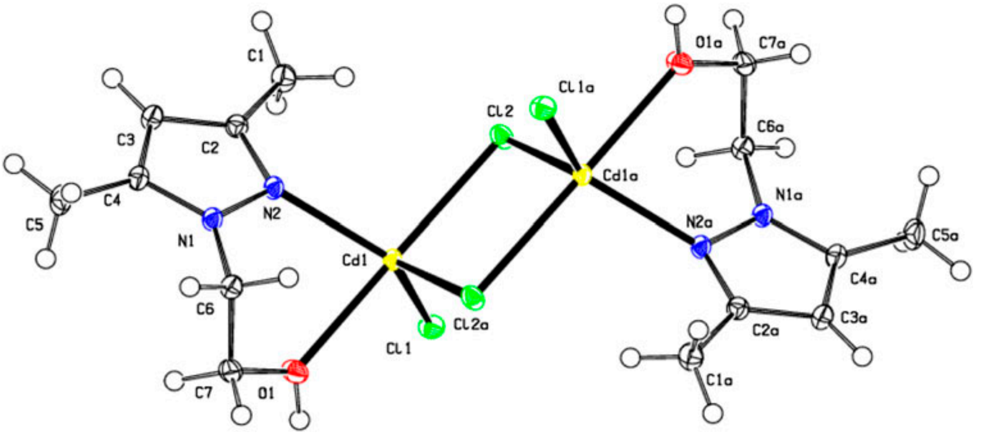


Figure 2. Molecular structure of **4** drawn with 50% probability.

Cd–$O_{nitrate}$ bond distance of 2.3510(10) Å in **3** is significantly shorter than the average bond distance of 2.4695(2) Å obtained for related complexes [15, 16, 25]. The shorter Cd–$O_{nitrate}$ bond distances in **3** may be attributed to the monodentate nitrate in **3** compared with varied coordination modes (monodentate, bidentate and anisodentate) displayed in the other complexes reported. As expected, the Cd–$Cl_{terminal}$ distance of 2.4356(4) Å is significantly shorter than the Cd–$Cl_{bridging}$ bond distance of 2.6329(4) Å in **4** and correlate well with those reported for related Cd(II) complexes [26].

3.2. *Liquid–liquid extraction of metal cations by (3,5-dimethyl-1H-*pyrazol-1-yl)*ethanol*

The ability of (3,5-dimethylpyrazol-1-yl)ethanol (**L1**) to remove Cu(II), Zn(II), Pb(II), and Cd(II) from aqueous media was studied by liquid–liquid extraction using dichloromethane-water biphasic system (table 3). Extraction efficiency was found to be dependent on the identity of the metal cation; Cu(II) exhibited the highest binding affinity of 92%, followed by Zn(II) at 90%, Pb(II) at 53%, and Cd(II) at 15% under similar experimental conditions. This trend is in agreement with Irvin-William series (ionic radii of Pb(II) > Cd(II) > Zn(II) > Cu(II)) except for the results obtained for Cd(II) and Pb(II). The higher extraction efficiency observed for Pb(II) (despite its larger ionic size) compared with Cd(II) could be explained using the Hard-Soft Acid-Base (HASB) theory [22]. Both Cu(II) and Zn(II) are

Table 3. Liquid–liquid extraction data of Cu(II), Zn(II), Pb(II), and Cd(II) by **L1**[a].

Entry	Metal (M^{2+})	Time (h)	M : L ratio	% Extraction[b]
1	Cu	2	1 : 1	90
2	Zn	2	1 : 1	87
3	Cd	2	1 : 1	15
4	Pb	2	1 : 1	53
5	Cu	4	1 : 1	92
6	Cd	4	1 : 1	55
7	Cd	4	1 : 2	61
8	Pb	2	1 : 2	70

[a] Conditions, Solvent system; water (20 ml) and dichloromethane (20 ml), initial concentration metal solutions, 1000 ppm.
[b] Determined by AAS.

borderline acids, while Cd(II) is a soft acid. The higher binding affinities of **L1** to Cu(II) and Zn(II) indicate **L1** is a borderline ligand. The lower binding efficiency of **L1** to Cd(II) could be attributed to weak interactions between a soft acid and a borderline base. Similar trends have been reported [27] for related pyrazolyl chelating ligands. For example, Bouabdallah and co-workers reported extraction efficiencies of 64 and 5% for Pb(II) and Cd(II), respectively, with tripodal N-donor pyrazoles [27a]. In comparison to our previous reports, the extraction efficiency of **L1** is relatively lower than that of (pyrazol-1-ylmethyl) pyridine [15, 16]. For instance, while **L1** exhibited binding affinities of 87, 53, and 15% for Zn(II), Pb(II), and Cd(II), respectively, bis(3,5-dimethylpyrazol-1-yl)pyridine showed percentages of 99, 66, and 31% [15]. The lower extraction efficiency for **L1** could arise from the presence of OH which is a hard donor in comparison to pyridine, a soft donor. On the other hand, **L1** displayed higher efficiencies than 5-pyrazolone-based Schiff bases [28] in the extraction of Cu(II). These Schiff bases showed only maximum extraction of 9% compared with 90% exhibited by **L1**, though under slightly different conditions.

The influence of metal/ligand ratio and contact time on the extraction abilities of **L1** was also investigated (table 3, entries 5–8). Increasing the contact time from 2 to 4 h resulted in a significant increase in extraction of Cd(II) from 15 to 55% (table 3, entries 3 and 6). Changing the metal/ligand ratio from 1 : 1 to 1 : 2 resulted in enhanced extraction ability of Cd(II) from 55 to 61%. This increase might be influenced by the coordination of two **L1** to one Cd(II), consistent with the solid-state structure of **3** (figure 1).

4. Conclusions

The coordination chemistry of (3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol ligand with Zn(II) and Cd(II) and its ability to extract Zn(II), Cd(II), Cu(II), and Pb(II) from aqueous media have been investigated. The (3,5-dimethyl-*1H*-pyrazol-1-yl)ethanol ligand is bidentate to Cd(II) metal. Both the size and electronic effects of the metal cations influence their relative binding efficiencies by **L1**. From the preferences displayed towards Zn(II), Cu(II) and Pb(II) and low extractions for Cd(II), **L1** behaves as a moderate donor.

Supplementary material

CCDC numbers 908001 and 908000 contain the supplementary crystallographic data for **3** and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors thank the International Foundation for Science (Grant no. W4857) for their financial assistance.

References

[1] (a) A.S. Mildvan, K. Cohm. *J. Biol. Chem.*, **241**, 1178 (1966); (b) S.S. Kidambi, D.-K. Lee, A. Ramamoorthy. *Inorg. Chem.*, **23**, 3142 (2003); (c) E. Kimura, In *Progress in Inorganic Chemistry*, K.K. Karlin (Ed.), Vol. 41, pp. 443–491, John Wiley and Sons, New York, NY (1994).

[2] (a) M.A. Mahmoud, M.M. Shoukry. *Polyhedron*, **20**, 343 (2001); (b) F. Ghebghoub, D. Barkat. *J. Coord. Chem.*, **62**, 1449 (2009); (c) F. Adjel, D. Barkat. *J. Coord. Chem.*, **64**, 574 (2011).

[3] (a) A. Aidi, D. Barkat. *J. Coord. Chem.*, **63**, 4136 (2010); (b) G.M.R. Tombo, D. Bellus. *Angew. Chem.*, **103**, 1689 (1991).
[4] E. Bouwman, W.L. Driessen, J. Reedijk. *J. Coord. Chem. Rev.*, **104**, 143 (1990).
[5] (a) X. Zhang, R. Van Eldik. *Inorg. Chem.*, **34**, 5606 (1995); (b) E. Kimura, I. Nakamara, T. Koike, M. Shionoya, Y. Kodama, T. Ikeda, M. Shiro. *J. Am. Chem. Soc.*, **116**, 4764 (1994).
[6] G. Parkin. *Chem. Rev.*, **104**, 699 (2004).
[7] J. Nriagu, J. Pacyna. *Nature*, **333**, 134 (1988).
[8] (a) R. Mukherjee. *Coord. Chem. Rev.*, **203**, 151 (2000); (b) F. Ghebghoub, D. Barkat. *J. Coord. Chem.*, **62**, 1449 (2009); (c) X.-J. Zhu, S.-T. Fu, W.-K. Wong, J.P. Guo, W.-Y. Wong. *Angew. Chem. Int. Ed.*, **45**, 3150 (2006); (d) L. Liu, Y.W. Lam, W.-Y. Wong. *J. Organomet. Chem.*, **691**, 1092 (2006).
[9] (a) D. Venkataraman, G.B. Gardner, S. Lee, J.S. Moore. *J. Am. Chem. Soc.*, **117**, 11600 (1995); (b) O.M. Yaghi, G. Li, H. Li. *Nature*, **378**, 703 (1995); (c) B. Mokhtari, K. Pourabdollah. *J. Coord. Chem.*, **64**, 4029 (2011).
[10] (a) A. Hachemaoui, K. Belhamel, H.-J. Bart. *J. Coord. Chem.*, **63**, 2337 (2010); (b) A.A.A. Hamid, C.P. Trip, A.E. Bruce, M.R.M. Bruce. *J. Coord. Chem.*, **3**, 731 (2010); (c) S. Trofimenko. *J. Am. Chem. Soc.*, **88**, 1842 (1996); (d) S. Trofimenko. *Chem. Rev.*, **93**, 943 (1993).
[11] (a) D.A. Atwood, M.M. Matlock, B.S. Howerton. *Water Res.*, **37**, 579 (2003); (b) G.J. Lumetta, T.G. Levitskaia, S.L. Latesky, R.V. Henderson, E.A. Edwards, J.C. Braley, S.I. Sinkov. *J. Coord. Chem.*, **65**, 741 (2012).
[12] H. Kantekin, M.B. Kilicaslan, F. Agin, H. Alp, U. Ocak. *J. Coord. Chem.*, **63**, 1921 (2010).
[13] (a) E.Y Tshuva, S.J. Lippard. *Chem. Rev.*, **104**, 987 (2004); (b) M.P. Walkes. *J. Inorg. Biochem.*, **79**, 241 (2000).
[14] J.O. Nriagu. *Nature*, **338**, 47 (1989).
[15] S.O. Ojwach, G.S. Nyamato, B. Omondi, J. Darkwa, A.O. Okoth. *J. Coord. Chem.*, **65**, 298 (2012).
[16] S.O. Ojwach, G.S. Nyamato, B. Omondi, J. Darkwa. *Inorg. Chim. Acta*, **392**, 141 (2012).
[17] J.L. van Wyk, B. Omondi, D. Appavoo, I.A. Guzei, J. Darkwa. *J. Chem. Res.*, **36**, 474 (2012).
[18] (a) SAINT Area-Detector Integration Software. Siemens Industrial Automation Inc., Madison, WI (1995); (b) Bruker-AXS. *APEX2, SADABS, and SAINT Software Reference Manuals,* Bruker-AXS, Madison, WI (2009).
[19] (a) SADABS Area-Detector Absorption Correction. Siemens Industrial Automation Inc., Madison, WI (1996); (b) G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).
[20] S. Munoz, J. Pons, J. Ros, M. Font-Bardia, C.A. Kinler, M.A. Halcrow. *Inorg. Chim. Acta*, **10**, 211 (2007).
[21] M.K. Ainooson, S.O. Ojwach, I.A. Guzei, L.C. Spencer, J. Darkwa. *J. Organomet. Chem.*, **696**, 1528 (2011).
[22] (a) S.D. Alexandratos, X.P. Zhu. *Macromolecules*, **38**, 5981 (2005); (b) R.G. Pearson. *J. Chem. Educ.*, **45**, 581 (1968); (c) M. Misono, E. Ochiai, Y. Saito, Y. Yoneda. *J. Inorg. Nucl. Chem.*, **29**, 2685 (1967).
[23] L.J. Shaw, P.K. Gwaltney, N. Keer. *Inorg. Chim. Acta*, **362**, 2396 (2009).
[24] M.C. Castellano, J. Pons, J. García-Antón, X. Solans, M. Font-Bardía, J. Ros. *Inorg. Chim. Acta*, **361**, 2923 (2008).
[25] (a) J. Pons, J. García-Antón, M. Font-Bardia, J. Ros, R. Jimenez, X. Solans. *Inorg. Chem. Commun.*, **10**, 1554 (2007); (b) W.N. Lipscomb, N. Strater. *Chem. Rev.*, **96**, 2375 (1996); (c) F.A. Allen. *Acta Cryst.*, **B58**, 380 (2002).
[26] M. Guerrero, J. Pons, T. Parella, M. Font-Bardia, T. Calvet, J. Ros. *Inorg. Chem.*, **48**, 8736 (2009).
[27] (a) I. Bouabdallah, I. Zidane, B. Hacht, R. Touzani, A. Ramdani. *ARKIVOC*, **11**, 1 (2006); (b) I. Bouabdallah, I. Zidane, B. Hacht, R. Touzani, A. Ramdani. *ARKIVOV,* **11**, 59 (2006); (c) S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, L. Janus. *Tetrahedron,* **60**, 939 (2009).
[28] N.J. Parmar, H.A. Barad, B.R. Pansuriya, R.A. Patel. *J. Coord. Chem.*, **64**, 688 (2011).