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Conjoint Experimental and Theoretical Evaluation of Zinc (II) Coordination Polymer as Potential Anion Receptors for Nitrate and Chromate

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A paradigm shift in supramolecular chemistry has drawn our attention to produce coordination polymers for anion separation. In this approach, we have successfully synthesized a one dimensional coordination polymer from combination of U-shaped diamide ligand, namely *N,N*-2,6-bis(4-pyridylmethyl)pyridine dicarboxamide **(L1)** and $Zn(NO_3)_2$ in methanol. This product is obtained as single crystal with formula molecule given by elemental analysis as $\{[Zn(\mathbf{L1})_2(H_2O)_2](NO_3)_2.4H_2O\}_n$. In this account, we also describe supramolecular interactions between this coordination polymer with two selected anions, nitrate and chromate using combination of experimental and theoretical studies. Observation *via* FTIR spectra indicates the presence of two distinctive peaks for Cr-O (931 cm^{-1}) and N-O (1384 cm^{-1}) confirming encapsulation of chromate and nitrate anions in the receptor. X-ray crystallography reveals the interaction between NH amide with the anions as expected. As resulted by Gaussian, coordination polymer with nitrate anion is found more stable compared to chromate with interaction energy 342.2729 kJ/mol.

Keywords: Coordination polymer, supramolecular, anions, hydrogen bonding, theoretical, chromate

I. INTRODUCTION

World has spent billions to treat waterways which have been polluted by wastes. This is excluding the clean-up remedies for water which has been polluted by toxic anions. As the pollution is invisible to the naked eyes, the action will only be taken after several indicators of contaminations are observed through nature. For instance, water or lake that has been contaminated by nitrate anions can only be declared after the dense growth of plant life is observed. Another example is contamination from perchlorate, arsenic or chromate, which can only be confirmed after the adverse health effects was diagnosed to the patients or after the death of aquatic life is reported [1] - [2]. Thus, realizing the importance in developing anion receptors or anion sensor that can detect toxic an-

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ions in waterways system, many scientists have produced new molecules as anion receptors [3]-[4]. Along with the development in this area, the presence of coordination polymers as anion receptors has continued to attract more attention due to their capability to shrink or expand the structure following the size of the guest molecules [5]-[7]. According to the reports, the synthesized coordination polymers exhibit large surface area and able to accommodate different size of guest molecules within their pores as observed in the solid state [8]-[9]. Recently, we have utilized monoamide and diamide ligands as the organic linker due to their great history in binding anion. Our reported diamide ligands have shown interactions with chromate, perchlorate, nitrate [10] and hexafluorophosphate anions either in neutral ligand or as discrete metallo-macrocycles complex. The work presented here is entirely different due to the introduction of the U-shaped organic linker, namely *N,N*-2,6-bis(4-pyridylmethyl)pyridine dicarboxamide is employed as the binding host in the coordination polymer. This ligand is equipped with two important criteria. Firstly, this molecule has NH amide moieties which are directed to the cavity of the molecule and second; the pendant arms are completed with N donor atoms as metal binding sites (Figure 1).

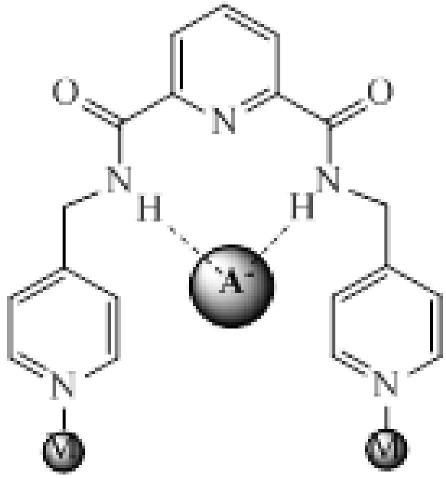

Figure 1. Molecular structure of ligand **(L1)** equipped with hydrogen bond to anion (A) and coordination to metal cation (M)

II. MATERIALS AND METHODS

Infrared spectra were collected on a Perkin Elmer Spectrum BX Infrared spectrometer as KBr disks. X-ray diffraction datasets of the complexes were collected with Mo-Kα radiation (λ=0.71073 Å) using Oxford Diffraction X-calibur single crystal X-ray diffractometer at 150(2) K. All datasets were corrected for absorption using a multi-scan method, and structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F2 by SHELXL-97 interfaced through the program X-Seed [11]. In general, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions. Table was generated from CIFTAB software [12]. Density functional theory (DFT) and Gaussian 09W software package were used in this study. The calculation was made at theoretical level of DFT/B3LYP with GEN (6-31G (d,p) for all compound and LANL2DZ for Zn and Cr) as basis set. GEN keyword in Gaussian 09W was used for a mixed basis set [13].

A. Synthesis of *N,N′*-2,6-bis(4-pyridylmethyl)pyridine dicarboxamide (L1) and coordination polymer

N,N′-2,6-Bis(4-pyridylmethyl)pyridine dicarboxamide was prepared with minor modification on the literature procedure [14]. 2,6-Dimethylpyridine dicarboxylate (1.02 g, 5.63 mmol) and 4-aminomethylpyridine (1.55 g, 11.8 mmol) were suspended in toluene, heated at reflux for 24 hours. Toluene was removed by using rotary evaporation (111°C at 77mbar). The oil residue obtained was dissolved in 75 mL of dichloromethane and washed with 50 mL of saturated sodium bicarbonate. The solvent was removed by using rotary evaporation before the residue was washed with 10 mL of hot diethyl ether to produce **(L1)** as cream solid. $Zn(NO_3)_2.4H_2O$ (0.0054 g, 0.018 mmol) was dissolved in methanol (5 mL) to give a colourless solution which, after being heated for few minutes, was added dropwise to a solution **(L1)** (0.0125 g, 0.036 mmol) prior dissolved in methanol (15 mL). The addition gave a colourless solution that was heated for 45 minutes and left to evaporate at room temperature. After a month, the solution afforded coordination polymer 1, $\{[Zn(\mathbf{L1})_2(H_2O)_2](NO_3)_2.4H_2O\}_n$ as colourless crystals (0.01g, 52%). Anal. found: C, 40.29; H, 4.25; N 15.08. $ZnC_{38}H_{46}N_{12}O_{16}$ requires C, 45.99; H, 4.68; N 16.94%. Selected IR bands (KBr disk, cm^{-1}): 3444 N-H str.; 1666 C=O str.; 1541, N-H bend; 1384, N-O str; 520, Zn-N; 803, Zn-O. Melting point (201°C)

B. Anion exchange experiment

K_2CrO_4 (0.0097 g, 0.05 mmol) was dissolved in deionized water (10 mL), before being added to a solution of $\{[Zn(\mathbf{L1})_2(H_2O)_2](NO_3)_2.4H_2O\}_n$ (0.0247 g, 0.025 mmol) which was also dissolved in deionized water (20 mL). This mixed solution was stirred for 2 hours at 40 °C. This reaction was left to evaporate off for two weeks at room temperature to give pale yellow precipitate in 65% (0.019 g). Anal. found: C, 39.85; H, 4.33; N, 12.45. $ZnC_{38}H_{46}N_{11}O_{21}Cr_2$ requires C, 39.26; H, 4.00; N, 13.26%. Selected IR bands (KBr disk, cm^{-1}): 3420 (s), 1668 (s), 1537 (s), 928 (s, Cr-O). Melting point (198°C).

III. RESULTS AND DISCUSSION

Ligands **(L1)** is a pre-organized amide ligands with U-shaped conformations in the solid-state, with the amide N-H directed internally into a pocket with potential for anion binding. This ligand was obtained in high yield and was fully characterized by spectroscopic techniques. The current data shows good agreement with the previous studies which confirm the success in obtaining compound [14]. Ligand *N,N*-2,6-bis(4-pyridylmethyl)pyridine dicarboxamide **(L1)** was then reacted with zinc nitrate in 1:2 ratio metal to ligand, using slow evaporation techniques to obtain coordination polymer as colourless crystals in moderate yield (51%). Based on CHN elemental analysis, this coordination polymer has formula molecule $\{[Zn(\mathbf{L1})_2(H_2O)_2](NO_3)_2.4H_2O\}_n$ with water molecules incorporated in the structure. This has led into expectation that the coordination polymer prepared in this study might have the structure as illustrated in Figure 2a and 2b.

FTIR spectrum of $\{[Zn(\mathbf{L1})_2(H_2O)_2](NO_3)_2.4H_2O\}_n$ shows the presence of ν(N-H), ν(C=O) and ν(C-N) at 3444, 1666 and 1541 cm^{-1}, respectively, appeared in common ranges as described in previous reports on the distinctive molecular frameworks [15]-[16]. There were obvious shift between the ligand and the complexes as listed in Table 2. For instance, the ν(N-H) of the ligand was shifted to the lower frequency indicating the weak hydrogen bonding between the NH amide with anion. New peaks appeared at 1384 cm^{-1} was assigned to ν(N-O) while 520 and 803 cm^{-1} were assigned for ν(Zn-N) and ν(Zn-O), respectively [17]-[18]. Table 1 shows the comparison of the IR bands for the coordination polymer with ligand **(L1)**.

As coordination polymer was obtained as crystals, it was subjected for X-ray crystallography analysis for structure determination. X-ray crystallography reveals that this compound crystallizes in the monoclinic space group $P21/c$. The asymmetric unit contains one zinc atom, two molecules ligand **(L1)**, two coordinated water molecules, two non-coordinated nitrate anions and four non-coordinated water solvate molecules (Figure 6). The zinc atoms occupy distorted octahedral environments with coordination by four pendant pyridyl groups and two water molecules and bond angles ranging from 85.9(2)-91.1(2)°. The bond lengths for the Zn-N bonds are in the range 2.158(6)-2.198(6) Å. The length between Zn-Zn is 12.894Å (1.894 nm) suggesting that this molecule is a porous coordination polymer. An intramolecular hydrogen bonding interactions between the NH donors of the ligands into a central pocket are indicated (Figure 3) and the bond lengths are common for weak hydrogen bonds as previously reported [19].

The result obtained meets our expectation where as ligand **(L1)** acts as a bridging ligand to link the two zinc atoms and forming a 1-D coordination polymer. The nitrate anions in this compound are bound to the coordination polymer *via* weak hydrogen bonding (C-H$\cdots$O, d = 2.665, D = 3.635 Å, C-H$\cdots$O, d = 2.222 Å, D = 3.101 Å). It was witnessed from the structure that the hydrogen bonding interactions involv-

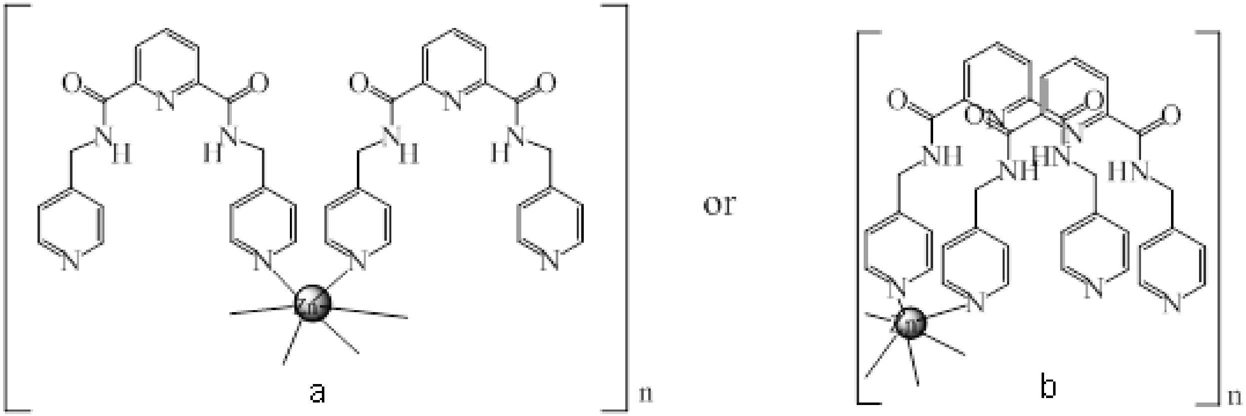

Figure 2. Illustration of the structure based on elemental analysis results

Table 1. Comparison of FTIR data for ligand **(L1)** and coordination polymer $\{[\mathrm{Zn}(\mathbf{L1})_2(\mathrm{H_2O})_2](\mathrm{NO_3})_2.4\mathrm{H_2O}\}_n$

Compounds	ν(N-H)	ν(C=O)	ν(C-N)	ν(N-O)	ν(Zn-N)	ν(Zn-O)
(L1)	3257	1653	1540	-	-	-
$\{[\mathrm{Zn}(\mathbf{L1})_2(\mathrm{H_2O})_2](\mathrm{NO_3})_2.4\mathrm{H_2O}\}_n$	3444	1666	1541	1384	520	803

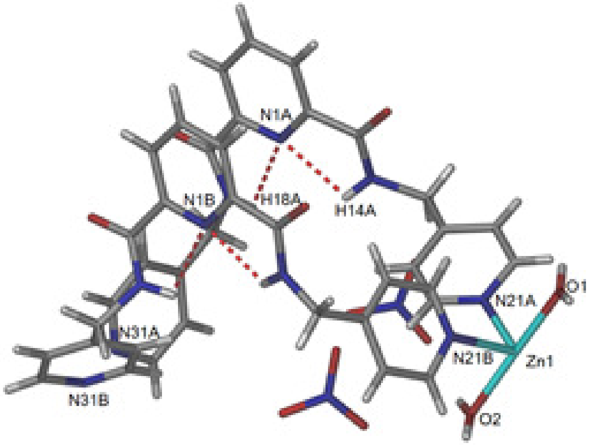

Figure 3. Perspective view of the asymmetric unit$\{[\mathrm{Zn}(\mathbf{L1})_2(\mathrm{H_2O})_2](\mathrm{NO_3})_2.4\mathrm{H_2O}\}_n$

ing the non-coordinated water molecules that occupy these pockets stabilized the packing of the anions in the structure (Figure 4). The structure of this coordination polymer is identical to the one we previously reported for cadmium ion, with the discrepancies only in bond lengths and angles [20],[14] .

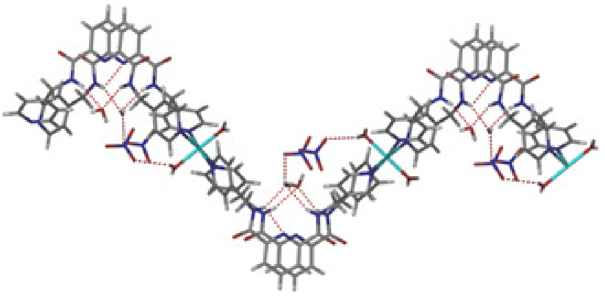

Figure 4. A perspective view of the hydrogen bonding in $\{[\mathrm{Zn}(\mathbf{L1})_2(\mathrm{H_2O})_2](\mathrm{NO_3})_2.4\mathrm{H_2O}\}_n$

Figure 5 shows the crystal packing of this complex when viewed down the *c* axis. It shows that this coordination polymer has two different types of large channels. One of the channels, lined with the 2,6-pyridine dicarboxamide moieties of the ligands hosts the hydrogen bonded water molecules and nitrate anions, while the second (shown empty) accommodates the water solvate molecules. The data of the crystal is shown in Table 3.

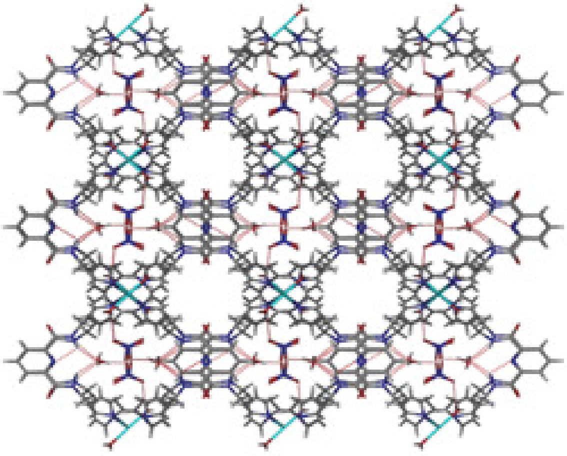

Figure 5. A perspective view of the crystal packing when viewed down the c axis

A. Anion study

Realizing the potential of this coordination compound to encapsulate or accommodate anions inside the porous cavities, this compound was further subjected for anion exchange experiments with chromate anions. In this experiment, potassium chromate was dissolved in aqueous solution before being combined with the aqueous solution of coordination polymer. The mixture was stirred for approximately 2 hours at controlled temperature to allow formation of yellow precipitate. The yellow precipitate was collected and dried under vacuum before being analysed by FTIR and elemental analysis. FTIR spectra show the presence of Cr-O stretching at 928^{-1} cm, indicating accomplishment incorporation of chromate anion in the structure. The nitrate peak (1384 cm^{-1}) is still remained but with reduced intensity (Figure 6b) thus giving us conclusive finding that not all nitrate is removed from the host. This is supported by elemental analysis that proposed the formula for the solid as $\mathrm{ZnC_{38}H_{46}N_{11}O_{21}Cr_2}$.

To determine the loss of nitrate from peak areas, the value of absorbance of nitrate is divided by the value of C=O stretches that act as the most constant peak in this spectrum. Based on the calculation, the percent of $\mathrm{NO_3}$ lost and replaced by $\mathrm{CrO_4}$ is approximately 82.30% as shown in table 2.

$$\frac{A(NO_3/ClO_4)}{A(C=O)} = X \quad \frac{A(NO_3/ClO_4)}{A(C=O)} = Y \qquad (1)$$

$$\frac{X-Y}{X} \times 100\% \quad = \%NO_3 \ \ lost \qquad (2)$$

B. Theoretical studies

Gaussian has been used in many ways, such as predicting interaction energy or finding the most stable form of molecules [21]. By using the same software, interaction energy between anions and NH-amide of the ligand in the coordination polymer is calculated (equation 3 and 4). To

Table 2. Crystal data of $\{[Zn(\mathbf{L1})_2(H_2O)_2](NO_3)_2.4H_2O\}_n$ with CCD number 1408542

Empirical formula	$C_{38}H_{42}ZnN_{12}O_{14}$
Formula weight	948.14
Crystal system	Monoclinic
Space group	*P21/c*
a (Å)	12.3568(3)
b (Å)	25.4241(6)
c (Å)	15.5652(5)
$\alpha(°)$	90
$\beta(°)$	108.468(3)
$\gamma(°)$	90
Volume (Å)	4638.1(2)
Z	4
Density (calculated) (Mg/m^3)	1.358
Absorption coefficient (mm^{-1})	0.604
F(000)	1952
Crystal size (mm^3)	0.16x0.15x0.15
Theta range for data (°)	2.36 - 29.95
Reflections collected	11993
Observed reflections [I>2s(I)]	6513
Data/restraints/parameters	11993/0/581
Goodness-of-fit on F^2	1.474
R1 [I>2s(I)]	0.1632
wR_2(all data)	0.2056
Largest diff. peak and hole (e.(Å)$^{-3}$)	7.211 and -1.861

A	:absorbance
(NO_3/ClO_4)	:peak absorbance for nitrate or perchlorate
$(NO_3/ClO_4)(CrO_4\ )$	:peak absorbance for nitrate or perchlorate that exchange with chromate
C=O	peak absorbance for carbonyl

achieve this, two most stable structure are proposed for study. Figure 7(a) shows the structure containing two nitrates in the amide cavity while structure with two chromates is shown in figure 7b. Comparison between the bond lengths and angles for calculated and experimental is shown in Table 3. It was observed that the bond lengths and angles for the calculated atoms are different from the experimental due to the position of the two ligands that cannot be overlapped in theory. However, our concerned is on the hydrogen

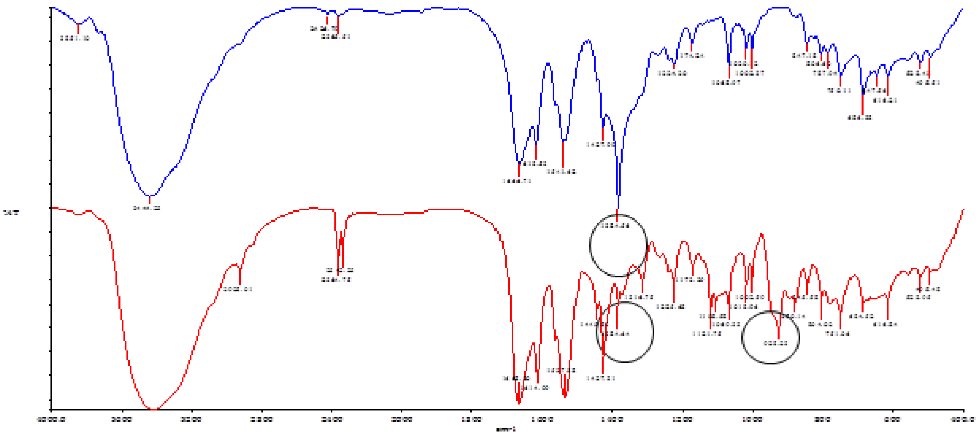

Figure 6. FTIR spectra before and after exchanged with chromate anions with signal for peak N-O (1384 cm^1) and Cr-O (928 cm^{-1})

Table 2. Calculation on the peak loss using ratio of peak area

	Original spectrum			Anion exchange spectrum			% loss of NO3
	$A_{c=o}$	A_{NO3}	Ratio: $A_{NO3}/A_{c=o}$=X	$A_{c=o}$	A_{NO3}	Ratio: $A_{NO3}/A_{c=o}$=Y	X-XY *100%
Batch							
1	17.4099	8.5916	0.4935	26.7708	2.3770	0.0888	82.00
2	19.000	9.0000	0.4737	24.0952	2.010	0.0834	82.39
3	22.2500	10.00	0.4494	30.7684	2.5402	0.0825	81.64
4	18.5101	8.2501	0.4457	27.0162	2.0355	0.0753	83.11
5	21.0951	10.9107	0.5173	29.5102	2.6954	0.0913	82.35
							Average=82.30±0.5

bonds that are particularly in agreement with the experimental data.

The calculation formulas for the interaction energy (uncorrected) and interaction energy (corrected) are written as in Equation (3) and (4) below:

Based on the calculation, anion coordination with nitrate is found to be more stable (-342.2729 KJ/mol) compared to chromate (291.1405 KJ/mol). This explains the reason why $CrO_4{}^{-2}$ anion cannot replaced all nitrate anions as determined in the FTIR spectra and elemental analysis results. The details of the theoretical calculation are listed in Table 4.

IV. SUMMARY

In conclusion, one dimensional coordination polymer has been successfully prepared and investigated for preliminary anion binding poten-

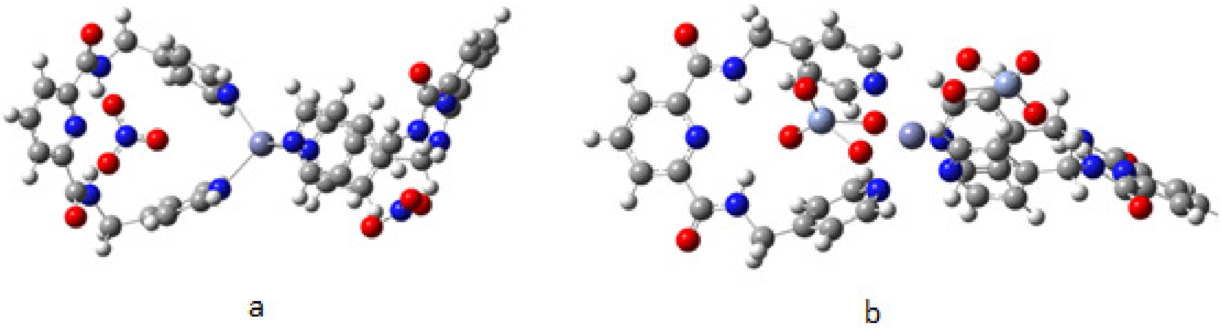

Figure 7. Gaussian view with (a) two nitrates (b) two chromates in the molecule cavity

Table 3. Comparison between the bond lengths and angles between calculated and experimental

Important Bonds	Calculated (Å)	Experimental (Å)	Angles	Calculated (°)	Experimental (°)
N(21A)-Zn(1)	2.143(2)	2.158(6)	O(1)-Zn(1)-N(21A)	90.7(3)	90.9(2)
N(21B)-Zn(1)	2.188(3)	2.198(6)	N(21A)-Zn(1)-N(31B)	85.3(2)	86.5(2)
N(31A)-Zn(1)	2.158(4)	2.197(7)	O(1)-Zn(1)-N(31A)	90.2(2)	91.1(2)
N(31B)-Zn(1)	2.112(3)	2.179(6)	O(2)-Zn(1)-N(21B)	84.9(3)	85.9(2)
Zn(1)-O1	2.121(3)	2.111(6)	C-H···O	85.4(3)	85.9(2)
N(21A)-H···O	2.529(4)	2.644(2)	N-H···N	105.71	106.59
N(21B)-H···O	2.532(4)	2.695(3)	N-H···N	103.22	103.69

$$\Delta\text{Einteraction (uncorrected)} = \text{Ecomplex - [- (Emetal}(\mathbf{L1})_2) + \text{E(anion)}_2] \quad (3)$$

$$\Delta\text{Einteraction (corrected)} = \Delta\text{Einteraction (uncorrected)} + \text{BSSE} \quad (4)$$

Table 4. Interaction energy calculation using Gaussion

	$\Delta E_{interaction}$(uncorrected), KJ/mol	BSSE, KJ/mol	$\Delta E_{interaction}$(corrected), KJ/mol
$[Zn(\mathbf{L1})_2(NO_3)_2]$	-738.8157, *(-369.4079)	+54.27	-684.5457, *(-342.2729)
$[Zn(\mathbf{L1})_2(CrO_4^{2-})_2]$	-661.1009, *(-330.5505)	+78.82	-582.2809, *(-291.1405)

*(Etotal)

tial. Conjoint results from theoretical and experimental studies have supported the potential applications of this compound as anions receptors for nitrate or chromate. This study can be pursued with other anions and accomplished by several kinetic works, towards the production of materials for river clean-up remedies.

V. ACKNOWLEDGMENT

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