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Responsive Nature of 1,2,4,5-Tetrakis(2-pyridylthiomethyl)benzene Toward Group 12 Metal Nitrates: Activity of Coordinated Nitrate in Metal Complexes

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Supporting Information

ABSTRACT: This study provides a detailed analysis on the responsive behavior of 1,2,4,5-tetrakis(2-pyridylthiomethyl)benzene (**L**) toward group 12 metal nitrates in both aqueous and nonaqueous media. The ligand **L** proved to be an environmentally responsive species, and structural investigations of its complexes with respective $M(NO_3)_2$ (M = Zn, Cd, and Hg) allowed one to remark on the inherent activity of the nitrate ion, resulting in a distinctively higher coordination number and dimensionality to the metal cations.

The chemistry of group 12 metal ions with various organic donors and structural aspects of their complexes has always been a fascinating area of research interest.[1] This has led to considerable effort in studying the interactive behavior of group 12 metal ions with various organic donor bases, in particular, having pyridyl nitrogen atoms as major coordination sites. Additionally, they also exhibit selective binding affinities toward Zn^{II}, Cd^{II}, and Hg^{II} ions when devised as chemosensors and biosensors.[2] In the past few decades, the design of organic donor bases bearing a combination of both nitrogen and sulfur donor atoms also received considerable attention because they show improved selectivity and have an exceptional background to explain the reactivity−selectivity of these metal ions in chemical and biological processes.[3] Despite the fact that widespread progress has been made in understanding the chemistry of group 12 metal ions, challenges remain in controlling the activity of the anion. In fact, the anion plays a crucial role in regulating the functional behavior of metal ions in chemical and biological processes.[4] Specified by our interest[5] in the chemistry of conformationally flexible organochalcogen ligands, herein we report the synthesis and structural aspect of 1,2,4,5-tetrakis(2-pyridylthiomethyl)benzene (**L**) bearing nitrogen and sulfur as donor sites and its complexation behavior with group 12 metal nitrates. The species **L** was synthesized by a known procedure and revealed as the "aabb" (a = above; b = below) pattern rather than the reported "abab" conformation for substituted thiopyridyl donor arms.[6] Primarily, the species **L** exhibited its preferred selectivity for M^{2+} (M = Zn, Cd, and Hg) ions over other competitive first-row transition-metal ions. The changes in the UV−vis spectra for **L** and further "turn-on" fluorescence responses ($\lambda_{ex} = 280$ nm; $\lambda_{em} = 340$ nm) with striking red shifts in emissions, with a shift of up to 5−10 nm upon the successive addition of M^{2+} ion (in H_2O) to a solution of the ligand (in CH_3CN), were notable. However, the "turn-on" responses in the fluorescence measurements continued to a 8:1 M/**L** stoichiometry. The availability of donor sites in ligand **L** reasonably offers the possibility of coordination to a maximum of two metal ions. The unusual spectroscopic behavior of the ligand toward M^{2+} (M = Zn, Cd, and Hg) ions in a mixed-solvent system was intriguing, and conclusions were drawn only when a crystal obtained from a solution titrated to a 8:1 M/**L** stoichiometry in mixed-solvent system was analyzed by X-ray crystallography. The single-crystal X-ray structure of this species revealed the formation of a protonated species ($\mathbf{H_4L}$) in the "aabb" conformation with protonation of all nitrogen atoms of the four thiopyridyl ring of the ligand. The influence of protonation on pyridyl nitrogen atoms is well noticeable as C═N−C bond angles of the pyridyl ring of the free ligand **L** expand from 117.0(1)−117.2(1)° to 123.7(2)−123.0(2)° in $\mathbf{H_4L}$ and well comparable to several pyridine-based receptors familiar for their selective nitrate-ion recognition.[7] In the present study, the possibility of protonation of the ligand likely occurs in the mixed-solvent system H_2O/CH_3CN because of the partial hydrolysis of metal salts $M^{n+} + xH_2O \leftrightarrow [M(H_2O)_x]^{n+} \leftrightarrow M(OH)_x^{(n-x)+} + xH^+$ ($n = 2$; $x = 4$ or 6) during titration. In the present conditions, the H^+ ions produced in solution were enough to protonate the pyridyl nitrogen atoms of the ligand. The behavior of **L** with other metal ions such as Ni^{2+} and Pd^{2+} was also examined in the same reaction conditions but led to recovery of the ligand in a new conformation ($\mathbf{L_1}$). These results reveal a complicated solution behavior, where possibilities of complexation followed by decomplexation, partial or complete hydrolysis of metal salts, and protonation of the ligand in an aqueous organic solvent are likely to occur. Therefore, metal−ligand interactions in an aqueous organic solvent medium may not be suggestive and are inconclusive, especially when quantification of the metal ion is being suggested on the basis of spectroscopic changes. The reaction event of **L** with different cations in a mixed-solvent system is outlined in Scheme 1. To explore and understand the coordinative behavior of the nitrogen center of **L** with group 12 metal nitrates, the metal/ligand titration experiments were also performed in an aprotic nonaqueous organic medium, i.e., in acetonitrile, and monitored by spectroscopic changes.

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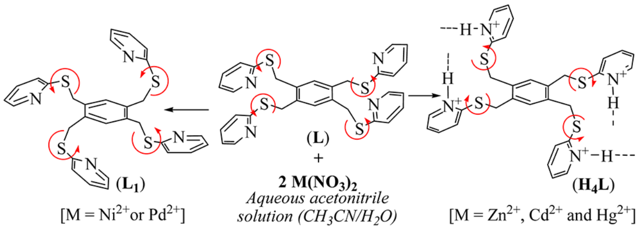
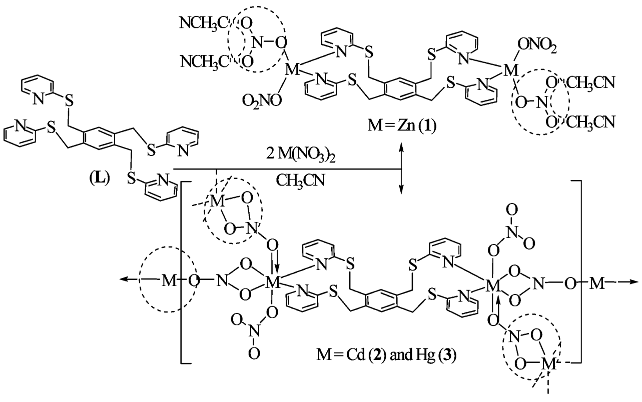
Scheme 1. Coordination Behavior of L with Metal Cations



The ligand **L** itself revealed temperature-dependent emissive changes in the fluorescence measurements and may be suggestive of rapid conformational changes above 35 °C (Figure S5 in the Ssupporting Information, SI). Indeed, the ligand **L** in acetonitrile proved to be a temperature-sensitive species. Considering the responsive nature of the ligand, the interactive behavior of **L** with M^{2+} (M = Zn, Cd, and Hg) ions was also monitored spectroscopically in CH_3CN at room temperature. The appearance of isosbestic points at ~235 nm (nearly at the same positions for respective M^{2+} ions) in UV–vis spectra and titration curves plotting the absorbance as a function of the added metal ions indicated a 2:1 M/**L** binding stoichiometry. Similarly, the acquisition of fluorescence emission spectra with the successive addition of M^{2+} ions (2×10^{-4} M in CH_3CN) to a solution of **L** (1×10^{-4} M in CH_3CN) revealed significant "turn-on" fluorescence responses (λ_{ex} = 280 nm; λ_{em} = 340 nm) to a maximum 2:1 M/**L** stoichiometry. Although spectroscopic changes can be taken into consideration for metal-ion speciation, real insight into the interactive behavior of **L** with M^{2+} ions and the structural parameters was required to establish the overall real reaction scenario. Complexes of Zn^{II}, Cd^{II}, and Hg^{II} (**1**–**3**) were also isolated as solid crystalline materials by reaction of the ligand with respective metal nitrate salts in acetonitrile at room temperature (Scheme 2).

Scheme 2. Synthesis and Coordination Environment in 1–3



Physicochemical and spectroscopic data for complexes **1**–**3** were consistent and in favor of 2:1 M/**L** complex formation. These complexes show moderate-to-poor solubility in common organic solvents. The IR spectra of complexes **1**–**3** evidence coordination of the ligand through its nitrogen-to-metal centers, yet it was not possible to distinguish unambiguously the bonding of nitrate because all three complex species exhibited comparable peak patterns in the range of ν 1490–1250 cm^{-1} for nitrate. The structural confirmation for **1**–**3** came from single-crystal X-ray diffraction studies.

The crystals of **1**–**3** were grown under strictly anhydrous and similar conditions upon the slow evaporation of a clear solution of the respective complexes **1**–**3** dissolved in acetonitrile. The complex **1** (M = Zn) revealed a discrete neutral unit, where the ligand forms a bridge between two metal centers by adopting its energetically least preferred "aaaa" conformation for all four of its thiopyridyl donor arms. Each Zn^{II} center is coordinated by the nitrogen atoms of two adjoining thiopyridyl arms of the bridging ligand. The remaining coordination site on zinc is completed by the involvement of two nitrate ions bonded in a unidentate manner. This overall coordination scenario around the Zn^{II} center provides a discrete molecular species in a slightly distorted tetrahedral configuration. The most interesting feature of this structure is the observation of the unexpected and rarest anion–solvent ($ONO_2\cdots CH_3CN$) interactions as one of the nitrate ions on each Zn^{II} center in complex **1** interacts with the solvent CH_3CN molecule (Figure 1).

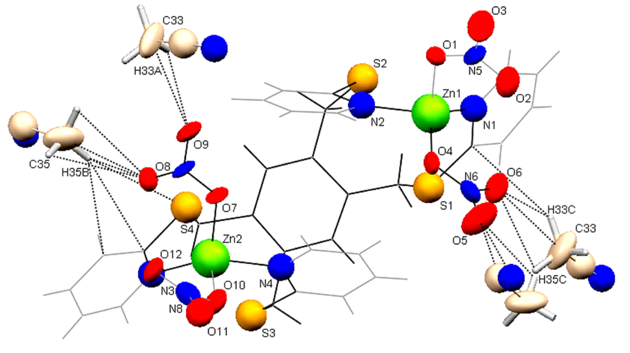


Figure 1. Perspective view of discrete Zn^{II} complex species **1** with $ONO_2\cdots CH_3CN$ interactions.

The influence of the solvent on metal-bonded nitrate is quite noteworthy because N–O and O–N–O bond lengths and bond angles respectively were observed in the ranges of 1.216(3)–1.282(2) Å and 117.6(2)–123(2)°. We believe that the observation of $ONO_2\cdots CH_3CN$ interactions is a positive indication of the perturbed symmetry of nitrate ions and suggests that complex **1** should remain active in the solution. Nevertheless, these interactions are valuable for new fundamentals because they should provide an experimental basis in understanding the upcoming activity of the anion, i.e., the structural outcome of a M/**L** combination attributable to structural and dynamical activities of nitrate in the present reaction conditions. Sensibly, structural investigations of Cd^{II} and Hg^{II} complexes obtained under conditions similar to those of Zn^{II} were necessary to study the structural trends in the same family group. A structural comparison of the crystal structures of Cd^{II} and Hg^{II} complexes revealed the close conformational and coordinative resemblance of the ligands in complexes **1**–**3**. The "aaaa" conformational pattern of the ligand upon metal-ion coordination provides a constrained coordination environment around metal centers. The M–N bonds of 2.001(18)–2.042(17) Å (M = Zn, **1**), 2.281(7)–2.304(5) Å (M = Cd, **2**), and 2.18(1) Å (M = Hg, **3**) predict an increase of the M–N bond upon moving from Zn^{II} to Cd^{II} but a decrease upon continuing from Cd^{II} to Hg^{II}. On the other hand, the M–O bonds (for nitrate ion bonded to metal in a unidentate mode) range from 1.989(16)–2.017(17) Å (**1**) to 2.331(7) Å (**2**) to 2.57(1) Å (**3**). Similarly, the N–M–N angles in the complexes increases from 126.93(7)° to 137.0(2)° to 147.6(4)° upon moving from **1** to **2** to **3**, respectively. The solvated nitrate ions, as seen in **1** with perturbed symmetry, corresponding to the nitrates in complexes **2** and **3** advance them to an extended structure in such a way that they bind in chelating bidentate mode to the same metal center and at the same time to the adjacent metal centers in bridging mode. The overall activity of the nitrate ion thus results in anion-assisted 2D structures for **2** and **3** (Figures S13−S16 in the SI). The shortest inter- and intramolecular (M−O) bonds due to nitrate ions bonded to neighboring metal centers were observed in the ranges of 2.378(5)−2.410(6) (M = Cd, **2**) and 2.44(1)−2.67(1) (M = Hg, **3**). The structural complexities due to nitrate ions are found to be similar in **2** and **3** and exhibit a close crystallographic resemblance. We considered all possible experimental factors and reasoned that the structural complexities in **2** and **3** were a result of the inherent activity of the nitrate ion, which is deeply related to solvation around it. The behavior of the nitrate ions in **2** and **3** could be rationalized in view of the fundamentals associated with nitrate chemistry. For instance, the nitrate ion (NO_3^-) in the gas phase is frequently encountered as a planar ion in D_{3h} symmetry, with the negative charge uniformly distributed on the three oxygen atoms.[8] In polar solvents, however, the D_{3h} symmetry of the nitrate ion is expected to be broken because of the nonsymmetric solvation environment and partially localizes the negative charge. There is also evidence in which nitrate bonded to a metal ion in its complexes exhibits a reduction in the local symmetry[9] from D_3h to C_{2v} symmetry. On the contrary, while working in aqueous or protic media, the nitrates usually act as charge-balancing counterions in their respective metal complexes. Considering the nature of the nitrate ion in different environments, it is more likely that a nonsymmetrical solvation environment of the anion in complex **1** adopts a nonplanar feature and partially localizes the negative charge on their nonbonded end. The partially localized negative charge on nitrate inevitably allows it to act as a weak nucleophile (the anion becomes a ligand), which, in turn, interacts with solvent molecules, as seen in the crystal structure of **1**. Apparently, the advances activity of the anion can be visualized provided that the geometrical preferences and charge-accepting ability of a metal ion allow it to proceed. On the basis of comparable experimental conditions and structural information obtained for complexes **1**−**3**, the extended coordination of nitrate in **2** and **3** may be anticipated because of the relativistic effect.[10] As relativistic effects become significant for the heaviest ions, the relativistic stabilization of the d and s orbitals of the heaviest ions enhances their charge-accepting ability relative to those of lighter ions in the same group of the periodic table. Because of the counterions bearing negative charges and the increased charge-accepting properties of metal ions in **2** and **3**, the structural characteristics are fundamentally different compared to **1**. The overall nitrate ion activity in these complexes results in an extended 2D coordination structure. Definitely, the role of external influences in the activity of the nitrate ion cannot be ignored because the nitrate ion in atmospheric and geochemical sciences is considered to be a photochemically active species and is believed to remain active in the dark.[11] It is difficult to make any further comment on the exact nature of the symmetry breaking of the nitrate ion in the solution state except that complexes **1**−**3** were prepared and crystallized from acetonitrile in comparable reaction conditions. It is important to note that the extended bonding of the nitrate ion has also been seen in a few of its metal complexes derived from silver(I), cadmium(II), and lead(II) nitrates either prepared or crystallized from acetonitrile and rationalized in terms of the coordination flexibility of the anion.[12]

Conclusively, the present findings provide a systematic experimental basis in understanding the "symmetry breaking", dynamics, and interactions of the anion with solvent molecules and serve as a tool in recognizing the "*inherent activity*" of the nitrate ion to some extent. These findings also provide *some basic insights into a rather arguable issue in inorganic chemistry, over the presence of nitrate ion as a mere counterion or play a vital role in determining the dimensionality and structure of the coordination polymer*.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, experimental details, and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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