Magnetic Properties

Synthesis, Crystal Structures and Magnetic Properties of Two Heterobridged μ-Phenoxo-μ₁,₁-Azide/Isocyanate Dinickel(II) Compounds: Experimental and Theoretical Exploration

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Abstract: This investigation deals with the syntheses, crystal structures and experimental and density functional theoretical magnetic properties of two heterobridged and isomorphous μ-phenoxo-μ₁,₁-azide/isocyanate dinickel(II) compounds of composition [Ni$^{II}_2$(L)$_2$(μ₁,₁-N$_3$)(CH$_3$CN)(CH$_3$OH)](ClO$_4$)·CH$_3$CN (**1**) and [Ni$^{II}_2$(L)$_2$(μ₁,₁-NCO)(CH$_3$CN)(CH$_3$OH)](ClO$_4$)·CH$_3$CN (**2**), where HL is the 1:1 condensation product of 3-ethoxysalicylaldehyde and 4-(2-aminoethyl)-morpholine. The two compounds are isostructural as well, except that **1** contains end-on azide and **2** contains end-on isocyanate. One metal ion is surrounded by O(μ-phenoxo), N(μ₁,₁-azide/μ₁,₁-isocyanate), N(imine), N(amine), O(ethoxy) and O(phenoxide, monodentate) atoms, while the second metal ion is surrounded by O(μ-phenoxo), N(μ₁,₁-azide/

μ₁,₁-isocyanate), N(imine), N(amine), O(methanol) and N(acetonitrile) atoms. Variable-temperature (2–300 K) magnetic susceptibility and variable-field (up to 5 T) magnetization data reveal ferromagnetic exchange interaction with J = 18.0 cm^{-1} for **1** and J = 11.4 cm^{-1} for **2**. Broken symmetry density functional calculations of exchange interaction have been performed on both complexes and the DFT-computed J values are nicely matched with the experimental J values [J(exp) = 18.0 cm^{-1} and J(DFT) = 17.2 cm^{-1} for **1**; J(exp) = 11.4 cm^{-1} and J(DFT) = 8.9 cm^{-1} for **2**]. The magnetic properties have been nicely rationalized in terms of spin density, magnetic orbitals and breakdown approach.

Introduction

Molecular magnetism has been an interdisciplinary research area. The major objectives in this area are as follows: (i) Determination of experimental[1–3] as well as theoretical[3–5] magneto-structural correlations; (ii) Development of magnetic materials, which may be single molecule magnets[6–8] and extended magnets;[9,10] (iii) Understanding of the intimate relationship of spin coupling and slow relaxation of magnetization by density functional theoretical and *ab initio* calculations.[1,3–5,7b–7d,11]

Understanding of the magnetic properties in terms of structures of heterobridged exchange coupled systems is much more complicated in comparison to the homobridged exchange coupled systems because of the involvement of more than one type of pathway in superexchange and the accompanied cooperativity in the former type. Magnetic properties of several heterobridged dicopper(II) compounds could be rationalized in terms of orbital-complementarity and orbital-counter-complementarity effects,[12] as copper(II) has only one magnetic

orbital. However, these approaches are less effective for hetero-bridged compounds of other metal ions (say, Ni^{II}) in which there are more than one magnetic orbital.[13–19] Few years back, we proposed some theoretical and experimental magneto-structural correlations in heterobridged μ-phenoxo-μ₁,₁-azide dinickel(II) compounds.[3a] In the meantime, few more compounds with a similar bridging moiety have been reported.[14c–14g] Therefore, enlightenment of the proposed correlations should deserve attention.

We observed that the 1:1 condensation products of 3-methoxysalicylaldehyde and ethanolamine or 1-(2-aminoethyl)-piperidine or 4-(2-aminoethyl)-morpholine, are useful ligands to derive μ-phenoxo-μ₁,₁-azide/isocyanate dinickel(II) compounds.[2b,3a,13] We though it relevant to investigate whether 3-ethoxysalicylaldehyde would also stabilize such heterobridged dinuclear compounds. Apparently, it may appear to someone that they would stabilize similar compounds as 3-ethoxysalicyl-aldehyde and 3-methoxysalicylaldehyde are closely similar molecules. However, our experience with the 1:2 condensation products (H$_2$L^{OMe} and H$_2$L^{OEt}, respectively) of these phenolic-ethereal aldehydes with diamines is that they stabilize different types of systems in a number of cases.[20] For example: (i) The products of mononuclear copper(II) metallo-ligands from H$_2$L^{OEt} with a number of second metal ions are frequently cocrystals while those from H$_2$L^{OMe} are discrete systems;[20a–20d] (ii) copper(II) metallo-ligands from H$_2$L^{OEt} can trap aquated proton but those from H$_2$L^{OMe} can't.[20e] Hence, it is relevant to check whether 1:1 condensation products of 3-ethoxysalicylaldehyde and ethanolamine or 1-(2-aminoethyl)-piperidine or 4-(2-amino-

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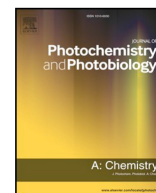
Experimental and theoretical exploration of sensing and magnetic properties of a triply bridged dicopper(II) complex: The first discrete metal complex to sense picric acid in pure water

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ABSTRACT

This article reports the syntheses, crystal structures, fluorescence spectra, picric acid (PA) sensing and magnetic properties of a μ-phenoxo-bis(μ-chloro) dicopper(II) compound of composition $[Cu_2L(\mu\text{-}Cl)_2]Cl\cdot4.5H_2O$ (**1**), where HL is the [1 + 2] condensation product of 2,6-diformyl-4-ethylphenol and 2-(2-aminoethyl)pyridine. Compound **1** is water soluble and exhibits fluorescence behaviour in pure water. Interestingly among the various aromatic, non aromatic nitro compounds as well as non nitro aromatic compounds screened, PA specifically quenches the fluorescence intencity of **1** significantly in water, revealing that **1** is a turn-off fluorosensor for PA. The sensing pathways have been investigated by spectral titration, time resolved fluorescence decay and DFT studies. Spectral and theoretical (DFT) studies suggest that the observed fluorescence quenching is associated with ground state (GS) charge transfer as well as electrostatic interactions between **1** and picrate ion. Unaltered fluorescence life time of **1** in the absence and presence of PA strongly suggests that quenching follows a static mechanism. Nature of binding modes or interactions between the complex **1** and PA was disclosed by the single crystal structure analysis of the corresponding association complex of composition $[Cu_2^{II}L(\mu\text{-}Cl)(H_2O)_2]$ 2Picrate·DMF (**2**). The quenching constant (K_{sv}), association constant (K_a) and detection limit (LOD) of the complex **1** for picric acid was found to be 1.1×10^5 M^{-1}, 4.64×10^{10} M^{-2} and 4.8 μM respectively. Variable-temperature (2.5–300 K) magnetic susceptibility measurement of the complex **1** reveals antiferromagnetic exchange interaction with $J = -132.40$ cm^{-1}. The magnetic property has been nicely rationalized in terms of spin density and magnetic orbitals within broken-symmetry (BS) framework. Compound **1** is the first example of a discrete metal compound to sense picric acid in pure water. Some other interesting aspects have been discussed.

1. Introduction

Development of cheap and efficient fluorescent chemosensors having high selectivity and sensitivity for detection of hazardous or explosives molecules/ions has attracted much attention in recent times for wide applications in both national security and environmental protection [1–4]. Trinitrophenol or picric acid (PA), being a powerful explosive among different nitroexplosives and a highly water-soluble hazardous pollutant, has received considerable attention recently in the field of chemosensors. In this regard, a wide variety of fluorosensors based on small organic molecules [5,6], organic polymers including conjugated polymers [7], discrete metallo-organic compounds [8], including macrocycles/cages [8i,8j], coordination polymers including MOFs [9–11], nanoaggregates [12], carbon or quantum dots [13], have been reported for detection of PA. The detection mechanism for PA is

mostly composed of proton transfer from the hydroxy group of PA to the chemosensor, leading to a hydrogen bonding network followed by electron transfer from the donor to the acceptor. However, most of them show one or more of the following drawbacks: (i) Real applicability is limited as most sensors function in non-aqueous media; (ii) There is synthetic difficulty because of the requirements of time consuming multi-step synthesis procedure (which usually ends in low yield of the final product), high temperature and expensive materials in the synthesis of most of the chemosensors. Moreover, structural evidence of the association complex formed between PA and fluorescent chemosensors, which is very important to gain deep insight into the exact interaction, is scarce. In this regards, Schiff base sensors deserve special attention due to their simplicity, sensitivity and low cost features. Their structures and solubility can be chemically tuned to increase the sensing selectivity. Therefore, it is highly desirable to explore new Schiff

Chemodosimetric Mechanistic Insight through Trapping Intermediate for Selective Detection of Picric Acid in Aqueous Medium by a Dinuclear Cd^{II} Complex

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A fluorescent dinuclear cadmium(II) based discrete metal complex of composition [Cd$^{II}_2$L(μ-Cl)Cl$_2$](1) is used {HL = 2,6-bis[2-(methylamino)ethyliminomethyl]-4-Ethylphenol} for the specific recognition of 2,4,6-trinitrophenol (picric acid; PA) via fluorescence quenching phenomenon among various nitro-aromatic compounds through a chemodosimetric approach. It has been established that **1** is a chemodosimeter in pure water. We have successfully been able to isolate three compounds: chemodosimeter **1**; an intermediate complex **2** of composition [Cd^{II}(LH$_2$)Cl$_2$](Picrate) and final association complex **3** of composition [NH$_3$(CH$_2$CH$_2$)NH$_2$CH$_3$](Picrate)$_2$. Compounds have been characterised by CHN elemental analyses, single crystal X-ray crystallography, PXRD, NMR and FTIR. Selective interaction of **1** with PA was evaluated by fluorescence, UV-Vis and life time measurements. Fluorescence quenching of **1** occurs definitely due to the formation of compound **3** via intermediate **2** involving partial decomplexation, hydrolysis and proton transfer phenomena in solution during the course of sensing. The quenching constant (K$_{sv}$), association constant (K$_a$) and detection limit (LOD) of the complex **1** for picric acid are ~1.55× 10^5 M^{-1}, ~1.8×10^{10} M^{-2} and ~0.47 μM (0.108 ppm), respectively. Mechanism of sensing is proposed and the very rare case of isolation and characterization of intermediate in picric acid sensing is discussed.

Introduction

Different hazardous chemicals or explosive molecules/ions are thrown out to the environment in industrial processes and obviously, their detection is an important aspect for national security and environmental issues. As a result, immense attention has been given in recent years for the design and studies of selective, sensitive and cost-effective fluorescent sensors.[1–4] Picric acid (PA; 2,4,6-trinitrophenol) is more powerful as an explosive than other common nitro-explosives and it is a highly water soluble hazardous chemical, which causes severe health anxieties. Therefore, detection of PA has received significant research attention in the field of chemosensors. In addition to fluorescence sensing methods, various analytical techniques (e.g. ion mobility spectrometry (IMS); gas chroma-tography-mass spectrometry (GC-MS); electrochemical methods; surface-enhanced Raman spectroscopy (SERS); nuclear quadru-pole resonance (NQR) etc.) have been applied so far for its detection.[5–9] However, fluorescence sensing method by using a fluorescent probe has drawn much interest because of its simplicity, sensitivity, short response time and low cost. For application purposes, it is highly desirable that a fluorescent probe can be synthesized easily, sufficiently soluble in water and effective as sensor in aqueous medium with high selectively. So far, a considerable number of fluorescent materials have been utilized for selective detection of PA. Those sensors include small organic molecules,[10–21] organic polymers including conjugated polymers,[22–26] discrete metallo-organic coordination compounds[27–41] including macrocycles/cages[30–32] or AIEgens[40,41] coordination polymers including MOFs,[42–73] nanoaggregates[74–76] and carbon or quantum dots.[77,78] However, apart from their complicated multistep preparation procedures, these sensor materials are found to be efficient in organic medium, which is not feasible for their practical application. Clearly, as the number of sensors in aqueous medium is much less than those in organic medium, it deserves significant importance to develop the aqueous medium sensors.

In order to get a clear and deeper insight into the sensing behaviour, various signalling mechanisms (e.g. photoinduced electron transfer (PET), intramolecular charge transfer (ICT), förster resonance energy transfer (FRET), inner filter effect (IFE) and chemodosimetry) along with various supramolecular inter-actions (e.g. hydrogen bonding, metal-ligand coordination, electrostatic interactions) are rationally considered. It is evident from previous studies that detection of PA by considering all above mentioned signalling mechanisms[10,12–37,42–78] except chemodosimetry[11,38] have been well explored. Clearly, fluores-cent chemodosimetric approach to detect PA needs special attention.

In general, for mechanistic interpretation of the sensing of any analyte, isolation/characterization of either intermediate or final association complex or both of these is required.

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