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Construction of a Novel Zn−Ni Trinuclear Schiff Base and a Ni^{2+} Chemosensor

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A novel Zn−Ni heterotrinuclear Schiff base compound bearing acacen^{2-} moieties was constructed through the selective assembly of a chemosensor Schiff base zinc compound with a Ni^{2+} ion. Its crystal structure not only clearly explains the binding mode between the chemosensor molecule and the detected metal ion but also represents the first trinuclear complex based on a symmetric acacen^{2-} base Schiff base.

In recent years, sensors based on the metal-ion-induced changes in fluorescence appear to be particularly attractive because of the simplicity and high detection limit of the fluorescence.[1] In this regard, metal-selective fluorescent chemosensors have served as useful tools for the detection of metal ions and thus have been widely exploited to detect biologically or environmentally relevant metal cations, such as Pb^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+} ions, etc.[1−3] Along with other transition metals, Ni^{2+} is a significant environmental pollutant, yet an essential trace element in biological systems such as respiration, biosynthesis, and metabolism.[4] For example, an undersupply of trace metals leads to deficiency and an oversupply results in toxic effects.[5] Nevertheless, no fluorescent probe for Ni^{2+} has been reported because of the fluorescence quenching nature of paramagnetic Ni^{2+}.[6] Furthermore, a few of the reported fluorescent probes for Cd^{2+}, Hg^{2+}, Fe^{2+}, and Cu^{2+} in the literature have been supported through the crystal structures of the final products explaining the binding mode between the chemosensor molecule and selective detected metal ions.[2b]

Over the past decades, coordination polymers based on a Schiff base composed of a primary amine and acetylacetone or analogues with biological and fluorescent properties have been successfully designed through the different synthetic strategies.[7,8] However, upon comparison with widely investigated hetero/homotrinuclear compounds based on salen-type symmetric di-Schiff base ligands,[9−14] trinuclear compounds containing acacen-type symmetric di-Schiff base ligands [sy-H$_2$L^2 = H$_2$acacen = bis(acetylacetone)ethylenediamine)] have not been reported to date and probably derive from this type of Schiff base ligand usually involving imino ($-CH_2-C{=}N-$), carbonyl [$-CH_2-C({=}O)-$], or enol [$-CH{=}C(R)-OH$] groups and the assembly of the metal

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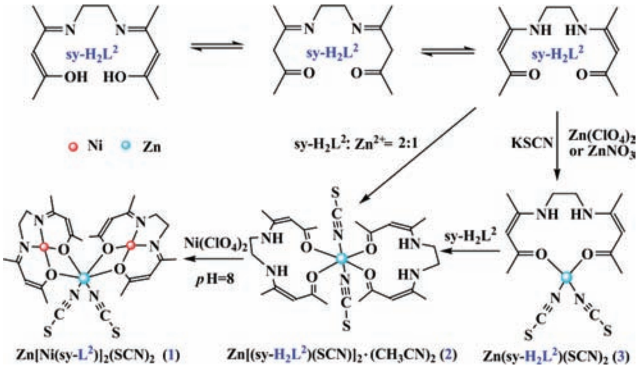
Scheme 1. Assembly Strategies of Compounds **1**−**3** Containing a Tetradentate N_2O_2 Schiff Base



complexes easily affected by external physical or chemical stimuli.[15]

As part of our ongoing study of metal complexes of the multifunctional Schiff base, herein we report the assembly of a novel Zn−Ni heterotrinuclear complex $\{(Zn[Ni(sy\text{-}L^2)]_2(SCN)_2\}$ (**3**) from $Zn[(sy\text{-}H_2L^2)(SCN)]_2\cdot(CH_3CN)_2$ (**2**). To the best of our knowledge, complex **2** is the first selective fluorescent chemosensor for the Ni^{2+} ion, and the resulting complex **3** represents the first trinuclear complex based on a symmetric acacen base Schiff base ligand.

The symmetrical Schiff base ligand bis(acetylacetone)ethylenediamine (sy-H_2L^2) was synthesized by condensation of the corresponding ethylenediamine with acetylacetone at room temperature in methanol. The resulting crystalline yellow solid was sy-H_2L^2.[16] In principle, compounds containing the imino ($-CH_2-C{=}N-$), carbonyl [$-CH_2-C({=}O)-$], or enol [$-CH{=}C(R)-OH$] groups are capable of exhibiting keto/enol tautomerism in solution. Therefore, the present Schiff base sy-H_2L^2 can exist either as a keto or an enol or as an equilibrium mixture of both forms (Scheme 1).[17] Thus, when *keto*-sy-H_2L^2 reacts with $Zn(ClO_4)_2$ or $Zn(NO_3)_2$ and KSCN in a 1:1:2 ratio, colorless crystals of $Zn(sy\text{-}H_2L^2)(SCN)_2$ (**1**)[18] were obtained. With an increase in the amount of metal-to-ligand ratio to 1:2, complex **2**[18] was obtained. Further, upon adjustment of the pH of the reaction mixture to 8, complex **2** in the presence of $Ni(ClO_4)_2$ results in complex **3**.[18] Interestingly, by investigating the fluorescence properties of complexes **1** and **2**, we found that only complex **2** shows selectivity toward Ni^{2+}. This could be due to the effective incorporation of a nickel ion in the cavity of complex **2** and the formation of a stable complex **3**, which is strong evidence for complex **2** as a nickel-ion-selective luminescent probe (Scheme 1).

Single-crystal X-ray analysis on complex **1** (Figure 1) shows that the asymmetric unit contains one neutral ligand sy-H_2L^2, one Zn^{2+} ion, and two N-terminal coordinated SCN^- anions. The Zn^{II} ion displays distorted tetrahedral coordination with two O atoms from the same Schiff base ligand sy-H_2L^2 and two N atoms from two terminal SCN^- anions. The Zn−O distances range from 1.934(9) to 1.985(9) Å and the Zn−N distances from 1.917(14) to 1.948(14) Å (Table S1 in the Supporting Information, SI). Because the Schiff base ligand sy-H_2L^2 is capable of exhibiting keto/enol tautomerism in solution, the intramolecular hydrogen bonds in **1** will contribute to an increase in the rigidity of the molecular conformation. If the weak intermolecular Zn···S interaction of 3.940 Å is considered, the coordination geometry around the Zn atom is best regarded as a distorted octahedron, with two O atoms occupying two axial positions. The two-dimensional layer of complex **1** is assembled through Zn···S interactions (Figure S1 and Table S2 in the SI).

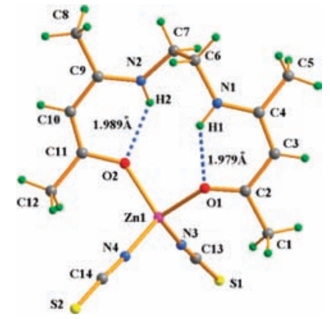


Figure 1. Molecular structure of **1** with atomic labels. The dashed lines denote the intramolecular hydrogen-bond (blue) N−H···O interactions.

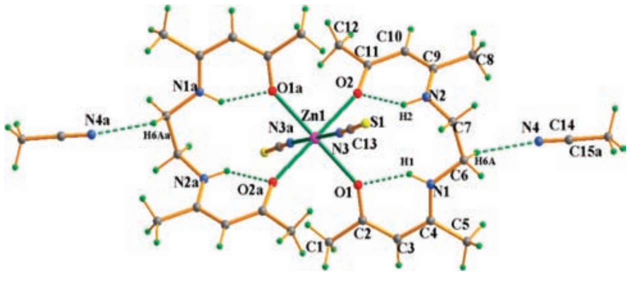


Figure 2. Molecular structure of complex **2** with atomic labels. Symmetric code: a, $1-x, 1-y, 1-z$. The dashed lines denote hydrogen-bond (green) N−H···O and C−H···N interactions.

Similar crystallographic analysis on complex **2** suggests a centrosymmetric framework consisting of two neutral sy-H_2L^2 ligands, two N-terminal SCN^- anions, one Zn^{2+} ion, and two solvent CH_3CN molecules. Compared to complex **1**, the Zn^{2+} ion in **2** is six-coordinated by four O atoms from two neutral ligands sy-H_2L^2 and two N atoms from two N-terminal SCN^- anions, in which the coordination geometry around the Zn ion can be regarded as octahedral with two N atoms in two axial positions (Figure 2 and Table S1 in the SI). Similar to complex **1**, intramolecular hydrogen bonds N−H···O in ligand sy-H_2L^2 of **2** accompanied by hydrogen bonds between solvent CH_3CN and ligand sy-H_2L^2 molecules contribute to the stability of the structure (Table S2 in the SI).

The asymmetric unit of complex **3**, shown in Figure 3, contains two independent heterotrinuclear Ni_2Zn molecules associated with intermolecular hydrogen bonds C−H···S, in which each Zn atom (Zn1/Zn2) is six-coordinated by four O atoms from two *cis*-*O*,*O*′-[Ni(sy-L^2)] building block units and two N atoms from two terminal SCN^- anions with a distorted octahedral environment, while each Ni atom (Ni1, Ni2, Ni3, and Ni4) is four-coordinated with a square-planar environment. The Zn−O distances range from 2.208(3) to 2.310(3) Å and the Zn−N distances from 2.089(4) to

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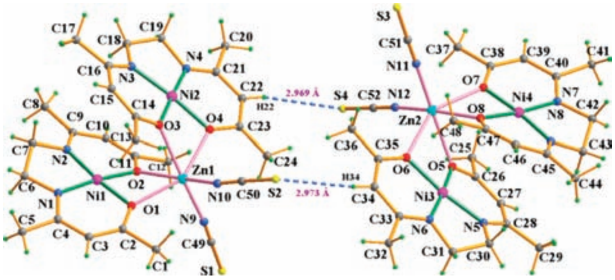

Figure 3. Molecular structure of trinuclear compound **3** with the atom-numbering scheme. The dashed lines denote the intermolecular hydrogen-bond (blue) C$-$H$\cdots$S interactions.

2.129(5) Å. The Ni$-$O distances range from 1.852(4) to 1.883(4) Å and the Ni$-$N distances from 1.825(4) to 1.874(4) Å. The Ni$-$Zn$-$Ni angles range from 80.63(3) to 81.45° (Table S2 in the SI), close to the Ni$-$Ni$-$Ni angles of 87.88° and 85.52° in the homotrinuclear [{Ni(Salpen)}$_2$Ni(NCS)$_2$] and [{Ni(Salen)}$_2$Ni(NCS)$_2$] reported by Ghosh (Salpen = *N*,*N*′-bis(salicylidene)-1,3-propanediamine, Salen = *N*,*N*′-bis(salicylidene)-1,3-pentanediamine).[19] After a complete survey of the related literature, we found that complex **3** is the first example of a trinuclear complex based on an acacen-type di-Schiff base ligand. Moreover, the trinuclear units in **3** pack alongside each other to give a three-dimensional supramolecular network (Figure S2 in the SI) in the *bc* plane by intermolecular hydrogen-bond C$-$H$\cdots$S interactions (Table S3 in the SI).

The fluorescence properties of the Schiff base ligand (sy-H_2L^2) and the three zinc(II) complexes **1**$-$**3** were studied at room temperature (298 K) in an *N*,*N*-dimethylformamide (DMF) solution (10^{-5} mol/L; Figure S3 in the SI). From Figure S3 in the SI, the emission spectra of complexes **1**$-$**3** resemble that of the ligand sy-H_2L^2 excluding peak positions (for **1** and **2**) and the emission intensity (for **1**$-$**3**), indicating the fluorescence emission spectra of these complexes. The structures of complexes **1** and **2** in the solid state are different; however, their intensity and emission peak positions (with λ_{max} = 361 and 363 nm upon excitation at 293 and 295 nm for **1** and **2**, respectively) are close to each other in a DMF solution. Compared with the emission spectra of the ligand sy-H_2L^2 (with λ_{max} = 450 nm upon excitation at 293 nm) and complex **3** (with λ_{max} = 446 nm upon excitation at 293 nm), the larger blue shifts of ca. 89 and 87 nm for the two complexes **1** and **2** have been given, which are considered to mainly arise from different existing modes of the ligand sy-H_2L^2 in the corresponding complexes (Scheme 1). Moreover, the incorporation of a Zn^{II}/Ni^{II} ion effectively increases the conformational rigidity of the ligand sy-H_2L^2/(sy-$L^2)^{2-}$ in the three compounds **1**$-$**3** and reduces the loss of energy via vibrational motions. Thus, the enhanced fluorescence intensities of the three complexes are detected, which open up the opportunity for photochemical applications of these complexes.[20]

Interestingly, the emission intensity of compound **2** increased gradually upon the addition of 1$-$3 equiv of Ni^{2+} ($NiCl_2$) with respect to **2**. To further understand this phenomenon, the same experiments were performed for the introduction of Cu^{2+} ($CuCl_2$), Mn^{2+} ($MnCl_2$), Ni^{2+} ($NiCl_2$), Al^{3+} ($AlCl_3$), K^+(KCl), Cd^{2+} ($CdCl_2$), Mg^{2+} ($MgCl_2$), and Na^+ (NaCl) into the system (Figure 4). When 1$-$3 equiv of Cu^{2+}, Mn^{2+}, Al^{3+}, K^+, Mg^{2+}, Cd^{2+}, and Na^+ were added to the DMF solution of **2**, the luminescent intensity decreased. These results suggest that complex **2** shows selectivity toward Ni^{2+}, and they can be considered as selective luminescent probes for the Ni^{2+} ion.

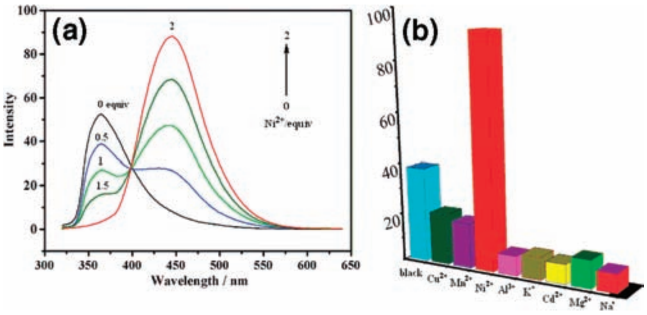

Figure 4. (a) Emission spectra of **2** in DMF (10^{-3} M) at room temperature (excited at 295 nm) in the presence of ~1$-$2 equiv of Ni^{2+} ions with respect to **2**: black, no addition; blue, 0.5 equiv; bright green, 1 equiv; green, 1.5 equiv; red, 2 equiv. (b) Luminescent intensity of compound **2** in DMF at room temperature with the addition of Ca^{2+}, Mn^{2+}, Ni^{2+}, Al^{3+}, K^+, Cu^{2+}, and Na^+ ions (excited at 295 nm).

To further support our evidence of the structural integrity of complex **2** in solution control experiments, in which the same amount of $NiCl_2$ was added to a solution of complex **1** in DMF, however, the luminescent intensity did not change significantly (Figure S4 in the SI). The result indicates that **2** does not decompose into a smaller discrete unit, namely, complex **1**, and retains its zero-dimensional structure in DMF. Considering two O and two N atoms from the same ligand sy-H_2L^2, this may create a favorable coordination environment for Ni^{2+} in complex **2** at pH = 8. At the same time, to confirm our hypothesis, the experiment of the reaction of complex **2** with $NiCl_2$ in a DMF solution was repeated several times, and finally the corresponding single crystal of **3** with an incorporated Ni^{2+} ion was obtained (Figure 3), which clearly explains the binding mode between molecule **2** and the Ni^{2+} ion.

In summary, on the basis of different ratios of ligand to metal ion, the two mononuclear zinc compounds **1** and **2** containing a N_2O_2-donor tetradentate symmetrical Schiff base ligand H_2L^2 have been synthesized at room temperature and structurally characterized. Fluorescent experimental results reveal that complex **2** shows selectivity toward Ni^{2+} and can be considered as a selective luminescent probe for the Ni^{2+} ion, which is further supported by the single-crystal structure of the resulting compound **3** explaining the binding mode between the sensor molecule **2** and the Ni^{2+} ion. Meanwhile, compound **3** also represents the first trinuclear compound based on a symmetric acacen base Schiff base ligand.

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Supporting Information Available: Synthesis, crystal data in Tables S1$-$S4, and additional Figures S1$-$S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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