Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 8051–8053 **8051**
DOI: 10.1021/ic9007944

Salen-Based [Zn_2Ln_3] Complexes with Fluorescence and Single-Molecule-Magnet Properties

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Received April 24, 2009

A family of four isostructural complexes with a V-shaped pentanuclear [Zn_2Ln_3] core of general formula [$Zn_2Ln_3(m\text{-salen})_3(N_3)_5(OH)_2$] [$Ln^{III} = Tb^{III}$ (**1**), Eu^{III} (**2**), Ho^{III} (**3**), Dy^{III} (**4**); m-salen = *N*,*N*′-ethylenebis(3-methoxysalicylideneamine)] were isolated and structurally characterized. The fluorescence and magnetic measurements of the four compounds were investigated. Complex **1** exhibits strong fluorescence properties, while single-molecule-magnet behavior is seen in complex **4**.

The development of lanthanide cluster chemistry has been largely stimulated by the recent discovery of lanthanide-based single-molecule magnets (SMMs).[1] Such nanoscale molecules exhibit slow relaxation of the magnetization and thus act as magnets at low temperatures.[2] This superparamagnet-like behavior generally results from the presence of the large spin ground state (S_T) and Ising-type magnetoanisotropy (D) in those systems.[2] The large amount of spin and spin−orbit coupling present in certain lanthanide (Ln) ions (i.e., Tb^{III}, Dy^{III}, or Ho^{III}) makes them attractive for use in SMMs.[1a−d] However, isolation of Ln-based SMMs proves a difficult challenge because the magnetic 4f orbitals of the Ln ions are less accessible than the d orbitals and interactions between spin carriers are therefore rather weak. One way to overcome this challenge is to promote stronger interactions between the Ln ions via overlapping bridging ligand orbitals. Moreover, the use of 3d metal systems in combination with 4f ions has been shown to yield better interactions between the spin carriers, thus producing unique SMMs.[1f,g]

In addition to their intriguing magnetic properties, lanthanide molecules also exhibit desirable fluorescence properties because of the long lifetime of emission and thus have potential for application in immunoassays, protein labeling, and NMR imaging.[3] Because f−f transitions are parity forbidden, Ln ions have low absorption coefficients.[4] As a result, much research is focused on using organic ligands as sensitizers/chromophores for fluorescence enhancement.[5] Multidentate salen-type Schiff base ligands are ideal for the chelation/encapsulation of Ln^{III} ions because they prevent coordination of solvent molecules, which tend to quench fluorescence.[6] In addition, such ligands tend to absorb the energy and transfer it efficiently to the metal ions, potentially enhancing the luminescent properties. Furthermore, salen-type ligands [i.e., *N*,*N*′-ethylenebis(3-methoxysalicylideneamine), H_2m-salen (see Figure S1 in the Supporting Information)] have been used in the study of magnetic interactions between heteronuclear metal centers.[7] Such compartmental ligands with inner (O, N, N, O) and outer (O, O, O, O) coordination pockets of different size and “hardness” are

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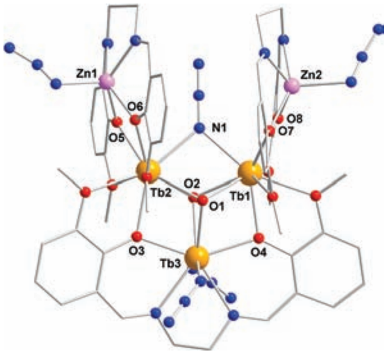

Figure 1. Partially labeled crystal structure of [$Zn_2Tb_3(OH)_2(N_3)_5$(m-salen)$_3$] (**1**) with H atoms omitted for clarity.

known to promote encapsulation of transition-metal (TM) and Ln^{III} ions. Hence, dinuclear TM−Ln^{III} complexes have been engineered using such ligand systems.[7]

By including potentially bridging azide ligands and basic conditions in our synthetic strategy, we have produced larger m-salen-based TM−Ln^{III} complexes with unique physical properties. Herein, we report the synthesis, structure, and fluorescence and magnetic properties of four pentanuclear [Zn_2Ln_3] complexes with an unprecedented V-shaped core.

To a solution of H_2m-salen (1 equiv), NaN_3 (3 equiv), and NEt_3 (2 equiv) in MeOH/MeCN (2:20 mL/mL) were added $ZnCl_2$ (1 equiv) and $Ln(NO_3)_3 \cdot H_2O$ (1 equiv) (Ln = Tb^{III}, Eu^{III}, Ho^{III}, and Dy^{III}) with stirring. After 1 h, the filtrate was allowed to crystallize at room temperature by slow evaporation. Four isostructural pentanuclear complexes of general formula [Zn_2Ln_3(m-salen)$_3(N_3)_5(OH)_2$] [Ln = Tb^{III} (**1**), Eu^{III} (**2**), Ho^{III} (**3**), Dy^{III} (**4**)] were obtained in 45−55% yield.[8]

All [Zn_2Ln_3] complexes are isostructural to the [Zn_2Tb_3] complex **1**, which is described below. Complex **1** crystallizes in space group $P\bar{1}$ and can be described as a V-shaped molecule. It consists of three m-salen ligands coordinated to two Zn^{II} ions in the inner pocket and three Tb^{III} ions (one in the inner pocket and two in the outer pocket) (Figure 1). The central, triangular [Tb_3] core is reminiscent of reported [Ln_3] complexes.[1c,9]

The two μ_3-OH ions lie 1.20/1.17 Å above/below the triangular plane and bridge all three Ln ions. The Tb···Tb separations are within a 3.57−3.67 Å range. The five metal centers are encapsulated by three m-salen ligands with one bridging and four terminal azido anions filling the remaining coordination environments, thus shielding them from potentially coordinating solvent molecules. Close inspection of the packing arrangement reveals that all [Zn_2Tb_3] molecules stack vertically along the *a* axis and horizontally along the *b* axis (see Figures S2 and S3 in the Supporting Information), with a Tb···Tb distance of 12.24 Å between adjacent molecules.

The use of NEt_3 is critical for the formation of this large complex because it serves to deprotonate the H_2m-salen ligand and promote the formation of the μ_3-OH bridges from H_2O molecules introduced by the starting metal salts. When other divalent TMs (M^{II}) such as Ni^{II}, Co^{II}, and Cu^{II} were employed instead of Zn^{II}, known dinuclear M^{II}Na complexes were isolated.[10]

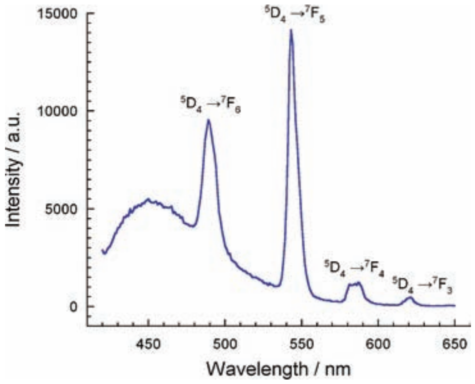

Figure 2. Solution emission spectrum of **1** in $CHCl_3$ excited at 400 nm.

Solid-state and solution luminescence studies of the four [Zn_2Ln_3] complexes revealed that the [Zn_2Tb_3] complex, **1**, exhibits fluorescence properties, as shown in Figures 2 and S4 in the Supporting Information.[11]

The emission spectrum of 0.024 g of complex **1** in 8 mL of $CHCl_3$ excited at 400 nm exhibits a broad peak at 460 nm, assigned to the fluorescence of zinc,[12] a well-defined peak at 492 nm, a sharp, high-intensity peak at 545 nm, and low-intensity peaks at 585 and 620 nm that are characteristic of Tb^{III} ions and are due to the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$ and $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$ transitions, respectively.[4] Such a long lifetime of emission of Tb^{III} ions is owed to the presence of the encapsulating m-salen ligands because the Tb^{III} ions are indirectly excited by the aromatic chromophore. It is noteworthy that the emission spectrum of the [Zn_2Eu_3] complex is rather weak (see Figure S5 in the Supporting Information); the energy level of the lowest triplet state of the ligand is closer to the energy of the emitting level of Eu^{III} than to that of Tb^{III}.[13] This leads to fast relaxation of the Eu^{III} ions via the competitive thermal relaxation pathway and thus the absence of significant fluorescence for the [Zn_2Eu_3] complex.

The direct-current (dc) magnetic susceptibilities for **1**−**4** were measured at 1000 Oe in the 1.8−300 K temperature range (see Figure S6 in the Supporting Information), and the observed paramagnetism arises uniquely from the 4f Ln^{III} ions because Zn^{II} metal ions are diamagnetic. At 300 K, the χT values of complexes **1**−**4** are 41.4, 4.1, 39.9, and 39.1 cm^3 K mol^{-1}, respectively. These values are reasonably close to the theoretical values (**1**, 35.4 cm^3 K mol^{-1}; **3**, 42.2 cm^3 K mol^{-1}; **4**, 42.5 cm^3 K mol^{-1}) for three of the isolated Ln ions: Tb^{III} ($^7F_6$), Ho^{III} ($^5I_8$), and Dy^{III} ($^6H_{15/2}$), respectively. Although **2** is expected to possess a diamagnetic ground state based on the presence of two Zn^{II} ions and three Eu^{III} ions (S = 0, $^7F_0$),[14] the χT product at 300 K of 4.14 cm^3 K mol^{-1} indicates that the compound is paramagnetic. The paramagnetism is likely induced by the presence of thermally populated excited states of the Eu^{III} ions that are magnetically active, while the ground state is diamagnetic. Indeed, the small χT product of 0.04 cm^3 K mol^{-1} at 1.8 K is

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[8] See the Supporting Information for X-ray data.

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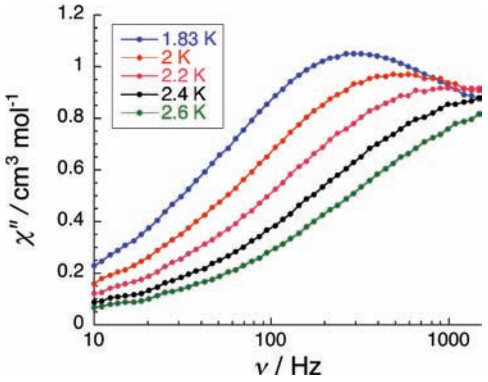

Figure 3. Frequency dependence of the out-of-phase ac susceptibility for **4** between 10 and 1000 Hz at $H_{dc} = 0$ Oe.

in good agreement with a diamagnetic ground state of **2**. As the temperature is decreased, the χT product of **1**, **3**, and **4** also decreases, suggesting the possible presence of intramolecular antiferromagnetic interactions between spin carriers. However, it should be noted that the thermal depopulation of the Ln^{III} excited states might also be partially or totally responsible for the rapid decrease of the χT product. It is therefore difficult to establish in a definitive manner the nature of intracomplex magnetic interactions. At lower temperatures, χT further decreases to reach 25.8, 18.0, and 11.6 cm^3 K mol^{-1} at 1.8 K for **1**, **3**, and **4**, respectively.

As seen in Figures S7−S10 in the Supporting Information, the field dependence of the magnetization below 8 K is not saturating even at 7 T for **1**−**4**. The main origin of this field behavior is certainly the presence of weak intramolecular antiferromagnetic interactions between Ln^{III} ions that makes the low-lying excited states accessible, even at 1.8 K, by applying a magnetic field. The presence of magnetic anisotropy is also likely to contribute to this lack of magnetization saturation. Although hysteresis effects have not been observed in the M vs H data above 1.8 K for these complexes, alternating-current (ac) susceptibility measurements were performed to probe the SMM properties.

For **1**−**3**, no out-of-phase ac signal was detected above 1.8 K; however, a frequency dependence of the ac susceptibility with a characteristic frequency of 280 Hz at 1.8 K is observed for **4**, indicating slow relaxation of the magnetization (see Figures 3 and S11 in the Supporting Information). This relaxation mode was followed by an increase in the temperature up to 2.6 K in order to determine the temperature dependence of the characteristic relaxation time. The relaxation time deduced from this data is consistent with an activated behavior (see Figure S12 in the Supporting Information), with an energy gap of 13.4 K and a preexponential factor, τ_0, of about 3.3×10^{-7} s.

Because of the fact that slow relaxation of the magnetization is experimentally observed only over a short range of temperature and frequency, the estimation of these characteristic parameters has a similar magnitude to other lanthanide-based SMM systems. It is worth mentioning that the ac data have also been recorded under small dc fields in order to suppress possible fast zero-field relaxation (see Figures S13 and S14 in the Supporting Information). Unfortunately, the relaxation time above 1.8 K stays unchanged under this magnetic field condition.

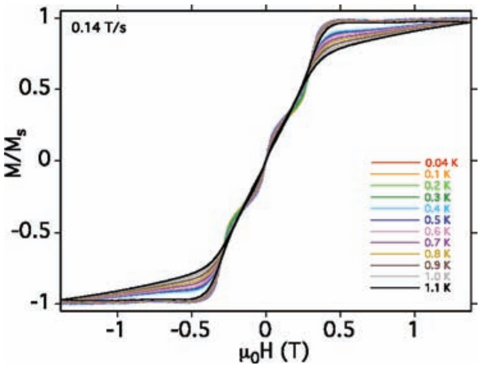

Figure 4. Magnetization (M) vs applied dc field sweeps for **4** at the indicated sweep rate and temperatures. M is normalized to its saturation value, M_s, at 1 T.

To further investigate the low-temperature behavior of complex **4**, single-crystal dc relaxation measurements were carried out on a micro-SQUID[15] in the temperature range 1.1−0.04 K (Figure 4). Below 1.1 K, unusual three-step shaped hysteresis loops were seen with a small opening. The shape of the loops are reminiscent of the reported Dy_3 system,[1c,1d] and steps are further accentuated upon cooling. For such Dy_3 systems, the shape and positioning of the steps generally originate from the weak exchange interactions and also depend on the orientation of the applied field in relation to the plane of the Dy_3 triangle. The latter plane was reported to be the easy plane of the magnetization, where the magnetic moments of the Dy^{III} centers are arranged in a toroidal fashion.[1c,1d] Below 0.4 K, the loops become temperature-independent, confirming the SMM behavior of **4** with very slow zero-field relaxation.

In conclusion, a structurally unique family of large penatanuclear $[Zn_2Ln_3]$ complexes of the m-salen ligand was isolated and characterized. Despite being isostructural, members of this family of $[Zn_2Ln_3]$ molecules demonstrate assorted physical properties; the Tb system was shown to exhibit fluorescence, while the Dy analogue shows slow relaxation of the magnetization, as seen in SMMs.

Acknowledgment. This work was supported by NSERC, CFI, FFCR, and the University of Ottawa. We thank Prof. T. Scaiano and his group for help with fluorescence measurements.

Supporting Information Available: Additional structural and magnetic data (Figures S1−S14) and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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