

Multinuclear Luminescent Schiff-Base Zn–Nd Sandwich Complexes

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Multinuclear 3d–4f complexes with sandwichlike molecular structures are formed with the Schiff-base ligand bis-(3-methoxysalicylidene)ethylene-1,2-phenylenediamine(H₂L). The stoichiometry and structures are dependent on the Zn:Nd ratio and counteranions present. They are trinuclear [Nd(ZnL)₂(NO₃)₂(H₂O)₂]·NO₃·EtOH·H₂O (**1**), [Nd-(ZnL)₂Cl₂(H₂O)₃]·Cl·2MeOH·5H₂O (**2**), and tetranuclear [Nd₂(ZnL)₂Cl₆(MeOH)₂]·MeOH (**3**). Dinuclear complex [NdZnL-(NO₃)₃MeCN]·MeCN (**4**) was also characterized. Near-infrared (NIR) lanthanide luminescence is observed in these complexes.

Introduction

Lanthanide(III) ions are often employed in probes for studies of biological systems as well as for the preparation of new materials because of their spectroscopic and magnetic properties.¹ Recently, there has been increased interest in the design of complexes with lanthanide ions that emit in the near-infrared (NIR) region (Yb³⁺, Nd³⁺, Er³⁺) because of their potential for use in fluoroimmunoassays, laser systems, and optical amplification.² For the lanthanide(III) ions, the f–f transitions are parity forbidden and the absorption coefficients are often very low. This has led to the use of suitable chromophores, which are used as sensitizers that can transfer energy to the lanthanide ions,

resulting in efficient emission (the antenna effect). There are now a number of reports on the use of organic dyes and 3d transition-metal complexes that absorb in the near-UV and visible ranges as sensitizers for the NIR luminescence of lanthanide(III) ions.³

Our studies have recently focused on the use of compartmental Schiff-base ligands designed to bind both 3d and 4f metal ions.⁴ These hetero-bimetallic systems were originally developed by Costes and co-workers in order to study magnetic properties. However, there have been relatively few reports on the luminescence properties of this class of compounds.⁵ Previous studies from our research groups have shown that various Zn(II) salen type Schiff-base complexes can act as sensitizers for NIR lanthanide luminescence.^{4,6} Of related interest is our recent report on two luminescent

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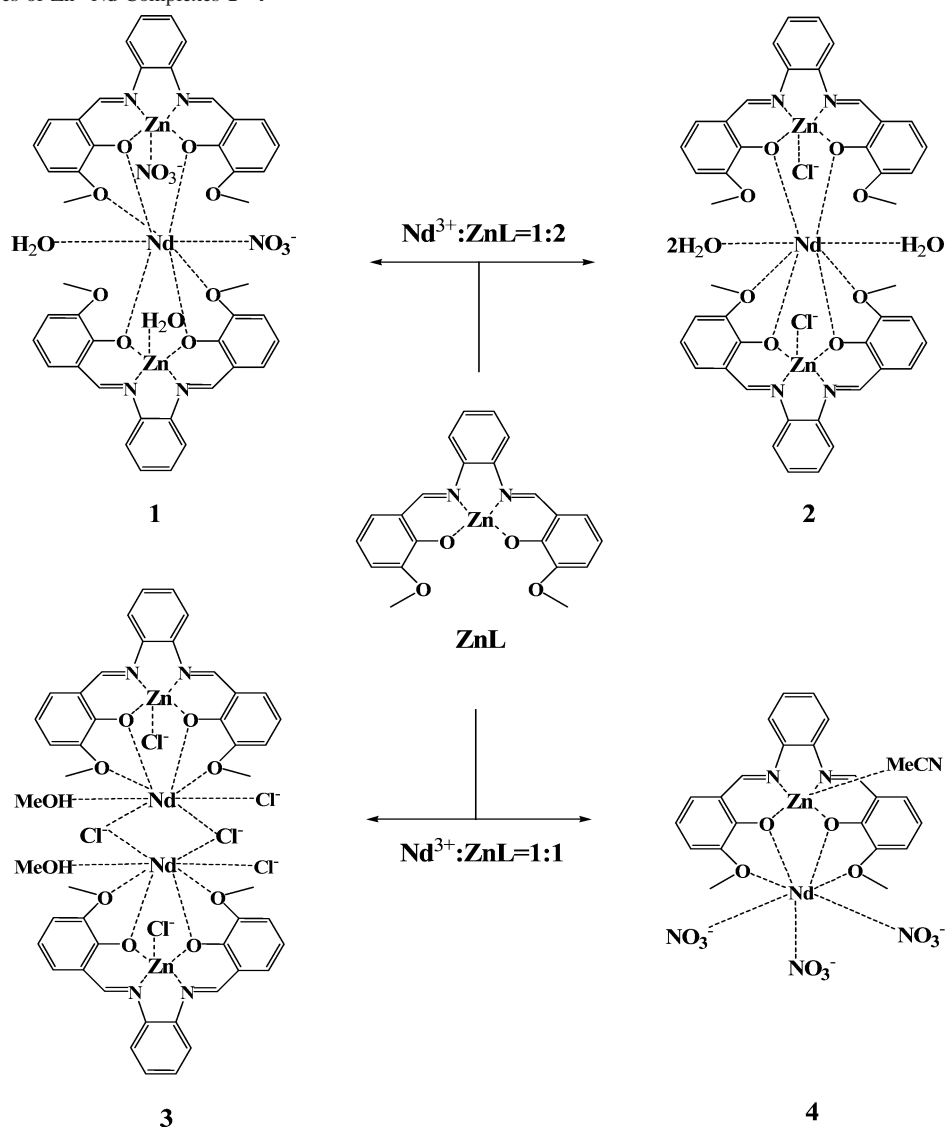
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Scheme 1. Syntheses of Zn–Nd Complexes 1–4



multidecker Tb(III) complexes, in which aromatic moieties of salen type ligands form π – π stacked structures.⁷ Other studies have also demonstrated that chromophoric ligands in multidecker frameworks can isolate centrally located Ln(III) ions from solvent molecules and thus enhance the emission properties.⁸ In this paper, we report the synthesis and structures of four luminescent multinuclear Zn–Nd Schiff-base complexes (Scheme 1). Whereas most 3d–4f salen type complexes have relatively simple dinuclear cores, two of the compounds (**1** and **2**) described here have novel π -stacked double-decker structures. Comparative photophysical studies support the idea that a π -stacked multidecker ligand arrangement helps to enhance luminescence properties over those of simple dinuclear Zn–Nd complexes such as **4**.

Experimental Section

All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. Metal salts, ethanol, acetonitrile, and methanol were purchased from Aldrich. Solvents for the photophysical investigations were dried over molecular sieves and freshly distilled under dry nitrogen before use. The Zn(II) complex ZnL was prepared from the Schiff base H₂L and Zn(OAc)₂·2H₂O as previously described.^{4,11} Physical measurements were taken by MS-ESI and MS-FAB using a Finnigan MAT TSQ 700 instrument. NMR readings were completed on a Varian 300 Unity Plus spectrometer (¹H, 300 MHz) at 298 K (chemical shifts referenced to the deuterated solvent). IR spectra were recorded on a Nicolet IR 200 FTIR spectrometer and UV–visible spectra were recorded on a Beckman DU 640 spectrophotometer. Microanalytical data (C, H, N) were obtained on **1–4**; however, data were inconsistent, possibly because of the variable loss of solvent molecules that occurred once the compounds were isolated. Melting

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points were obtained in sealed glass capillaries under dinitrogen and are uncorrected. Photoluminescence measurements were made at room temperature with a one-meter SPEX 1704 spectrometer and a liquid-nitrogen-cooled Ge detector. The excitation was provided by an argon ion laser using either the UV multiline optics (333.6–363.8 nm range) or the laser line at 300.0 nm.

[Nd(ZnL)₂(NO₃)₂(H₂O)₂]·NO₃·EtOH·H₂O (1). A solution of ZnL (0.044 g, 0.10 mmol) in ethanol (10 mL) was added to a solution of Nd(NO₃)₃·6H₂O (0.022 g, 0.05 mmol) in ethanol (10 mL), and the mixture was stirred and heated under reflux (30 min). The solution was then cooled to room temperature and filtered. Volatile materials were removed under reduced pressure to give the crude product in ca. 90% yield. Pale yellow, X-ray quality crystals of **1** were obtained after 3 weeks by allowing the reaction mixture to evaporate in the air. Yield: 0.034 g (52%). Mp: >286 °C (dec). ESI-MS (MeOH) *m/z*: 1183 [*M* – NO₃[–] – EtOH – H₂O]⁺. ¹H NMR (400 MHz, CD₃OD): δ –4.162 (1H), –0.260 (3H), –0.026 (2H), 1.144 (1H), 1.197 (1H), 2.023 (3H), 3.187 (1H), 3.515 (1H), 4.438 (3H), 4.684 (2H), 5.394 (2H), 5.742 (1H), 6.211 (2H), 6.257 (2H), 6.458 (2H), 7.883 (1H), 8.144 (2H), 10.872 (3H), 13.231 (2H), 13.444 (1H). IR (CH₃OH, cm^{–1}): 3496 (s), 2960 (m), 1646 (s), 1637 (s), 1455 (m), 1406 (m), 1245 (w), 1117 (w), 1035 (s), 619 (m). UV–vis (CH₃OH, 25 °C; λ_{max} (nm)): 307, 344.

[Nd(ZnL)₂Cl₂(H₂O)₃]·Cl·2MeOH·5H₂O (2). A solution of ZnL (0.044 g, 0.10 mmol) in 2:1 MeOH:MeCN (15 mL) was added to a solution of NdCl₃·6H₂O (0.018 g, 0.05 mmol) in MeOH (10 mL). The mixture was heated under reflux (30 min), allowed to cool to room temperature, and filtered. Volatile materials were removed under reduced pressure to give the crude product in ca. 90% yield. Yellow, X-ray quality crystals of **1** were obtained after 2 weeks by allowing the reaction mixture to evaporate in the air. Yield: 0.026 g (40%). Mp: >285 °C (dec). ESI-MS (MeOH) *m/z*: 1112 [*M* – Cl[–] – 2MeOH – 6H₂O]⁺. IR (CH₃OH, cm^{–1}): 3412 (s), 2946 (s), 2835 (m), 1655 (s), 1641 (s), 1448 (m), 1416 (m), 1112 (w), 1033 (s), 620 (m). UV–vis (CH₃OH, 25 °C; λ_{max} (nm)): 235, 302, 350.

[Nd₂(ZnL)₂Cl₆(MeOH)₂]·MeOH (3). A solution of NdCl₃·6H₂O (0.036 g, 0.10 mmol) in MeOH (10 mL) was added to a solution of ZnL (0.044 g, 0.10 mmol) in 2:1 MeOH:MeCN (15 mL). The mixture was stirred and heated under reflux for 20 min. The solution was then allowed to cool to room temperature and was filtered. Volatile materials were removed under reduced pressure to give the crude product in ca. 90% yield. X-ray quality crystals were obtained by allowing diethyl ether to diffuse slowly into the solution in a sealed container. Yellow single crystals of **3** were formed after two weeks. Yield: 0.024 g (32%). Mp: >235 °C (dec). ESI-MS (MeOH) *m/z* (%): 1377 [*M* – Cl[–] – 2MeOH]⁺. IR (CH₃OH, cm^{–1}): 3400 (s), 2945 (m), 2829 (m), 2053 (w), 1652 (s), 1638 (s), 1451 (m), 1404 (m), 1116 (w), 1030 (s), 622 (m). UV–vis (CH₃OH, 25 °C; λ_{max} (nm)): 305, 351.

[NdZnL(NO₃)₃MeCN]·MeCN (4). A solution of Nd(NO₃)₃·6H₂O (0.044 g, 0.10 mmol) in MeOH (10 mL) was added to a solution of ZnL (0.044 g, 0.10 mmol) in 2:1 MeOH:MeCN (15 mL). The mixture was stirred and heated under reflux for 30 min. The solution was allowed to cool to room temperature and was filtered. Volatile materials were removed under reduced pressure to give the crude product in ca. 90% yield. X-ray quality crystals were obtained by allowing diethyl ether to diffuse slowly into the solution in a sealed container. Yellow single crystals of **4** were obtained after two weeks. Yield: 0.049 g (58%). Mp: >277 °C (dec). ESI-MS (MeOH) *m/z*: 707 [*M* – NO₃[–] – 2MeCN]⁺. IR (CH₃OH, cm^{–1}): 3438 (s), 2969 (m), 1650 (s), 1638 (s), 1566 (m),

1479 (m), 1457 (m), 1290 (m), 1119 (w), 619 (m), 578 (m). UV–vis (CH₃OH, 25 °C; λ_{max} (nm)): 236, 307, 345.

X-ray Crystallography. Data were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 153 K. Absorption corrections were applied using GAUSSIAN. The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX97 program package.⁹ The coordinates of the non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.¹⁰

Results and Discussion

Solutions of the Schiff-base complex ZnL^{4,11} were treated with salts of Nd(III) under reflux, followed by slow evaporation of the solvent or slow diffusion of diethyl ether in sealed containers. The reactions proceed in ca. 30 min, and high yields of the crude products can be obtained by evaporation of the solvent under a vacuum. X-ray quality crystalline materials were obtained after several weeks by allowing the reaction mixtures to evaporate in the air or via the diffusion of diethyl ether into the reaction mixtures in sealed containers (Scheme 1). Using a 2:1 Zn:Nd molar ratio produced trimetallic Zn₂Nd complexes with both Nd(NO₃)₃·6H₂O and NdCl₃·6H₂O (**1** and **2**). When a 1:1 Zn:Nd molar ratio was employed, the nuclearity of the complex isolated was dependent on the salt used. Thus, NdCl₃·6H₂O gave a tetrametallic Zn₂Nd₂ complex **3**, whereas the nitrate salt afforded the simple heterodinuclear Zn–Nd complex **4**. The X-ray structures of **1–4** were determined, and details of crystallographic parameters, data collection, and refinements are listed in Table 1. See the Supporting Information for crystallographic data for compounds **1–4** in CIF format. Selected bond lengths and angles for **1–4** are given in Tables 2–5, respectively. Views of the two trinuclear Zn₂Nd complexes **1** and **2** are shown in Figures 1 and 2, respectively. In **1**, the two Zn²⁺ ions are bound to the inner N₂O₂ cores of the two Schiff-base ligands and have distorted square pyramidal geometries. For Zn(1), the axial site is occupied by the oxygen atom of an NO₃[–] group, whereas Zn(2) bears a H₂O molecule in this position. The zinc atoms lie slightly above their respective N₂O₂ planes (Zn(1), 0.579 Å; Zn(2), 0.575 Å). The Nd³⁺ ion is sandwiched between the two ZnL units, which are virtually parallel to each other. The Nd–Zn distances are similar (Zn(1), 3.526 Å; Zn(2), 3.561 Å). The Nd³⁺ center is nine-coordinate, surrounded by nine oxygen atoms; four are from phenolic groups, two from methoxy groups, two from a bidentate nitrate ligand, and one from a water molecule. A third NO₃[–] group is present in the crystal lattice but is not within bonding distance of any of the metals.

The reaction of ZnL with NdCl₃·6H₂O instead of the nitrate salt used for **1** produces **2**, which has an overall structure similar to that of **1** (Figure 2). The Zn²⁺ ions in **2** have square-based pyramidal geometries but are now further removed from their N₂O₂ planes vs **1** (Zn(1), 0.690 Å; Zn(2), 0.774 Å). Each Zn²⁺ also bears a chloride ligand in an axial position. A third Cl[–] anion is present in the unit cell but is not coordinated. For **2**, the position of the Nd³⁺ ion is

Table 1. Crystal Data and Structure Refinement for Complexes 1–4

	1	2	3	4
formula	C ₄₆ H ₄₈ N ₇ NdO ₂₁ Zn ₂	C ₄₆ H ₆₀ Cl ₃ N ₄ NdO ₁₈ Zn ₂	C ₄₇ H ₄₈ Cl ₆ N ₄ Nd ₂ O ₁₁ Zn ₂	C ₂₆ H ₂₄ N ₇ NdO ₁₃ Zn
fw	1309.89	1338.35	1476.81	852.13
cryst syst	monoclinic	orthorhombic	triclinic	orthorhombic
space group	<i>P</i> 2(1) <i>c</i>	<i>P</i> 2(1)2(1)2(1)	<i>P</i> 1	<i>P</i> na2(1)
<i>a</i> (Å)	14.0805(9)	13.271(3)	13.516(3)	9.5124(19)
<i>b</i> (Å)	13.9988(9)	13.470(3)	14.284(3)	16.439(3)
<i>c</i> (Å)	26.2151(17)	31.170(6)	14.358(3)	19.317(4)
α (deg)	90	90	82.55(3)	90
β (deg)	100.2770(10)	90	76.20(3)	90
γ (deg)	90	90	72.59(3)	90
<i>V</i> (Å ³)	5084.4(6)	5571.8(19)	2563.7(9)	3020.7(11)
<i>Z</i>	4	2	2	4
<i>D</i> _{calcd} (g cm ⁻³)	1.711	1.612	1.913	1.874
<i>T</i> (K)	293(2)	153(1)	153(1)	153(1)
<i>F</i> (000)	2644	2748	1456	1692
μ (mm ⁻¹)	2.03	1.988	3.292	2.573
θ range (deg)	1.58–27.50	2.91–25.00	2.93–25.00	3.25–27.50
no. of reflns measured	28 889	8403	16 810	6482
no. of reflns used	11 322	6977	8976	5406
no. of params	694	646	654	439
R ^a (<i>I</i> > 2σ(<i>I</i>))	0.0367	0.0729	0.0508	0.0341
wR2 ^a (<i>I</i> > 2σ(<i>I</i>))	0.0954	0.1762	0.1084	0.0760
R1 ^a (all data)	0.0557	0.0936	0.1049	0.0501
wR2 ^a (all data)	0.1024	0.1874	0.1277	0.0824
<i>S</i>	0.978	1.062	1.036	1.024

^a R1 = $\sum |F_o| - |F_c| / \sum |F_o|$, wR2 = $[\sum w[(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Nd(1)–O(1)	2.380(2)	O(2)–Nd(1)–O(3)	118.56(8)
Nd(1)–O(2)	2.406(2)	O(1')–Nd(1)–O(3)	162.77(8)
Nd(1)–O(1')	2.407(2)	O(2')–Nd(1)–O(3)	105.34(7)
Nd(1)–O(2')	2.520(2)	O(1)–Nd(1)–O(3')	176.26(9)
Nd(1)–O(3)	2.807(3)	O(2)–Nd(1)–O(3')	112.80(8)
Nd(1)–O(3')	2.934(3)	O(1')–Nd(1)–O(3')	56.14(7)
Zn(1)–O(2)	1.996(2)	O(2')–Nd(1)–O(3')	111.30(8)
Zn(1)–O(1)	2.012(2)	O(3)–Nd(1)–O(3')	120.67(8)
Zn(1)–N(1)	2.028(3)	O(2)–Zn(1)–O(1)	81.26(10)
Zn(1)–N(2)	2.048(3)	O(2)–Zn(1)–N(1)	149.40(11)
Zn(2)–O(1')	2.004(2)	O(1)–Zn(1)–N(1)	89.19(11)
Zn(2)–O(2')	2.012(2)	O(2)–Zn(1)–N(2)	89.00(11)
Zn(2)–N(2')	2.038(3)	O(1)–Zn(1)–N(2)	144.05(11)
Zn(2)–N(1')	2.075(3)	N(1)–Zn(1)–N(2)	81.83(12)
O(1)–Nd(1)–O(2)	66.09(8)	O(1')–Zn(2)–O(2')	82.30(9)
O(1)–Nd(1)–O(1')	125.87(8)	O(1')–Zn(2)–N(2')	143.11(11)
O(2)–Nd(1)–O(1')	74.95(8)	O(2')–Zn(2)–N(2')	91.19(11)
O(1)–Nd(1)–O(2')	72.21(8)	O(1')–Zn(2)–N(1')	88.26(10)
O(2)–Nd(1)–O(2')	79.64(8)	O(2')–Zn(2)–N(1')	151.21(11)
O(1')–Nd(1)–O(2')	64.84(7)	N(2')–Zn(2)–N(1')	80.20(11)
O(1)–Nd(1)–O(3)	58.52(8)		

not as symmetrical as that found in **1** (Zn(1)–Nd, 3.530 Å; Zn(2)–Nd, 3.455 Å). The Nd³⁺ ion in **2** is again nine-coordinate, being bound to six oxygen atoms from two L ligand and three water molecules. Despite the fact that the structures of **1** and **2** have a Nd³⁺ ion sandwiched between two ZnL moieties, the planar aromatic groups of each ligand are sufficiently close to each other to assume that there is appreciable aromatic π – π stacking present in both molecules. Thus for example, in **1**, the N(2)–N(2') distance is 3.388 Å, and the shortest distance between aryl units in **2** is 3.498 Å. The dihedral angles between the heterocyclic rings of the L groups themselves range from 11.6 to 17.9° in **1** and **2**.

By changing the Zn:Nd ratio in the synthesis to 1:1, we were able to prepare two additional complexes. Reaction of NdCl₃·6H₂O with ZnL under conditions similar to those used for **1** and **2** gave the tetranuclear complex [Nd₂(ZnL)₂Cl₆–

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

Nd(1)–O(2')	2.326(4)	O(3')–Nd(1)–O(4')	61.79(16)
Nd(1)–O(3')	2.336(5)	O(2)–Nd(1)–O(4')	139.72(16)
Nd(1)–O(2)	2.341(4)	O(3)–Nd(1)–O(4')	87.93(15)
Nd(1)–O(3)	2.415(5)	O(2')–Nd(1)–O(1')	60.83(14)
Nd(1)–O(4')	2.590(5)	O(3')–Nd(1)–O(1')	120.63(15)
Nd(1)–O(1')	2.759(5)	O(2)–Nd(1)–O(1')	69.22(15)
Zn(1)–O(3)	2.048(4)	O(3)–Nd(1)–O(1')	127.05(14)
Zn(1)–N(2)	2.079(5)	O(4')–Nd(1)–O(1')	144.85(15)
Zn(1)–O(2)	2.084(4)	O(3)–Zn(1)–N(2)	86.5(2)
Zn(1)–N(1)	2.090(6)	O(3)–Zn(1)–O(2)	78.43(18)
Zn(2)–O(3')	1.986(5)	N(2)–Zn(1)–O(2)	137.2(2)
Zn(2)–O(2')	2.041(4)	O(4')–Zn(1)–N(1)	140.8(2)
Zn(2)–N(1')	2.044(5)	N(2)–Zn(1)–N(1)	78.9(2)
Zn(2)–N(2')	2.051(6)	O(2)–Zn(1)–N(1)	88.0(2)
O(2')–Nd(1)–O(3')	65.62(15)	O(3')–Zn(2)–O(2')	77.70(18)
O(2')–Nd(1)–O(2)	85.51(15)	O(3')–Zn(2)–N(1')	142.3(2)
O(3')–Nd(1)–O(2)	129.99(16)	O(2')–Zn(2)–N(1')	87.7(2)
O(2')–Nd(1)–O(3)	87.82(15)	O(3')–Zn(2)–N(2')	88.7(2)
O(3')–Nd(1)–O(3)	72.11(17)	O(2')–Zn(2)–N(2')	140.8(2)
O(2)–Nd(1)–O(3)	66.60(15)	N(1')–Zn(2)–N(2')	81.0(2)
O(2')–Nd(1)–O(4')	125.87(16)		

(MeOH)₂·MeOH (**3**) in 32% yield. The use of Nd(NO₃)₃·6H₂O under similar conditions gave the simple heterodinuclear complex [NdZnL(NO₃)₃MeCN]·MeCN (**4**). The structure of **3** is shown in Figure 3 and comprises two ZnNdL units linked together by two bridging chlorine atoms bound to both Nd³⁺ ions. The Zn²⁺ and Nd³⁺ ions in **3** are located in the inner N₂O₂ and O₂O₂ cavities of each Schiff-base ligand. Each Nd³⁺ ion is eight-coordinate from four oxygen atoms of L, three chlorides, and one methanol molecule. The Zn–Nd distances are 3.479 and 3.504 Å for Zn(1) and Zn(2), respectively. These distances are comparable to the Zn–Nd separation in **4** (3.493 Å) and to those in Zn–Nd Schiff-base complexes previously reported.^{4,6} The Nd–Nd separation is 4.477 Å, which effectively rules out the possibility of any π – π stacking between the aromatic groups of the ligands. As found in **2**, the Zn²⁺ ions in **3** have square pyramidal geometries, with chlorine atoms occupying the

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**

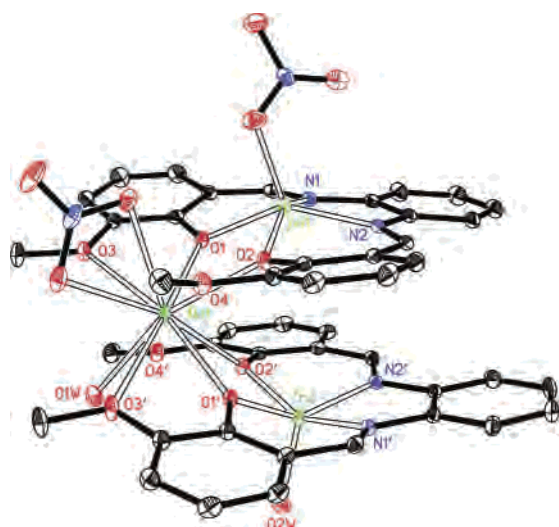
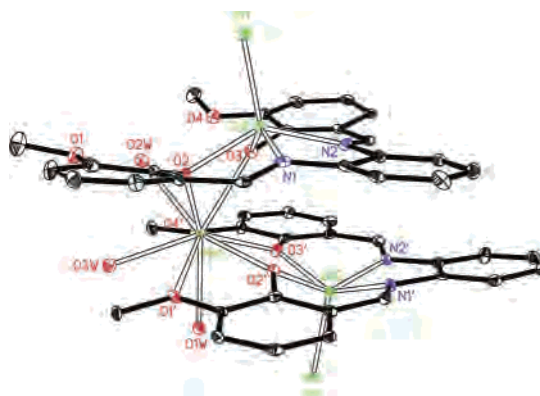
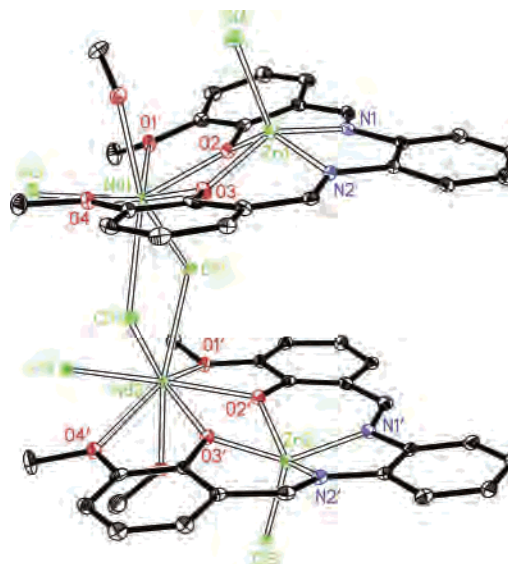
Nd(1)–O(3)	2.268(6)	O(2)–Nd(1)–O(1)	62.27(19)
Nd(1)–O(2)	2.309(6)	O(4)–Nd(1)–O(1)	144.57(19)
Nd(1)–O(4)	2.645(6)	O(3')–Nd(2)–O(2')	65.6(2)
Nd(1)–O(1)	2.659(6)	O(3')–Nd(2)–O(4')	61.81(19)
Nd(2)–O(3')	2.293(6)	O(2')–Nd(2)–O(4')	123.4(2)
Nd(2)–O(2')	2.299(6)	O(3')–Nd(2)–O(1')	124.66(19)
Nd(2)–O(4')	2.658(6)	O(2')–Nd(2)–O(1')	61.43(19)
Nd(2)–O(1')	2.668(6)	O(4')–Nd(2)–O(1')	145.84(18)
Zn(1)–N(1)	2.027(7)	N(1)–Zn(1)–O(3)	141.8(3)
Zn(1)–O(3)	2.027(6)	N(1)–Zn(1)–O(2)	88.2(3)
Zn(1)–O(2)	2.029(6)	O(3)–Zn(1)–O(2)	76.6(2)
Zn(1)–N(2)	2.049(7)	N(1)–Zn(1)–N(2)	81.5(3)
Zn(2)–N(1')	2.027(7)	O(3)–Zn(1)–N(2)	88.1(3)
Zn(2)–O(3')	2.032(6)	O(2)–Zn(1)–N(2)	140.2(3)
Zn(2)–O(2')	2.032(6)	N(1')–Zn(2)–O(3')	141.0(3)
Zn(2)–N(2')	2.054(7)	N(1')–Zn(2)–O(2')	89.2(3)
O(3)–Nd(1)–O(2)	66.6(2)	O(3')–Zn(2)–O(2')	75.5(2)
O(3)–Nd(1)–O(4)	62.19(19)	N(1')–Zn(2)–N(2')	80.9(3)
O(2)–Nd(1)–O(4)	122.99(19)	O(3')–Zn(2)–N(2')	88.9(3)
O(3)–Nd(1)–O(1)	127.31(19)	O(2')–Zn(2)–N(2')	141.2(3)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **4**

Nd(1)–O(2)	2.411(3)	O(3)–Nd(1)–O(1)	122.92(10)
Nd(1)–O(3)	2.421(3)	O(2)–Nd(1)–O(4)	122.57(10)
Nd(1)–O(1)	2.625(3)	O(3)–Nd(1)–O(4)	60.66(9)
Nd(1)–O(4)	2.645(3)	O(1)–Nd(1)–O(4)	149.59(11)
Zn(1)–O(2)	1.991(3)	O(2)–Zn(1)–O(3)	80.48(13)
Zn(1)–O(3)	1.995(3)	O(2)–Zn(1)–N(2)	147.04(14)
Zn(1)–N(2)	2.025(4)	O(3)–Zn(1)–N(2)	91.78(13)
Zn(1)–N(1)	2.040(4)	O(2)–Zn(1)–N(1)	91.20(14)
O(2)–Nd(1)–O(3)	64.40(10)	O(3)–Zn(1)–N(1)	152.87(14)
O(2)–Nd(1)–O(1)	60.99(10)	N(2)–Zn(1)–N(1)	81.22(14)

axial positions. The structure of **4** is similar to those found in analogous complexes (Figure 4).^{4,5} The Zn²⁺ ion has a molecule of MeCN coordinated in an axial position, whereas the 10-coordinate Nd³⁺ ion is surrounded by four ligand (L) oxygen atoms and six oxygens from three bidentate NO₃[−] groups. In all complexes, the Schiff-base ligands are essentially planar, with the dihedral angles between three heterocyclic rings ranging from 11.3 to 31.1°.

Spectroscopic Studies. The ¹H NMR spectrum of **1** in CD₃OD at 298 K shows 20 signals corresponding to two complexed Schiff base ligands (Figure S1). These signals remain unchanged over a two-week period, indicating that

**Figure 1.** View of the molecular structure of **1**. H atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 25% probability level.**Figure 2.** View of the NdZn₂ core of **2**. H atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 25% probability level.**Figure 3.** View of the molecular structure of **3**. H atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 25% probability level.

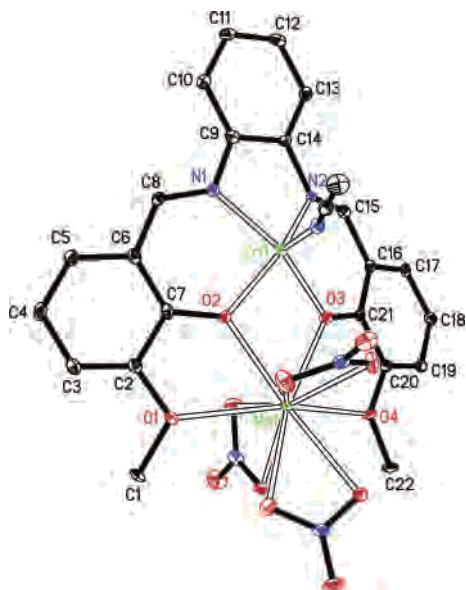
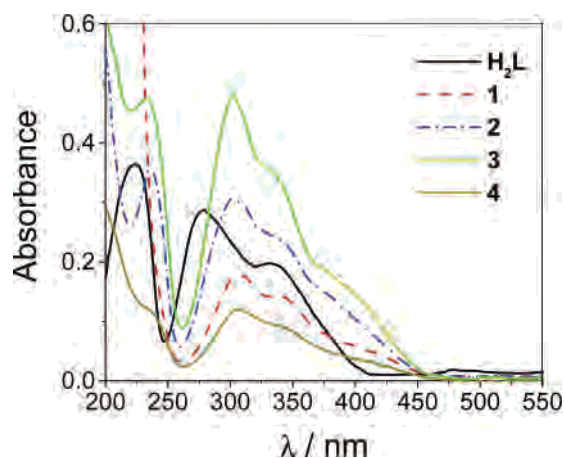
the sandwich structure is stable in this solvent. In MeOH, the free ligand H₂L exhibits absorption bands at 223, 279, and 331 nm in the UV–vis spectrum. These bands are red-shifted on metal-ion coordination in all four of the complexes (Figure 5). Ligand-centered absorption properties of complexes **1–4** in CH₃OH are listed in Table 6. Complexes **1–3** show higher molar absorption coefficients than **4**. Excitation of the ligand-centered absorption bands resulted in Nd³⁺ NIR emission bands assigned to the ⁴F_{3/2} → ⁴I_{j/2} (*j* = 9, 11, 13) transitions. The emission spectra of **1** and **4** are shown in Figure 6. Emissions near 876 and 905 nm are assigned to ⁴F_{3/2} → ⁴I_{9/2}, near 1066 nm to ⁴F_{3/2} → ⁴I_{11/2} and near 1355 nm to ⁴F_{3/2} → ⁴I_{13/2} transitions.

We were interested in the influence of structural differences in these complexes on their photophysical properties. However, the complexes have different structures, stoichiometries, and types of ancillary ligands (e.g., H₂O, NO₃[−], Cl[−], MeCN); therefore, direct comparison of their photophysical properties will be less meaningful than if they were all structurally similar. We used solutions with their concentrations adjusted to give the same absorbance values at 300 nm; the relative emission intensities near 1066 nm for **1** and **4** in CH₃OH and CH₃OD are listed in Table 6 (λ_{ex} =

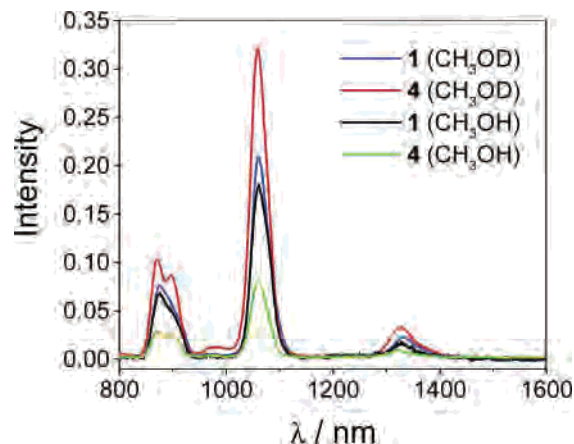
Table 6. Ligand-Centered Absorption Properties of Complexes **1–4** in CH₃OH and Relative Emission Intensities (*I*) near 1066 nm^a for Complexes **1** and **4** in CH₃OH and CH₃OD at 298 K

complex	λ_{\max} (nm) (ϵ (M ⁻¹ cm ⁻¹))	<i>I</i> in CH ₃ OH	<i>I</i> in CH ₃ OD
1	307 (35580), 340 (28260, sh)	2.3	2.6
2	236 (44400), 302 (38210), 338 (29910, sh)		
3	233 (43150), 301 (43650), 350 (25760, sh)		
4	235 (19930, sh), 306 (20130), 350 (13790, sh)	1	3.9

^a The concentrations were adjusted to give the same absorbance value at 300 nm for **1** and **4** in CH₃OH and CH₃OD ($\lambda_{\text{exc}} = 300$ nm).

**Figure 4.** View of the molecular structure of **4**. H atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 25% probability level.**Figure 5.** UV-vis spectra of free H₂L and complexes **1–4** in CH₃OH. (Concentrations: 1×10^{-6} to 1×10^{-5} M).

300 nm). In CH₃OH, we note that **1** has better luminescence than **4** despite the fact that it has a coordinated H₂O molecule. This may be due to the fact that **1** contains two chromophores vs one in **4**, which could increase the rate of energy-transfer processes in **1**. Interestingly the relative emission intensity of **1** is similar in CH₃OH and CH₃OD (2.3 vs 2.6), whereas for **4**, the relative emission intensity is much higher in CH₃

**Figure 6.** NIR luminescence of **1** and **4** in CH₃OH and CH₃OD at room temperature with the same absorbance value at 300 nm (λ_{exc}).

OD vs CH₃OH (3.9:1). Thus in CH₃OD, the relative emission intensities of **1** and **4** are reversed. Conductivity studies showed that **4** is a 1:1 electrolyte in CH₃OH, which suggests the loss of NO₃⁻ from the Nd³⁺ ion. This dissociation could allow the coordination of solvent in **4**, and the luminescence would be less in CH₃OH.¹² The data suggest that interactions with solvent (methanol) are not as important in the photochemical processes in **1** as they are in **4**.

Conclusions

A series of four multinuclear Zn–Nd Schiff-base complexes have been prepared and their structures determined and photophysical properties examined. The stoichiometry and structures of these complexes are dependent on the Zn:Nd ratio employed in their syntheses as well as the nature of the anion present (Cl⁻ vs NO₃⁻). Studies show that the photochemical properties of these complexes are dependent on their structures as well as the solvents employed.

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Supporting Information Available: ¹H NMR spectrum of **1** in CD₃OD; X-ray crystallographic data for **1–4** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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