DOI: 10.1002/ejic.200500699

Self-Assembly and Characterization of Homo- and Heterodinuclear Complexes of Zinc(II) and Lanthanide(III) Ions with a Tridentate Schiff-Base Ligand

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Keywords: Dinuclear complexes / Lanthanides / Tridentate Schiff-base ligand / Self-assembly / Zinc

Tridentate Schiff-base ligand H**L** (L = $C_{12}H_9N_2O$) reacts with lanthanide(III) nitrates to give complexes of formulae [M_2**L**$_3(NO_3)_3$], where M = Y^{3+} (**1**), La^{3+} (**2**), Nd^{3+} (**3**), Sm^{3+} (**4**), Eu^{3+} (**5**), Gd^{3+} (**6**), Tb^{3+} (**7**), Dy^{3+} (**8**), Ho^{3+} (**9**), Lu^{3+} (**10**), and [MM^1**L**$_3(NO_3)_x$], where M = Eu^{3+}, and M^1 = Dy^{3+} (**11**), Zn^{2+} (**12**); x = 3 for **11** and 2 for **12**. The structures of the complexes have been assigned on the basis of the spectroscopic data (solution analysis) and microanalyses. In the case of complexes **3**, **5**, **8** and **12** the structures have been confirmed by X-ray crystallography. The structural analysis of the dinuclear complexes showed the presence of two metal atoms [M(1) and M(2)] and three ligands, **L**. Each lanthanide atom is coordinated to by 9 donor atoms with typical Ln–N and Ln–O distances. Zinc(II) is coordinated to by two oxygen atoms and four nitrogen atoms from two ligands. The metal ions are bridged by the phenoxo oxygen atoms of the ligands. We have obtained a heterodinuclear complex by a rapid one-step reaction. Quantum mechanical calculations indicated that the formation of heterodinuclear complex **12** is slightly favored energetically over the homodinuclear complex **5**.
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Introduction

Schiff-base ligands with N,O-donor sets may be employed in the metal ion directed assembly of coordination architectures.[1,2] These ligands are fascinating and versatile complexing agents because their metal complexes are known to serve as luminescent probes in the visible and near-IR spectral domains,[3,4] as precursors for doped materials where the metal centers must be at fixed distances from each other, as catalysts for specific DNA[5] and RNA[6] cleavage reactions, and as analytical sensors for the in vivo mapping of Ca^{2+} concentration.[7,8] The complexes of paramagnetic ions have been tested as contrast enhancement agents, especially the complexes of gadolinium(III).[9–15] Dinuclear lanthanide complexes are continuing to attract considerable research interest due to their potential biological,[16–18] medical,[19] chemical and technological importance.[20] A dinuclear terbium(III) complex containing phthalocyanines is very good example of the effect of f-f interactions on dynamic magnetism.[21,22]

There is increasing interest in heterometallic 3d-4f complexes because of their magnetic[23,24] and luminescent properties.[25–29] Thermodynamic assembly processes lead to the strongly luminescent triple-helical heterodinuclear complexes of lanthanides (Ln = La to Lu) and zinc.[30,31] Dinuclear d-f complexes with Schiff-base ligands have been reported.[32–34] A novel synthetic approach for a $(3d)_2(4f)$ heterotrinuclear complex by transmetallation has been described.[35] We have obtained the heterodinuclear complex by a rapid one-pot reaction.

In view of the successful synthesis of the Zn^{II}, Cd^{II},[36] and Mn^{II} [37] complexes with H**L** (Figure 1), we attempted to prepare an analogous series of lanthanide complexes. Previously obtained complexes with zinc and cadmium had the M/L stoichiometry of 1:2. However, all of the syntheses that we attempted using lanthanides resulted in compounds with a M/L stoichiometry of 2:3 in the solid state, which was confirmed by X-ray analyses of complexes **3**, **5**, **8**, and **12**. The ESI-MS spectra of all the complexes included the [M**L**$_2$]$^{n+}$ and [**L**]$^+$ signals, which means that in solution significant dissociation of the M_2L_3 complexes to mononulcear species and ligand molecules occurs. We also performed quantum mechanical calculations to gain an insight into the factors that affect the stability of heterodinuclear and homodinuclear complexes.

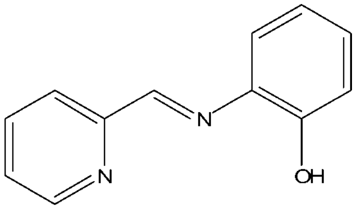

Figure 1. Structure of ligand H**L** – (*E*)-2-[(pyridin-2-yl)methyleneamino]phenol.

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Herein we report that our investigations into the lanthanide coordination chemistry of the ligand H**L** have successfully demonstrated that this ligand is able to form novel dinuclear complexes. We describe and compare the structures of the complexes formed.

Results and Discussion

Synthesis and Characterization of the Complexes

Schiff-base ligands with N,O-donor type sets have been employed infrequently in the metal ion directed assembly of coordination architectures.[38] Ligand H**L** leads to the generation of $[M_2L_3(NO_3)_3]$, where M = Y^{3+} (**1**), La^{3+} (**2**), Nd^{3+} (**3**), Sm^{3+} (**4**), Eu^{3+} (**5**), Gd^{3+} (**6**), Tb^{3+} (**7**), Dy^{3+} (**8**), Ho^{3+} (**9**), Lu^{3+} (**10**), and $[MM^1L_3(NO_3)_x]$, where M = Eu^{3+}, M^1 = Dy^{3+} (**11**), Zn^{2+} (**12**); x = 3 for **11** and 2 for **12**. The structures of the complexes have been assigned on the basis of the spectroscopic data (solution analysis), microanalyses, and in the case of complexes **3**, **5**, **8** and **12**, confirmed by X-ray crystallography.

ESI-MS is a highly sensitive and accurate analytical tool widely used for the characterization of large charged biomolecules, such as proteins and DNA. The technique has also been found to be particularly suited for the identification of large metallosupramolecular architectures present in solution, in which multiply charged ions are generated by the sequential loss of counterions resulting in characteristic isotopic patterns in the spectrum.[39] The ESI-MS investigations were performed with the complexes dissolved in acetonitrile at an approx concentration of 10^{-4} M. For the samarium(III) complex (**4**) the ESI mass spectrum showed a mixture of the following complexes: 1171 (5%) $[Sm_2L_3(NO_3)_3(H_2O)_5 + H]^+$, 1153 (5%) $[Sm_2L_3(NO_3)_3(H_2O)_4 + H]^+$, 546 (100%) $[SmL_2]^+$, 450 (30%) $[SmL(NO_3)(H_2O)_2]^+$, 413 (5%) $[SmL(NO_3)]^+$, 341 (5%) $[Sm_2L(NO_3)_3]^{2+}$, 253 (5%) $[Sm_2L_2(NO_3)]^{3+}$, 199 (20%) $[L]^+$. This result confirmed the previously observed behavior of lanthanide complexes in solution.[40]

Crystallographic Characterization of Complexes 3, 5, 8, and 12

Crystals of complexes **3**, **5**, **8**, and **12** were obtained by diffusion of diethyl ether into a solution of the complex in acetonitrile. Compounds **3** (Figure 2), **5**, and **8** are isostructural. In all three complexes both lanthanide ions are nine-coordinate, albeit unsymmetrically; one of the ions is coordinated by two ligand molecules and one nitrate ion, while the other lanthanide ion binds to one ligand and two nitrate ions. The ligand molecules are tridentate, and they coordinate to the metal ions by the pyridine nitrogen atom N1, the N8 atom and by the hydroxy oxygen atom. The latter bridges the two metal ions. The bond lengths and angles are quite typical. There are also molecules of solvent (acetonitrile) in the crystal structures. In the mixed complex **12** (Figure 3), the Eu^{III} ion is nine-coordinate, while the Zn^{II} ion is six-coordinate and has distorted octahedral geometry.

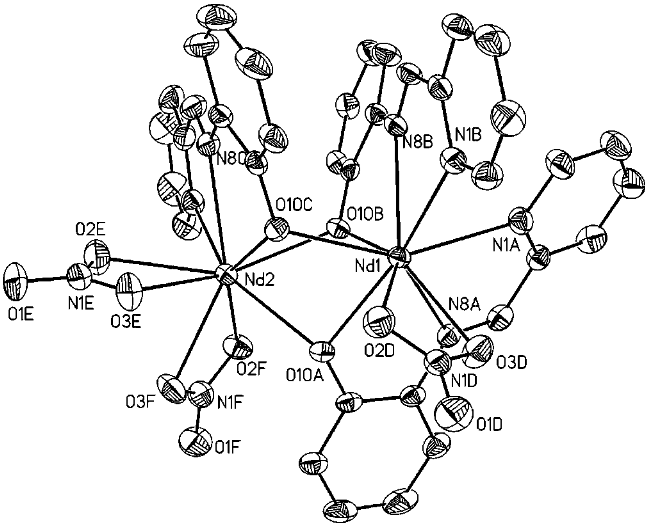

Figure 2. Anisotropic-ellipsoid representation of molecule **3** together with numbering scheme. The ellipsoids are drawn at the 50% probability level; hydrogen atoms are represented by spheres of arbitrary radii.

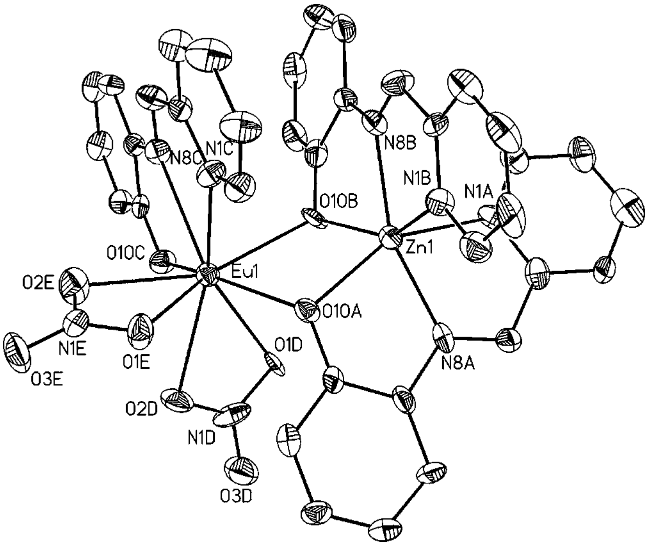

Figure 3. Anisotropic-ellipsoid representation of molecule **12** together with numbering scheme. The ellipsoids are drawn at the 50% probability level; hydrogen atoms are represented by spheres of arbitrary radii.

Stability of Heterodinuclear and Homodinuclear Complexes

In order to assess the energy difference between heterodinuclear complex **12** and homodinuclear complex **5**, the energetics of the *fictitious* reaction of complex **12** with $Zn(NO_3)_2$, leading to the complex **5** with $Eu(NO_3)_3$, was calculated. Table 1 presents absolute energies for these species calculated with a SDD basis set. The energy difference between the species on both sides of the fictitious reaction is small, about 1.8 kcal/mol, and favours the reaction leading to the heterodinuclear complex. This seems to indicate that the formation of the heterodinuclear Eu/Zn complex **12** is slightly preferred over the formation of the homodinuclear complex **5**, due to larger energy gain and thus larger thermodynamic stability of the complex **12**. This is further supported by an experimental observation – the heterodinuclear complex **12** is formed in a rapid one-step reaction.

Table 1. Absolute energies (in Hartrees) for the species involved in the fictitious reaction connecting complexes **5** and **12**.

Molecule	Energy
$[Eu_2L_3(NO_3)_3]$	–1779.179268
$Zn(NO_3)_2$	–342.946213
$[EuZnL_3(NO_3)_2]$	–1238.050066
$Eu(NO_3)_3$	–884.078243

Conclusions

We were able to synthesize homo- and heterodinuclear zinc(II) and lanthanide(III) complexes comprising a tridentate Schiff-base ligand. The complexes were characterized in solution by ESI-MS spectroscopy. The molecular structures of complexes **3**, **5**, **8**, and **12** were investigated by X-ray crystallography, which confirmed that the coordination number is 9 for the lanthanide(III) ions, and 6 for the zinc(II) ions. Quantum mechanical calculations indicated that energetic factors slightly favour the formation of heterodinuclear as opposed to homodinuclear complexes, at least for Eu and Zn. The present results provide a facile and rapid synthetic protocol for the preparation of heterodinuclear complexes by a one-pot reaction.

In conclusion, the investigated complexes may be of use in several fields of lanthanide coordination chemistry, in nanotechnology, and as functional components of molecular electronic devices. Hydroxo-bridged Zn complexes are attractive because of their potential relevance as models for sugar-metabolizing enzymes.[41]

Experimental Section

General: CH_3CN was freshly distilled under argon over CaH_2. Ligand H**L** was prepared according to a published method.[37,42] The metal salts were used as supplied by Aldrich without further purification. Mass spectra were recorded by a Waters Micromass ZQ spectrometer in positive-ion mode. The samples were dissolved in acetonitrile (10^{-4} mol dm^{-3}). Sample solutions were introduced into the mass spectrometer source with a syringe pump at flow rate of 40 μL min^{-1} with a capillary voltage of +3 kV, and a desolvation temperature of 300 °C. The source temperature was 120 °C. The cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation occuring. Scanning was performed from *m/z* = 200 to 1000 for 6 s, and 10 scans were summed to obtain the final spectrum. Microanalyses were obtained using a Perkin–Elmer 2400 CHN microanalyzer. IR spectra were obtained with a Perkin–Elmer 580 spectrophotometer, and are reported in cm^{-1}.

Y Complex (1): A mixture of $Y(NO_3)_3{\cdot}6H_2O$ (40 mg, 0.1 mmol) and ligand H**L** (40.0 mg, 0.2 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The red solution was evaporated under reduced pressure to give complex **1** as an orange solid in quantitative yield. ESI-MS: *m/z* = 893 (5%) $[Y_2\mathbf{L}_3(NO_3)_2]^+$, 483 (100%) $[Y\mathbf{L}_2]^+$, 366 (25%) $[Y\mathbf{L}(NO_3)(H_2O)]^+$, 348 (45%) $[Y\mathbf{L}(NO_3)]^+$, 288 (75%) $[Y_2\mathbf{L}(NO_3)_3(H_2O)]^{2+}$, 199 (5%) $[\mathbf{L}]^+$. IR (KBr $[\text{cm}^{-1}]$): ṽ = 3609 (OH), 3210 (OH), 3066 (CH arom), 3029 (CH imin), 1733 (NO_3^-), 1652 (CN), 1596 (py), 1587 (py), 1489 (py), 1470 (py), 1384 (NO_3^-), 1299 (py), 1272 (py), 1153 (py), 1032 (py), 870 (OH), 809 (NO_3^-), 750 (py), 592 (py), 536 (py). $Y_2(\mathbf{L})_3(NO_3)_3{\cdot}H_2O$ (973.48): calcd. C 44.25, H 3.00, N 12.95; found C 44.13, H 2.98, N 12.87.

La Complex (2): A mixture of $La(NO_3)_3{\cdot}6H_2O$ (44 mg, 0.1 mmol) and ligand H**L** (40.0 mg, 0.2 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The orange solution was evaporated under reduced pressure to give complex **2** as a yellow solid in quantitative yield. ESI-MS: *m/z* = 533 (100%) $[La\mathbf{L}_2]^+$, 466 (20%) $[La_2\mathbf{L}_3(NO_3)]^{2+}$, 398 (20%) $[La\mathbf{L}(NO_3)]^+$, 290 (10%) $[La_2\mathbf{L}_3]^{3+}$, 199 (5%) $[\mathbf{L}]^+$. IR (KBr $[\text{cm}^{-1}]$): ṽ = 3421 (OH), 3066 (CH arom), 3021 (CH imin), 1638 (CN), 1586 (py), 1567 (py), 1552 (py), 1486 (py), 1470 (py), 1451 (py), 1384 (NO_3^-), 1300 (py), 1265 (py), 1180 (py), 1148 (py), 868 (OH), 801 (NO_3^-), 748 (py), 587 (py), 526 (py). $La_2(\mathbf{L})_3(NO_3)_3{\cdot}H_2O$ (1073.48): calcd. C 40.28, H 2.72, N 11.74; found C 40.27, H 2.63, N 11.57.

Nd Complex (3): A mixture of $Nd(NO_3)_3{\cdot}6H_2O$ (45 mg, 0.1 mmol) and ligand H**L** (40.0 mg, 0.2 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The orange solution was evaporated under reduced pressure to give complex **3** as a yellow solid in quantitative yield. ESI-MS: *m/z* = 1138 (5%) $[Nd_2\mathbf{L}_3(NO_3)_3{\cdot}4H_2O]^+$, 1004 (10%) $[Nd_2\mathbf{L}_3(NO_3)_2]^+$, 540 (50%) $[Nd\mathbf{L}_2]^+$, 471 (20%) $[Nd_2\mathbf{L}_3(NO_3)]^{2+}$, 199 (35%) $[\mathbf{L}]^+$, 155 (100%) $[Nd_2\mathbf{L}(NO_3)(H_2O)]^{4+}$. IR (KBr $[\text{cm}^{-1}]$): ṽ = 3591 (OH), 3382 (OH), 3061 (CH arom), 3020 (CH imin), 1728 (NO_3^-), 1588 (py), 1569 (py), 1486 (py), 1465 (py), 1384 (NO_3^-), 1312 (py), 1182 (py), 1111 (py), 868 (OH), 803 (NO_3^-), 777 (py), 751 (py), 588 (py). $Nd_2(\mathbf{L})_3(NO_3)_3{\cdot}4H_2O$ (1138.19): calcd. C 37.99, H 3.10, N 11.08; found C 37.87, H 2.89, N 11.01.

Sm Complex (4): A mixture of $Sm(NO_3)_3{\cdot}6H_2O$ (45 mg, 0.1 mmol) and ligand H**L** (40.0 mg, 0.2 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The red solution was evaporated under reduced pressure to give complex **4** as an orange solid in quantitative yield. ESI-MS: *m/z* = 1171 (5%) $[Sm_2\mathbf{L}_3(NO_3)_3(H_2O)_5]$, 1153 (5%) $[Sm_2\mathbf{L}_3(NO_3)_3(H_2O)_4]$, 557 (100%) $[Sm\mathbf{L}_2]^+$, 450 (30%) $[Sm\mathbf{L}(NO_3)(H_2O)_2]^+$, 413 (5%) $[Sm\mathbf{L}(NO_3)]^+$, 341 (5%) $[Sm_2\mathbf{L}(NO_3)_3]^{2+}$, 253 (5%) $[Sm_2\mathbf{L}_2(NO_3)]^{3+}$, 199 (20%) $[\mathbf{L}]^+$. IR (KBr $[\text{cm}^{-1}]$): ṽ = 3345 (OH), 3068 (CH arom), 3021 (CH imin), 1623 (CN), 1586 (py), 1570 (py), 1559 (py), 1487 (py), 1469 (py), 1442 (py), 1384 (NO_3^-), 1297 (py), 1271 (py), 1185 (py), 1153 (py), 869 (OH), 808 (NO_3^-), 750 (py), 591 (py), 534 (py). $Sm_2(\mathbf{L})_3(NO_3)_3{\cdot}5H_2O$ (1168.45): calcd. C 37.01, H 3.19, N 10.79; found C 37.55, H 3.67, N 11.02.

Eu Complex (5): A mixture of $Eu(NO_3)_3{\cdot}5H_2O$ (43 mg, 0.1 mmol) and ligand H**L** (40.0 mg, 0.2 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The red solution was evaporated under reduced pressure to give complex **5** as a red solid in quantitative yield. ESI-MS: *m/z* = 1155 (5%) $[Eu_2\mathbf{L}_3(NO_3)_3(H_2O)_4]$, 547 (15%) $[Eu\mathbf{L}_2]^+$, 450 (100%) $[Eu\mathbf{L}(NO_3)(H_2O)_2]^+$, 253 (10%) $[Eu_2\mathbf{L}_2(NO_3)]^{3+}$, 199 (30%) $[\mathbf{L}]^+$. IR (KBr $[\text{cm}^{-1}]$): ṽ = 3608 (OH), 3342 (OH), 3068 (CH arom), 3025 (CH imin), 1728 (NO_3^-), 1596 (py), 1586 (py), 1570 (py), 1488 (py), 1467 (py), 1441 (py), 1384 (NO_3^-), 1297 (py), 1269 (py), 1185 (py), 1155 (py), 868 (OH), 807

(NO_3^-), 778 (py), 751 (py), 590 (py). $Eu_2(\mathbf{L})_3(NO_3)_3\cdot 4H_2O$ (1153.64): calcd. C 37.48, H 3.06, N 10.93; found C 37.43, H 2.98, N 10.87.

Gd Complex (6): A mixture of $Gd(NO_3)_3\cdot 6H_2O$ (45 mg, 0.1 mmol) and ligand H**L** (40.0 mg, 0.2 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The red solution was evaporated under reduced pressure to give complex **6** as a red solid in quantitative yield. ESI-MS: m/z = 552 (100%) $[Gd\mathbf{L}_2]^+$, 484 (30%) $[Gd_2\mathbf{L}_3(NO_3)]^{2+}$,435 (25%) $[Gd\mathbf{L}(NO_3)H_2O]^+$, 417 (80%) $[Gd\mathbf{L}(NO_3)]^+$, 199 (5%) $[\mathbf{L}]^+$. IR (KBr [cm^{-1}]): $\tilde{\nu}$ = 3609 (OH), 3313 (OH), 3064 (C Harom), 3025 (C Himin), 1733 (NO_3^-), 1595 (py), 1586 (py), 1569 (py), 1487 (py), 1468 (py), 1384 (NO_3^-), 1296 (py), 1270 (py), 1249 (py), 1154 (py), 868 (OH), 807 (NO_3^-), 778 (py), 751 (py), 590 (py). $Gd_2(\mathbf{L})_3(NO_3)_3\cdot H_2O$ (1110.17): calcd. C 38.95, H 2.63, N 11.36; found C 38.11, H 2.21, N 11.19.

Tb Complex (7): A mixture of $Tb(NO_3)_3\cdot 6H_2O$ (45 mg, 0.1 mmol) and ligand H**L** (40.0 mg, 0.2 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The red solution was evaporated under reduced pressure to give complex **7** as a yellow solid in quantitative yield. ESI-MS: m/z = 553 (100%) $[Tb\mathbf{L}_2]^+$, 418 (80%) $[Tb\mathbf{L}(NO_3)]^+$, 199 (20%) $[\mathbf{L}]^+$. IR (KBr [cm^{-1}]): $\tilde{\nu}$ = 3611(OH), 3368 (OH), 3066 (CH arom), 3026 (CH imin), 1732 (NO_3^-), 1594 (py), 1586 (py), 1492 (py), 1469 (py), 1384 (NO_3^-), 1297 (py), 1184 (py), 1108 (py), 869 (OH), 807 (NO_3^-), 777 (py), 750 (py), 590 (py).$Tb_2(\mathbf{L})_3(NO_3)_3\cdot H_2O$ (1113.52): calcd. C 38.83, H 2.63, N 11.32; found C 38.95, H 2.69, N 11.45.

Dy Complex (8): A mixture of $Dy(NO_3)_3\cdot 6H_2O$ (44 mg, 0.1 mmol) and ligand H**L** (40.0 mg, 0.2 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The orange solution was evaporated under reduced pressure to give complex **8** as an orange solid in quantitative yield. ESI-MS: m/z = 1141 (5%) $[Dy_2\mathbf{L}_3(NO_3)_2]^+$, 558 (35%) $[Dy\mathbf{L}_2]^+$, 339 (10%) $[Dy_2\mathbf{L}_3]^{3+}$, 261 (100%) $[Dy_2\mathbf{L}_2(NO_3)]^{3+}$, 199 (30%) $[\mathbf{L}]^+$, 146 $[Dy_2\mathbf{L}(NO_3)]^{4+}$. IR (KBr [$cm^{-1}$]): $\tilde{\nu}$ = 3554 (OH), 3470 (OH), 3103 (CH arom), 3027 (CH imin), 1725 (NO_3^-), 1555 (py), 1530 (py), 1486 (py), 1467 (py), 1384 (NO_3^-), 1297 (py), 1202 (py), 1106 (py), 868 (OH), 819 (NO_3^-), 778 (py), 751 (py), 588 (py). $Dy_2(\mathbf{L})_3(NO_3)_3\cdot 2H_2O$ (1138.68): calcd. C 37.97, H 2.74, N 11.07; found C 37.99, H 2.78, N 11.28.

Ho Complex (9): A mixture of $Ho(NO_3)_3\cdot 5H_2O$ (44 mg, 0.1 mmol) and ligand H**L** (40.0 mg, 0.2 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The red solution was evaporated under reduced pressure to give complex **9** as a yellow solid in quantitative yield. ESI-MS: m/z = 559 (70%) $[Ho\mathbf{L}_2]^+$, 489 (5%) $[Ho_2\mathbf{L}_3(NO_3)]^{2+}$, 460 (100%) $[Ho\mathbf{L}(NO_3)(H_2O)_2]^+$, 420 (15%) $[Ho\mathbf{L}(NO_3)]^+$, 260 (40%) $[Ho_2\mathbf{L}_2(NO_3)]^{3+}$, 199 (30%) $[\mathbf{L}]^+$. IR (KBr [cm^{-1}]): $\tilde{\nu}$ = 3609 (OH), 3375 (OH), 3067 (CH arom), 3027 (CH imin), 1722 (NO_3^-), 1586 (py), 1530 (py), 1487 (py), 1469 (py), 1384 (NO_3^-), 1297 (py), 1185 (py), 1109 (py), 869 (OH), 808 (NO_3^-), 772 (py), 750 (py), 591 (py). $Ho_2(\mathbf{L})_3(NO_3)_3\cdot 2H_2O$ (1143.54): calcd. C 37.81, H 2.73, N 11.02; found C 37.06, H 2.68, N 11.23.

Lu Complex (10): A mixture of $Lu(NO_3)_3\cdot xH_2O$ (36 mg, 0.1 mmol) and ligand H**L** (40.0 mg, 0.2 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The red solution was evaporated under reduced pressure to give complex **10** as an orange solid in quantitative yield. ESI-MS: m/z = 569 (100%) $[Lu\mathbf{L}_2]^+$, 452 (15%) $[Lu\mathbf{L}(NO_3)(H_2O)]^+$, 434 (20%) $[Lu\mathbf{L}(NO_3)]^+$, 331 (5%) $[Lu_2\mathbf{L}_3(NO_3)]^{3+}$, 199 (5%) $[\mathbf{L}]^+$. IR (KBr, [cm^{-1}]): $\tilde{\nu}$ = 3611 (OH), 3335 (OH), 3055 (CH arom), 3024 (CH imin), 1732 (NO_3^-), 1594 (py), 1588 (py), 1570 (py), 1483 (py), 1472 (py), 1383 (NO_3^-), 1297 (py), 1272 (py), 1250 (py), 1154 (py), 868 (OH), 806 (NO_3^-), 777 (py), 752 (py), 590 (py). $Lu_2(\mathbf{L})_3(NO_3)_3\cdot H_2O$ (1145.60): calcd. C 37.74, H 2.55, N 11.00; found C 38.01, H 2.34, N 10.89

Eu-Dy Complex (11): A mixture of $Eu(NO_3)_3\cdot 5H_2O$ (36 mg, 0.084 mmol), $Dy(NO_3)_3\cdot 6H_2O$ (37 mg, 0.084 mmol) and ligand H**L** (50.0 mg, 0.25 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The red solution was evaporated under reduced pressure to give complex **11** as an orange solid in quantitative yield.

Table 2. Crystal data collection and structure refinement details.

Compound	3	5	8	12
Formula	$C_{36}H_{27}N_9Nd_2O_{12}\cdot C_2H_3N$	$C_{36}H_{27}N_9Eu_2O_{12}\cdot C_2H_3N$	$C_{36}H_{27}N_9Dy_2O_{12}\cdot C_2H_3N$	$C_{36}H_{28}EuN_8O_9Zn\cdot 2(CH_4O)$
Formula weight [$g\,mol^{-1}$]	1107.20	1122.64	1143.72	997.07
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	Cc
a [Å]	12.418(1)	12.383(1)	12.382(1)	20.764(2)
b [Å]	23.921(1)	23.959(1)	23.975(1)	10.891(1)
c [Å]	14.702(1)	14.524(1)	14.599(1)	17.298(2)
β [°]	111.69(1)	111.61(1)	111.64(1)	93.01(1)
V [$Å^3$]	4058.1(8)	4005.9(8)	4028.5(8)	3906.6(8)
Z	4	4	4	4
D_x [$g\,cm^{-3}$]	1.81	1.86	1.89	1.70
μ [mm^{-1}]	2.61	3.18	3.76	2.28
Crystal size [mm]	0.18×0.15×0.12	0.2×0.2×0.1	0.2×0.2×0.1	0.2×0.15×0.1
Θ range [°]	2–30	2–30	2–30	2–30
hkl range	$-17 \le h \le 16$	$-17 \le h \le 11$	$-16 \le h \le 16$	$-29 \le h \le 28$
	$-31 \le k \le 31$	$-32 \le k \le 32$	$-31 \le k \le 31$	$-14 \le k \le 7$
	$-20 \le l \le 17$	$-17 \le l \le 19$	$-17 \le l \le 20$	$-23 \le l \le 23$
Reflections:				
measured	38181	36004	26034	18429
unique (R_{int})	10602 (0.038)	10463 (0.063)	10144 (0.036)	9339 (0.086)
with $I > 2\sigma(I)$	7267	9263	7160	4577
Number of parameters	559	559	559	536
$R(F)$	0.036	0.063	0.041	0.060
$wR(F^2)$	0.064	0.144	0.096	0.093
Goodness of fit	0.98	1.13	1.00	0.82
max./min. $\Delta\rho$ [$e\,Å^{-3}$]	1.67/–0.88	2.68/–3.50	1.53/–0.95	1.12/–0.66

ESI-MS: *m*/*z* = 1166 (5%) [EuDy**L**$_3$(NO$_3$)]$^{2+}$, 556 (100%) [Dy**L**$_2$]$^+$, 547 (80%) [Eu**L**$_2$]$^+$, 199 (30%) [**L**]$^+$. IR (KBr [cm^{-1}]): $\tilde{\nu}$ = 3636 (OH), 3367 (OH), 3085 (CH arom), 3025 (CH imin), 1731 (NO$_3^-$), 1564 (py), 1543 (py), 1483 (py), 1459 (py), 1384 (NO$_3^-$), 1301 (py), 1248 (py), 1102 (py), 866 (OH), 805 (NO$_3^-$), 780 (py), 751 (py), 592 (py). EuDy(**L**)$_3$(NO$_3$)$_3$·2H$_2$O (1128.15): calcd. C 38.33, H 2.77, N 11.17; found C 38.06, H 2.54, N 10.99.

Eu-Zn Complex (12): A mixture of Eu(NO$_3$)$_3$·5H$_2$O (36 mg, 0.084 mmol), Zn(NO$_3$)$_2$·6H$_2$O (16 mg, 0.084 mmol) and ligand H**L** (50.0 mg, 0.25 mmol) in MeCN (15 mL) was stirred at room temperature for 24 h. The red solution was evaporated under reduced pressure to give complex **12** as an orange solid in quantitative yield. ESI-MS: *m*/*z* = 1155 (5%) [Eu$_2$**L**$_3$(NO$_3$)$_3$(H$_2$O)$_4$+H]$^+$, 870 (5%) [EuZn**L**$_3$(NO$_3$)]$^+$, 545 (15%) [Eu**L**$_2$]$^+$, 459 (100%) [Zn**L**$_2$]$^+$, 199 (15%) [**L**]$^+$. IR (KBr [cm^{-1}]): $\tilde{\nu}$ = 3612 (OH), 3348 (OH), 3069 (CH arom), 3027 (CH imin), 1733 (NO$_3^-$), 1569 (py), 1487 (py), 1468 (py), 1383 (NO$_3^-$), 1296 (py), 1250 (py), 1107 (py), 868 (OH), 807 (NO$_3^-$), 778 (py), 750 (py), 590 (py). EuZn(**L**)$_3$(NO$_3$)$_2$·4H$_2$O (1067.07): calcd. C 40.52, H 3.31, N 11.81; found C 40.21, H 3.23, N 12.02.

Crystal Structure Determination of Complexes 3, 5, 8 and 12: Data were collected by the ω-scan technique in the θ range of 2–30° on a KUMA KM4CCD four-circle[43] diffractometer equipped with a CCD detector, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Accurate cell parameters were determined by the least-squares fit of 10137 (for **3**), 13161 (for **5**), 8403 (for **8**) and 2785 (for **12**) reflections of highest intensity chosen from the complete dataset. Data were corrected for Lorentz-polarization effects[44] and for absorption.[45] The structure was solved by direct methods with SHELXS-97[46] and refined with SHELXL-97.[47] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined with a 'riding model' with their isotropic thermal parameters set to 1.2 times the U_{eq} of the appropriate carrier atom. Relevant crystal data and refinement details are listed in Table 2. Selected geometrical parameters for complexes **3**, **5**, **8** and **12** are listed in Table 3.

Table 3. Selected geometrical parameters.

M	Nd (**3**)	Eu (**5**)	Dy (**8**)
M1–O10A	2.436(2)	2.392(4)	2.411(3)
M1–O10B	2.467(2)	2.428(4)	2.442(3)
M1–O10C	2.408(2)	2.363(5)	2.367(3)
M1–N1A	2.674(3)	2.628(6)	2.649(4)
M1–N1B	2.689(3)	2.654(6)	2.666(4)
M1–N8A	2.567(3)	2.518(5)	2.542(4)
M1–N8B	2.581(3)	2.534(5)	2.547(4)
M1–O2D	2.585(2)	2.551(5)	2.557(4)
M1–O3D	2.542(3)	2.489(5)	2.514(4)
M2–O10A	2.493(2)	2.452(5)	2.466(3)
M2–O10B	2.461(2)	2.399(4)	2.414(3)
M2–O10C	2.428(2)	2.396(5)	2.404(3)
M2–N1C	2.652(3)	2.626(6)	2.633(4)
M2–N8C	2.575(3)	2.530(6)	2.555(4)
M2–O2E	2.560(3)	2.524(6)	2.537(4)
M2–O3E	2.529(3)	2.489(6)	2.505(4)
M2–O2F	2.494(2)	2.446(5)	2.466(3)
M2–O3F	2.547(2)	2.503(6)	2.526(4)
M1–O10A–M2	95.49(7)	95.0(1)	95.0(1)
M1–O10B–M2	95.53(7)	95.5(1)	95.6(1)
M1–O10C–M2	97.96(8)	97.3(2)	97.9(1)
	12		
Eu1–O10A	2.406(7)	Zn1–O10A	2.126(8)
Eu1–O10B	2.409(6)	Zn1–O10N	2.115(6)
Eu1–O10C	2.326(6)	Zn1–N1A	2.282(8)
Eu1–N1C	2.622(9)	Zn1–N1B	2.190(7)
Eu1–N8C	2.547(7)	Zn1–N8A	2.075(8)
Eu1–O1D	2.476(6)	Zn1–N8B	2.119(7)
Eu1–O2D	2.480(7)		
Eu1–O1E	2.579(7)		
Eu1–O2E	2.510(7)		
Eu1–O10A–Zn1	102.1(3)		
Eu1–O10B–Zn1	102.3(2)		

CCDC-274721 (for **8**), -274722 (for **5**), -274723 (for **3**), and -274724 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum Mechanical Calculations: The set of Cartesian coordinates determined by X-ray diffraction for the atoms in complexes **5** and **12** served as a starting point for geometry optimization utilizing the density functional theory (DFT). The B3LYP method[48,49] was utilized, and a composite basis set in which Eu, and Zn were treated with a SDD basis set in which Stuttgart-Dresden pseudopotentials[50,51] substituted for the innermost electrons to account for relativistic effects was applied. Ligands atoms from the first coordination sphere were treated with a 6-31G basis set,[52] while the remaining atoms were treated with a STO-3G basis set.[53] Single point energies were calculated with a SDD basis set[50,51] for all atoms. All calculations were preformed with Gaussian 03.[54]

Acknowledgments

This work was partially supported by grant No. 4T09A 049 24 from the Polish Ministry of Scientific Research and Information Technology.

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Received: August 3, 2005