Dalton
Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 11449

www.rsc.org/dalton

PAPER

Anion-dependent construction of two hexanuclear 3d–4f complexes with a flexible Schiff base ligand†‡

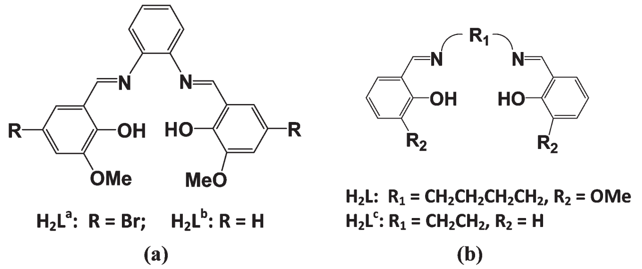
Xiaoping Yang,[a] Christopher Chan,[a] Daniel Lam,[a] Desmond Schipper,[a] Julie M. Stanley,[a] Xiaoyan Chen,[a] Richard A. Jones,*[a] Bradley J. Holliday,*[a] Wai-Kwok Wong,*[b] Shengchun Chen[a] and Qun Chen*[c]

Received 12th June 2012, Accepted 27th July 2012
DOI: 10.1039/c2dt31268a

Two hexanuclear 3d–4f Ni–Eu and Cu–Eu complexes $[Eu_4Ni_2L_2(OAc)_{12}(EtOH)_2]$ (**1**) and $[Eu_4Cu_2L_2(OAc)_{12}]\cdot 2H_2O$ (**2**) are reported which are formed from the salen type Schiff-base ligand H_2L (H_2L = *N*,*N*′-bis(3-methoxysalicylidene)butane-1,4-diamine). In both complexes, four Eu^{3+} cations are bridged by eight OAc^- groups and the chain is terminated at each end by two ML (M = Ni and Cu) units. The structures of **1** and **2** were determined by single crystal X-ray crystallographic studies and the luminescence properties of the free ligand and metal complexes in solution were measured.

Introduction

The design and construction of polynuclear metal complexes have received extensive attention due to the fascinating physical and chemical properties associated with this class of materials.[1] Heteropolynuclear complexes comprised of d-block transition metals and lanthanide ions are currently of interest for potential applications in materials which harness unique optical and magnetic properties.[2] However, it is difficult to control the structures of polynuclear assemblies based on lanthanide ions because they often display high and variable coordination numbers and have no strong stereochemical preferences. Complex structures are often influenced by a variety of factors such as ligand architecture, the nature of counter ions, and ionic radii.[3] The majority of d–f polynuclear compounds reported so far have employed carboxylates, amino acids, betaines, and 2-pyridonates as ligands.[4] Compartmental Schiff bases with two dissimilar metal-binding sites, one being specific for the d metal ion and another for the f metal ion, are classical ligands which have been used for the synthesis of 3d–4f heteronuclear complexes.[5a–d] Our recent studies have focused on the synthesis of polynuclear 4f homometallic and 3d–4f heterometallic complexes with Schiff-base ligands.[5e–i] We have employed essentially two kinds of "salen" style Schiff-base ligands in which one is a conjugated ligand with a phenylene backbone $H_2L^{a,b}$ (Scheme 1a) and the other is exemplified by the flexible Schiff-base ligands H_2L^c and H_2L (Scheme 1b). In past studies, we discovered that "multi-decker" 4f and 3d–4f complexes with lanthanide ions sandwiched between alternating layers of the Schiff-base ligand L^a or ZnL^b units could be isolated.[5e–g] A key feature in these kinds of structures is the presence of intramolecular π–π stacking interactions between planar conjugated Schiff base ligands, which can further add to the stability of the complex. When the more flexible Schiff base ligands H_2L^c and H_2L were used in the synthesis, a variety of 1-D coordination polymers were formed by bridging H_2L^c units or by OAc^- (acetate) anions.[5h,i] The flexible Schiff-base ligands show a "stretched" configuration to bridge lanthanide ions, forming coordination polymeric structures in which π–π stacking interactions do not occur. We are interested in the influence of anions on the structures of these lanthanide complexes. For example, a 1-D coordination polymer $\{YbNiLCl(OAc)_2(H_2O)\}_n$ was obtained from the reaction of *N*,*N*′-bis(3-methoxysalicylidene)butane-1,4-diamine (H_2L) with $Ni(OAc)_2\cdot 4H_2O$ and $YbCl_3\cdot 6H_2O$ when there were two kinds of anions present in the reaction mixture, OAc^- and Cl^-. In contrast, a heterobinuclear complex $[YbNiLCl_3(H_2O)_3]$ was formed from



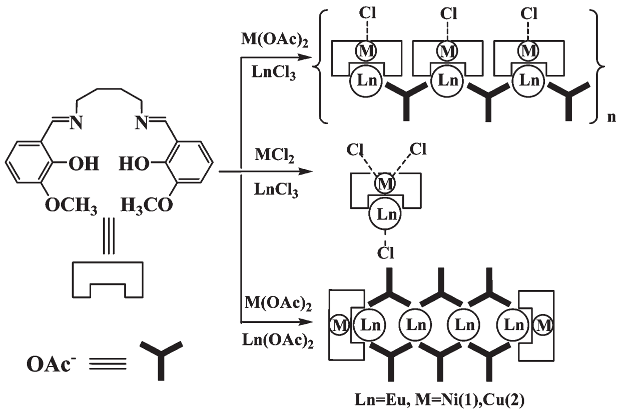
Scheme 1 Salen-type Schiff base ligands.

---

[a] *Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station, A5300, Austin, 78712-0165 TX, USA. E-mail: rajones@mail.utexas.edu, bholliday@cm.utexas.edu*
[b] *Department of Chemistry and Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, China. E-mail: wkwong@hkbu.edu.hk*
[c] *Key Laboratory of Fine Petrochemical Technology, Changzhou University, Changzhou 213164, China. E-mail: chenqunjpu@yahoo.com*

† Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contributions to transition metal catalysis and Inorganic Chemistry.

‡ Electronic supplementary information (ESI) available: NMR spectra of **1** and **2** (2 pages). CCDC 869086 and 869087. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31268a



Scheme 2 Synthesis of 3d–4f complexes **1** and **2**.

the reaction of H_2L with $NiCl_2 \cdot 6H_2O$ and $YbCl_3 \cdot 6H_2O$ when the only anion that was present was Cl^- (Scheme 2).[5i] As part of our continuing studies focused on the construction of high nuclearity frameworks, we describe here two 3d–4f hexanuclear complexes $[Eu_4Ni_2L_2(OAc)_{12}(EtOH)_2]$ (**1**) and $[Eu_4Cu_2L_2(OAc)_{12}] \cdot 2H_2O$ (**2**) which are obtained from reactions of H_2L with $M(OAc)_2 \cdot 4H_2O$ (M = Ni(II) and Cu(II)) and $Eu(OAc)_3 \cdot 4H_2O$ (Scheme 2). In these examples only OAc^- was present in the reaction mixture. Of the known heterometallic 3d–4f Schiff base complexes, most are binuclear and there exist very few reports of high nuclearity 3d–4f salen based systems.[2,5b,6] Interestingly, **1** and **2** have a similar hexanuclear structures in the solid state with four Eu^{3+} cations bridged by eight OAc^- groups and clamped between two ML (M = Ni and Cu) units. Intramolecular π–π stacking interactions between phenylene units of H_2L are absent in the structures of **1** and **2**.

Experimental section

General considerations

All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. Metal salts and other solvents were purchased from Aldrich and used directly without further purification. The Schiff-base ligand H_2L was prepared according to well-established procedures.[7] Physical measurements: NMR: VARIAN UNITY-plus. 600 spectrometer (^1H, 600 MHz) at 298 K; Mass spec: HRESI, Finnigan MAT TSQ 700; IR: Nicolet IR 200 FTIR spectrometer. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected. Absorption spectra were obtained on a BECKMAN DU 640 spectrophotometer, excitation and visible emission spectra on a QuantaMaster PTI fluorimeter.

Synthesis of complexes 1 and 2

$[Eu_4Ni_2L_2(OAc)_{12}(EtOH)_2]$ (1). A mixture of the Schiff-base ligand H_2L (0.178 g, 0.5 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.124 g, 0.5 mmol) in CH_3CN/EtOH (1 : 3, 20 ml) was stirred and heated under reflux for 10 minutes. The reaction mixture was allowed to cool briefly, $Eu(OAc)_3 \cdot 4H_2O$ (0.165 g, 0.5 mmol) was added and the mixture was again heated under reflux (15 minutes). It was allowed to cool and was then filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and blue crystals were obtained after two weeks. The crystals were filtered off and washed with EtOH (5 ml). Yield (based on $Eu(OAc)_3 \cdot 4H_2O$): 0.083 g (30%). m.p. > 290 °C (dec.). ESI-MS (MeOH) *m*/*z*: 1550 ($[NiEu_3L(OAc)_8(EtOH)_4]^+$). ^1H NMR (600 MHz, CD_3OD): δ (ppm) 91.990 (1H, EtOH), 40.157 (2H), 16.249 (6H), 10.044 (4H), 3.599 (2H), 3.480 (3H), 1.166 (10H), −1.511 (18H). IR (CH_3OH, cm^{-1}): 3420 (m), 2951 (m), 1621 (s), 1553 (m), 1540 (m), 1451 (s), 1420 (s), 1340 (s), 1222 (m), 1075 (m), 856 (m), 730 (s).

$[Eu_4Cu_2L_2(OAc)_{12}] \cdot 2H_2O$ (2). The procedure was the same as that for **1** using $Cu(OAc)_2 \cdot H_2O$ (0.100 g, 0.5 mmol). Green blue single crystals of **2** were formed after two weeks. Yield (base on $Eu(OAc)_3 \cdot 4H_2O$): 0.135 g (48%). m.p. > 275 °C (dec.). ESI-MS (MeOH) *m*/*z*: 694 ($[CuEuL(OAc)_2]^+$). ^1H NMR (600 MHz, CD_3OD): δ (ppm) 40.164 (2H), 18.487 (6H), 10.189 (2H), 8.809 (2H), 0.088 (6H), −2.340 (22H). IR (CH_3OH, cm^{-1}): 3379 (m), 1630 (s), 1557 (s), 1460 (s), 1418 (m), 1223 (s), 1156 (m), 1078 (m), 1001 (m), 855 (m), 732 (s).

X-ray crystallography

Data were collected on a Rigaku MiniFlex II CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 223 K. The data set was corrected for absorption based on multiple scans and reduced using standard methods. The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.[8] Coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[9]

Results and discussion

Reactions of the Schiff-base ligand H_2L with $M(OAc)_2 \cdot nH_2O$ (M = Ni and Cu) and $Eu(OAc)_3 \cdot 4H_2O$ in refluxing MeCN/EtOH (1 : 3) produced dark blue solutions from which the hexanuclear Ni–Eu and Cu–Eu complexes **1** and **2** were isolated as blue crystalline solids in 30 and 48% yields, respectively. The solid state structures of **1** and **2** were determined by single crystal X-ray crystallographic studies. Crystallographic data for both complexes are presented in Table 1 and selected bond lengths and angles are given in Tables 2 and 3.

A view of the crystal structure of **1** is shown in Fig. 1, and reveals a hexanuclear centrosymmetric core containing two equivalent $NiEu_2L$ moieties linked by two tridentate OAc^- anions. In the $NiEu_2L$ moiety, Ni(1) is located in the inner N_2O_2 cavity of the Schiff base ligand and has a bi-pyramidal geometry with two oxygen atoms from two bridged OAc^- anions occupying the axial positions. Eu(1) is bound to the O_2O_2 cavity of the Schiff-base ligand and surrounded by nine oxygen atoms from one L group and five OAc^- anions. Ni(1) and Eu(1) are bridged by two bidentate OAc^- anions in addition to the phenolic oxygen atoms of the Schiff base ligand. The Ni(1)–Eu(1) separation is 3.346 Å. Eu(2) and Eu(1) are linked by three OAc^- anions with a separation of 4.113 Å. Eu(2) is 9 coordinate being

Table 1 Crystal data and structure refinement for complexes **1** and **2**

	1	**2**
Formula	$C_{68}H_{92}N_4O_{34}Ni_2Eu_4$	$C_{64}H_{88}N_4O_{36}Cu_2Eu_4$
Fw	2234.72	2224.24
Cryst syst.	Monoclinic	Triclinic
Space group	$P21/n$	$P\bar{1}$
a (Å)	12.803(3)	10.765(2)
b (Å)	16.488(3)	12.646(3)
c (Å)	19.716(4)	19.068(4)
α (°)	90	95.39(2)
β (°)	108.40(3)	104.23(3)
γ (°)	90	112.35(3)
V (Å^3)	3949.3(14)	2275.9(10)
Z	2	1
D_{calc} (g cm^{-3})	1.879	1.617
Temp (K)	153(1)	153(1)
F(000)	2216	1090
μ (mm^{-1})	3.685	3.251
θ rang (°)	1.65–25.00	1.13–25.00
Reflns meads	10 575	19 984
Reflns used	6850	7993
Params	505	516
R^a ($I > 2\sigma(I)$)	$R_1 = 0.0367$	$R_1 = 0.0570$
	$wR_2 = 0.1101$	$wR_2 = 0.1662$
R^a (all data)	$R_1 = 0.0446$	$R_1 = 0.0829$
	$wR_2 = 0.1358$	$wR_2 = 0.2038$
S	1.221	1.171

[a] $R_1 = \Sigma|F_o| - |F_c|\Sigma|F_o|$. $wR_2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 2 Selected bond lengths (Å) and angles (°) for **1**

Eu(1)–O(3)	2.336(5)
Eu(1)–O(2)	2.337(4)
Eu(1)–O(9)	2.359(5)
Eu(1)–O(8)	2.390(4)
Eu(1)–O(6)	2.397(4)
Eu(1)–O(13)	2.495(4)
Eu(1)–O(11)	2.542(5)
Eu(1)–O(4)	2.643(5)
Eu(1)–O(1)	2.667(5)
Ni(1)–O(3)	2.063(5)
Ni(1)–O(7)	2.080(5)
Ni(1)–N(1)	2.087(6)
Ni(1)–O(2)	2.092(5)
Ni(1)–O(5)	2.099(5)
Ni(1)–N(2)	2.126(6)
O(3)–Eu(1)–O(2)	75.80(16)
O(3)–Eu(1)–O(4)	62.73(15)
O(2)–Eu(1)–O(4)	133.64(15)
O(3)–Eu(1)–O(1)	131.67(16)
O(2)–Eu(1)–O(1)	63.03(16)
O(4)–Eu(1)–O(1)	134.77(17)
O(3)–Ni(1)–N(1)	171.9(2)
O(3)–Ni(1)–O(2)	87.40(17)
N(1)–Ni(1)–O(2)	85.2(2)
O(3)–Ni(1)–N(2)	87.5(2)
O(7)–Ni(1)–N(2)	94.33(19)
N(1)–Ni(1)–N(2)	100.0(2)
O(2)–Ni(1)–N(2)	174.6(2)

Table 3 Selected bond lengths (Å) and angles (°) for **2**

Eu(1)–O(6)	2.309(7)
Eu(1)–O(3)	2.372(6)
Eu(1)–O(9)	2.396(7)
Eu(1)–O(11)	2.414(7)
Eu(1)–O(2)	2.441(6)
Eu(1)–O(7)	2.495(8)
Eu(1)–O(8)	2.525(7)
Eu(1)–O(1)	2.663(8)
Eu(1)–O(4)	2.794(7)
Cu(1)–O(2)	1.955(7)
Cu(1)–N(1)	2.003(8)
Cu(1)–O(3)	2.006(7)
Cu(1)–N(2)	2.012(9)
Cu(1)–O(5)	2.156(7)
O(3)–Eu(1)–O(2)	63.9(2)
O(3)–Eu(1)–O(1)	125.3(2)
O(2)–Eu(1)–O(1)	61.7(2)
O(3)–Eu(1)–O(4)	59.2(2)
O(2)–Eu(1)–O(4)	104.7(2)
O(1)–Eu(1)–O(4)	141.1(3)
O(2)–Cu(1)–N(1)	91.1(3)
O(2)–Cu(1)–O(3)	80.0(3)
N(1)–Cu(1)–O(3)	146.4(3)
O(2)–Cu(1)–N(2)	170.5(3)
N(1)–Cu(1)–N(2)	95.9(3)
O(3)–Cu(1)–N(2)	90.6(3)

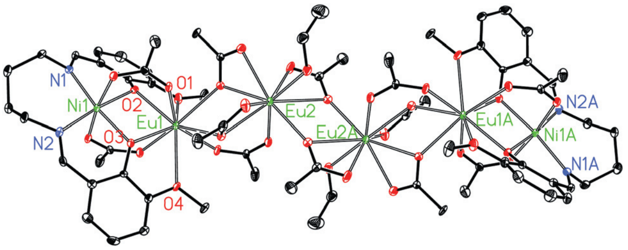


Fig. 1 A view of the crystal structure of **1**. H atoms have been omitted for clarity and thermal ellipsoids drawn at the 30% probability level. Symmetry operator (−*x*, −*y*, −*z*) generates equivalent atoms marked with “A”.

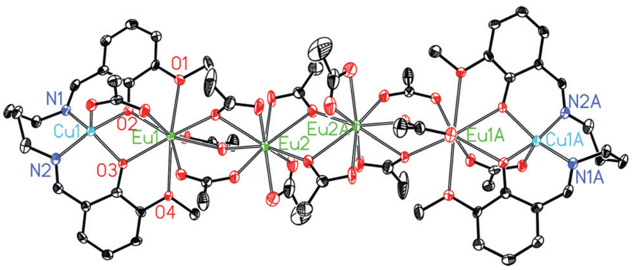


Fig. 2 A view of the crystal structure of **2**. H atoms have been omitted for clarity and thermal ellipsoids drawn at the 30% probability level. Symmetry operator (−*x*, −*y*, −*z*) generates equivalent atoms marked with “A”.

bound by five OAc^- anions and one EtOH molecule. The distance between the two central Eu(2) ions is 4.231 Å.

A view of the crystal structure of **2** is shown in Fig. 2. Complex **2** has a similar hexanuclear structure to **1**, thus there is a centrosymmetric core with two equivalent $CuEu_2L$ moieties that are bridged by two tridentate OAc^- anions. The distance between the two equal Eu(2) ions is 4.144 Å. In the $CuEu_2L$ moiety, Cu(1) and Eu(1) are located in the inner N_2O_2 and O_2O_2 cavities of the Schiff-base ligand, respectively, with a separation of 3.467 Å. The Cu^{2+} ion has a square based pyramidal geometry *via* the coordination of an oxygen atom of OAc^- anion in the axial position. Eu(1) has a nine-coordinate environment similar to that found in **1**. Eu(2) and Eu(1) are also linked by three OAc^- anions with a separation of 4.087 Å. However, unlike **1** there is no EtOH molecule coordinated to Eu(2). Eu(2) is 9 coordinate being bound by six OAc^- anions. In **1** and **2**, the average distances for the Ni–N (2.107 Å), Ni–O (phenolic) (2.078 Å), Cu–N (2.009 Å), Cu–O (phenolic) (1.980 Å), Eu–O (phenolic) (2.337 Å **1**, 2.408 Å **2**) and Eu–O(methoxy) (2.655 Å **1**, 2.732 Å **2**) bonds are comparable to those found in the literature.[5,6]

^1H NMR spectrum of **1** in CD_3OD at room temperature revealed the presence of 7 broadened peaks ranging from −2 to +41 ppm, corresponding to the 45 C–H protons from one Schiff base ligand, six coordinated OAc^- groups and one coordinated EtOH molecule (Fig. S1, ESI‡). A very broad O–H proton peak assigned to the coordinated EtOH is observed at +92 ppm. The ^1H NMR spectrum of **2** in CD_3OD at room temperature shows the presence of 6 broadened peaks ranging from −3 to +41 ppm. These peaks correspond to the 40 C–H protons from one Schiff base ligand and six coordinated OAc^- groups. The broad and unresolved nature of the signals caused by the paramagnetic 3d metal ions and the 4f lanthanide ions precluded further study by COSY 2-D analysis. The data is consistent with multinuclear structures for **1** and **2** persisting in solution.

Luminescence studies

There is considerable interest in luminescent lanthanide complexes since lanthanide ions exhibit long-lived lifetimes and line-like emission bands at characteristic wavelengths. The photophysical properties of lanthanide ions depend markedly on the environment surrounding the metal center. For example, solvents containing O–H (*i.e.* H_2O and CH_3OH) can efficiently quench the luminescence of lanthanide ions. However, if the O–H is replaced by O–D, this process becomes much less efficient.[10] Since complexes **1** and **2** are soluble in methanol the photophysical properties were studied in both CH_3OH and CD_3OD.

The absorption spectra of the free ligand H_2L, and complexes **1** and **2** in MeOH are shown in Fig. 3. The free ligand H_2L exhibits absorption bands at 219, 240, 259, 291 and 415 nm, which are strongly perturbed upon co-ordination to Ln^{3+} in complexes **1** and **2**. Complexes **1** and **2** exhibit similar solution absorption spectra. The excitation and emission spectra of the free ligand H_2L and complex **1** are shown in Fig. 4. Excitation of the absorption band at 275 nm of the free ligand H_2L produces two broad emission bands at λ_{max} = 319 and 496 nm. The excitation spectrum of the free ligand H_2L, monitoring the intensity of the emission at 496 nm, displays two peaks centered at 275 and 350 nm. For complexes **1** and **2**, the typical narrow emission bands of the Eu^{3+} ion ($^5D_0 \rightarrow {}^7F_j$ transitions, j = 0, 1, 2, 3 and 4) can be detected upon excitation of the ligand-centered absorption bands (λ_{ex} = 308 and 281 nm for **1** and **2**, respectively) in CD_3OD at room temperature (Fig. 4). However, the emission intensities are reduced sharply in CH_3OH, indicating that the photophysical properties are significantly affected by solvent O–H bonds in the solvent molecules. The overall quantum yield (Φ_{em}) of **1** in CD_3OD was determined as 0.0011 relative to $[Ru(bipy)_3]Cl_2$ in water (bipy = 2,2′-bipyridine; Φ_{em} = 0.028),[11] which is less than that of the polymeric complex $[Eu_2(H_2L)(OAc)_6]_n$ that does not bear 3d metal ions (Φ_{em} = 0.015).[5i] The luminescence of **2** in CD_3OD is also weak with a quantum yield less than 10^{-4}. For both **1** and **2**, the weak luminescence of Eu^{3+} ions maybe due to lanthanide to transition metal (4f → 3d) energy transfer which can efficiently quench lanthanide ions.[12] Studies of other d-block metals (*i.e.* d^{10} monovalent metal ions[13]) in the synthesis of d–f complexes, which may result in the transition metal to lanthanide (d → 4f) energy transfer, are in progress.

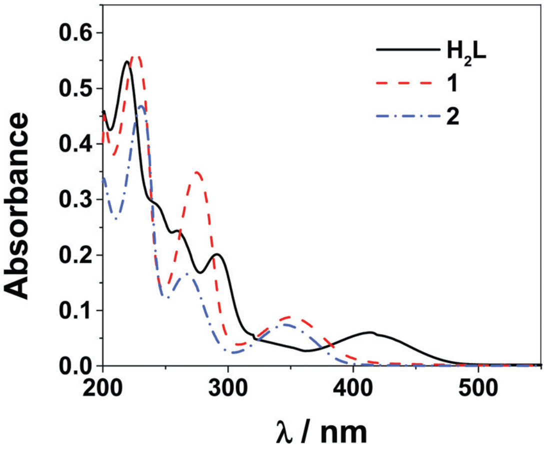


Fig. 3 Absorption spectra of the free H_2L and complexes **1** and **2** in CH_3OH.

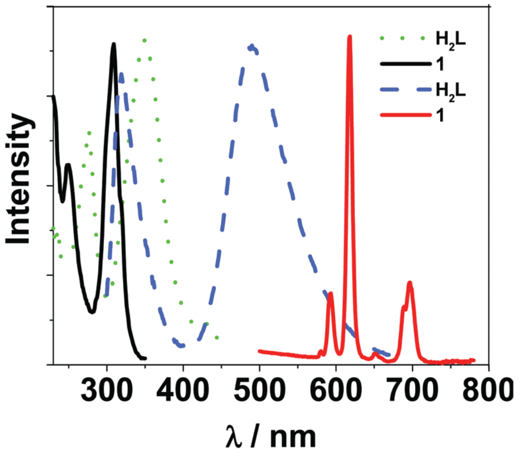


Fig. 4 Excitation and emission spectra of the free ligand H_2L (···; ---) in CH_3OH and **1** (—) in CD_3OD at room temperature.

Conclusions

Two hexanuclear Ni–Eu and Cu–Eu complexes **1** and **2** with the flexible Schiff-base ligand H_2L have been prepared and structurally characterized. In complexes **1** and **2**, four Eu^{3+} anions bridged by eight OAc^- groups are clamped between two ML (M = Ni and Cu) units. The overall structures of **1** and **2** comprise two crystallographically equivalent MEu_2L units related by a center of symmetry and linked by two OAc^- groups. Both **1** and **2** show visible emissions of Eu^{3+} ions in methanol. However, the overall quantum yields of **1** and **2** are much less than that of $[Eu_2(H_2L)(OAc)_6]_n$, indicating that the energy transfer from the Eu^{3+} ions to the transition metals (Ni^{2+} and Cu^{2+}) may happen in **1** and **2**.

Acknowledgements

The authors acknowledge the Freshman Research Initiative, funded in part by HHMI Undergraduate Science Education Award (52005907) and the National Science Foundation (CHE-0629136). Single crystal X-ray data were collected using instrumentation purchased with funds provided by the National Science Foundation (CHE-0741973). BJH wishes to acknowledge the Welch Foundation (F-1631), the National Science Foundation (CHE-0847763, CHE-0629136), and the UT-CNM and UT-Austin for financial support of this research. RAJ wishes to acknowledge the Welch Foundation (F-816). WKW wishes to thank Hong Kong Baptist University (FRG/06-07/II-16) and the Hong Kong Research Grants Council (HKBU 202407) financial support. QC wishes to acknowledge the financial support from A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) and Open Foundation of Jiangsu Province Key Laboratory of Fine Petrochemical Technology (KF1005).

Notes and references

1 (*a*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*b*) M. Eddaoudl, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*c*) C. Piguet and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 1999, **28**, 347; (*d*) P. Zanello, S. Tamburini, P. A. Vigato and G. A. Mazzocchin, *Coord. Chem. Rev.*, 1987, **77**, 165; (*e*) *Clusters and Colloids: From Theory to Applications*, ed. G. Schmidt, VCH, Weinheim, 1994.

2 (*a*) R. E. P. Winpenny, *Chem. Soc. Rev.*, 1998, **27**, 447; (*b*) H. Deng, S. Chun, P. Florian, P. J. Grandinetti and S. G. Sore, *Inorg. Chem.*, 1996, **35**, 3891; (*c*) O. Reany, T. Gunnlaugsson and D. Parker, *Chem. Commun.*, 2000, 473; (*d*) H. Mass, A. Currao and G. Calzaferri, *Angew. Chem., Int. Ed.*, 2002, **41**, 2495; (*e*) G. Blasse, *Mater. Chem. Phys.*, 1992, **31**, 3.

3 (*a*) J.-C. G. Bünzli, *Lanthanides Probes in Life, Chemical and Earth Sciences*, Elsevier, Amsterdam, The Netherlands, 1989, vol. 1989; (*b*) J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; (*c*) C. Piguet and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 1999, **28**, 347; (*d*) P. Guerriero, S. Tamburini and P. A. Vigato, *Coord. Chem. Rev.*, 1995, **139**, 17; (*e*) C. Piguet, *Chimia*, 1996, **50**, 144.

4 M. Sakamoto, K. Manseki and H. Ōkawa, *Coord. Chem. Rev.*, 2001, **219–221**, 379.

5 (*a*) M. Andruh, *Chem. Commun.*, 2011, **47**, 3025; (*b*) M. P. Hogerheide, J. Boersma and G. V. Konten, *Coord. Chem. Rev.*, 1996, **155**, 87; (*c*) E. Cremades, S. Gómez-Coca, D. Aravena, S. Alvarez and E. Ruiz, *J. Am. Chem. Soc.*, 2012, **134**(25), 10532; (*d*) T. D. Pasatoiu, J.-P. Sutter, A. M. Madalan, F. Z. C. Fellah, C. Duhayon and M. Andruh, *Inorg. Chem.*, 2011, **50**(13), 5890; (*e*) X.-P. Yang and R. A. Jones, *J. Am. Chem. Soc.*, 2005, **127**, 7686; (*f*) X.-P. Yang, R. A. Jones and W.-K. Wong, *Dalton Trans.*, 2008, 1676; (*g*) W.-K. Wong, X.-P. Yang, R. A. Jones, J. H. Rivers, V. Lynch, W.-K. Lo, D. Xiao, M. M. Oye and A. L. Holmes, *Inorg. Chem.*, 2006, **45**, 4340; (*h*) X.-P. Yang, R. A. Jones, J. H. Rivers and W.-K. Wong, *Dalton Trans.*, 2009, 10505; (*i*) X.-P. Yang, D. Lam, C. Chan, J. M. Stanley, R. A. Jones, B. J. Holliday and W.-K. Wong, *Dalton Trans.*, 2011, **40**, 9795.

6 M. Sakamoto, K. Manseki and H. Okawa, *Coord. Chem. Rev.*, 2001, **219**, 379.

7 F. Lam, J.-X. Xu and K. S. Chan, *J. Org. Chem.*, 1996, **61**, 8414.

8 G. H. Sheldrick, *SHELX 97, A software package for the solution and refinement of X-ray data*, University of Göttingen, Göttingen, Germany, 1997.

9 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, vol. 4, 1974, Table 2.2A.

10 N. Sabbatini, M. Guardigli and J. M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201.

11 K. Nakamaru, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2697.

12 (*a*) E. Wolcan, L. Villata, A. L. Capparelli and M. R. Feliz, *Photochem. Photobiol. Sci.*, 2004, **3**, 322; (*b*) B. C. Barja, A. Remorino, M. J. Roberti and P. F. Aramendia, *J. Argent. Chem. Soc.*, 2005, **93**, 81; (*c*) Q.-Y. Chen, C.-J. Li and Q.-H. Luo, *Synth. React. Inorg. Met.-Org. Chem.*, 2003, **33**(9), 1701.

13 (*a*) M. A. Rawashdeh-Omary, C. L. Larochelle and H. H. Patterson, *Inorg. Chem.*, 2000, **39**, 4527; (*b*) Z. Assefa, G. Shankle, H. H. Patterson and R. Reynolds, *Inorg. Chem.*, 1994, **33**, 2187; (*c*) Z. Assefa and H. H. Patterson, *Inorg. Chem.*, 1994, **33**, 6194.