Reversible guest molecule encapsulation in the 3-D framework of a heteropolynuclear luminescent Zn_4Eu_2 cage complex†‡

Xiaoping Yang,[a] Benjamin P. Hahn,[a] Richard A. Jones,*[a] Keith J. Stevenson,*[a] J. Steven Swinnea[b] and Qiaoyin Wu[a]

Received (in Berkeley, CA, USA) 19th May 2006, Accepted 8th July 2006
First published as an Advance Article on the web 3rd August 2006
DOI: 10.1039/b607183j

Guest molecules of diethyl ether or methanol are reversibly encapsulated in cavities formed by the 3-dimensional supramolecular framework of heteropolynuclear, luminescent $[Eu_2Zn_4L_4(OAc)_6(NO_3)_2(OH)_2]\cdot 2Et_2O$.

The assembly of 3-dimensional open metal–organic frameworks and supramolecular materials are currently of interest for potential uses in gas separation, hydrogen storage, catalysis, guest inclusion and ion exchange applications.[1] Since heteropolynuclear f and d-block complexes are of interest due to their unusual magnetic and luminescent properties,[2] open framework assemblies which feature these mixed-metal building blocks will be of additional interest. Although the use of higher nuclearity lanthanide complexes in 3-D open frameworks is known,[3] there are relatively few examples of such materials constructed from combinations of heteronuclear (d–f) metals.[4] The development of polymetallic lanthanide complexes has been limited due to the difficulty in controlling the variable coordination environment of Ln^{3+} ions.[5] Relatively few 3d–4f polynuclear compounds have been reported which employ carboxylates, amino acids, betaines, and 2-pyridonates as ligands.[4] We report here the synthesis, structure and properties of $[Eu_2Zn_4L_4(OAc)_6(NO_3)_2(OH)_2]\cdot 2Et_2O$ (**1**) (HL = 5-bromo-3-methoxysalicylaldehyde). Molecules of **1** have an unusual central cage-like cavity, and, in the solid state a combination of short intermolecular Br···O interactions and π–π stacking give rise to a 3-dimensional framework which contains open channels. These openings ($\sim 8 \times 9$ Å) loosely encapsulate Et_2O guest molecules.

Reaction of the bromo substituted vanillin, 5-bromo-3-methoxysalicylaldehyde (HL), with $Eu(NO_3)_3\cdot 6H_2O$ and $Zn(OAc)_2\cdot 2H_2O$ (1 : 1 : 1) in MeCN–EtOH gave **1** in *ca.* 65% yield.§ Vanillin based ligands, having multiple oxygen donor capabilities, are known to coordinate to lanthanides in a variety of ways. For example Costes and coworkers recently described a triangular Gd_3 derivative of 3-methoxysalicylaldehyde.[6] We have also described an unusual Tb_{10} complex formed from the reaction of HL with $TbCl_3\cdot 6H_2O$ in methanol in the presence of $Zn(OAc)_2\cdot 2H_2O$.[7] In this system the absence of $Zn(OAc)_2\cdot 2H_2O$ resulted in trinuclear $[Tb_3L_3(\mu_3\text{-}OH)_2Cl_3(MeOH)_2H_2O]\cdot Cl\cdot 3MeOH$ similar to the Gd_3 complex of Costes. The present work demonstrates that further variations in lanthanide salt (*i.e.* nitrate *vs.* chloride.) and reactions conditions (solvents) can have a significant effect on the outcome of these reactions. The X-ray structure of **1** (Fig. 1) revealed a centrosymmetric core with two equivalent Zn_2Eu moieties.¶ A cage-like structure is formed by four bidentate acetate (OAc^-) groups which link the two trinuclear cores. Each triangular Zn_2Eu unit bears two deprotonated salicylaldehyde L groups which bridge each Eu–Zn edge. The Eu–Zn distances are similar at 3.568 and 3.520 Å for Eu(1)–Zn(1) and Eu(1)–Zn(2), respectively. The two Zn atoms are bridged by a single acetate group and are separated by 3.364 Å. Each Zn_2Eu unit is capped by a μ_3-OH group. The distance between the two oxygen atoms of these μ_3-OH groups across the cage is 3.530 Å. However, the distance between the O atom of each μ_3-OH unit and an oxygen of a bridging OAc^- group is relatively short (O(7)–O(11A) = 2.899 Å), which indicates that hydrogen bonding further stabilizes the bonding between the two Zn_2Eu halves. The two unique zinc atoms are 5-coordinate but each has a different geometry. Zn(1) has a distorted square based pyramidal geometry while Zn(2) is distorted trigonal bipyramidal. As expected the average Zn–O (methoxy) distance (2.318 Å) is significantly longer than the average Zn–O (phenolic) distance (2.028 Å) (dative *vs.* ionic bonding). The Eu^{3+} ion is 9-coordinate with average Eu–O (phenolic) and Eu–O (aldehyde) distances of 2.463 and 2.499 Å respectively. Both are slightly longer than those found in the literature.

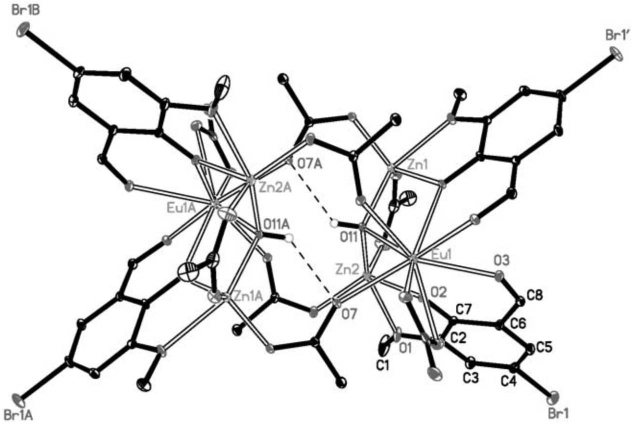

Fig. 1 Crystal structure of **1** showing the inner cage and intramolecular O–H···O interactions. Other hydrogen atoms have been omitted for clarity. The complex resides about a crystallographic inversion center at ½, 0, 0. Atoms whose labels are appended by A are related by $1 - x, -y, -z$.

---

[a] *Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A 5300, Austin, TX, 78712-0165. E-mail: rajones@mail.utexas.edu; stevenson@mail.cm.utexas.edu*
[b] *Texas Materials Institute, The University of Texas at Austin, Austin, TX, 78712*

† Electronic supplementary information (ESI) available: X-Ray diffraction patterns and experimental. See DOI: 10.1039/b607183j

‡ Dedicated in Memoriam to Professor Ian O. Rothwell

The 3-dimensional supramolecular framework of **1** is generated by a combination of short intermolecular Br···O interactions together with π–π stacking interactions between aryl units (center to center distances: 3.981 Å). For example, the Br(1C)···O(12F) distance is 2.940 Å which is shorter than the sum of the van der Waals radii for Br and O (3.350 Å). Analogous short Br (acceptor)···Y (donor, Y = N, O, S, F or Br) have been well documented in the stabilization of supramolecular architectures.[8] These interactions create a two-dimensional layer as shown in Fig. 2. Adjacent layers are further crosslinked by N···H–C (N···H, 2.613 Å, N–H–C, 139.36°) and O···H–C (O···H, 2.650 Å, O–H–C, 165.25°) interactions between NO_3^- and the aldehyde (CH) group (C(8)).[9] The resulting three-dimensional open network has extended channels running along the *b*-axis which measure approximately 8 × 9 Å. Guest molecules of diethyl ether are accommodated within these channels (Fig. 3). There are no short interactions between the Et_2O molecules and the surrounding supramolecular framework suggesting that they could be easily removed. Elemental analysis indicated that approximately 90% of the Et_2O molecules are removed after 2 h of drying under vacuum (10^{-2} torr). These observations led us to explore the host–guest properties of **1** in more detail. Key questions were whether **1** returned the mesoporous structure after removal of Et_2O and could other small molecules be reversibly encapsulated. Powder XRD patterns of **1** after exposure to vacuum for 2 h were similar to the simulated patterns generated from single crystal X-ray data.† We were also able to study the reversible encapsulation of volatile organic compounds (VOC's) by the Et_2O free form of **1** using a quartz crystal microbalance (QCM). The QCM technique is a proven nanogravimetric method for detecting the gas phase insertion and removal of VOC's from a host material.[10]† Preliminary studies show that both Et_2O and MeOH demonstrate a true host–guest interaction with the mesoporous framework of **1**.† Fig. 4 shows the sorption isotherm for Et_2O using a quartz crystal coated with **1** (1.2×10^{-8} mol). The distribution of the concentration of vapor in the host, C_s, relative to the concentration of VOC in vapor phase, C_v, can quantified by a partition coefficient, K. An experimental, or apparent partition coefficient, K_{exp}, can be obtained from the frequency response of the QCM as a result of VOC's interacting with the host complex.[11] If partitioning is described in terms of $K_{exp} \times$ MW, the QCM data can be expressed with respect to normalized partial pressures (P/P_0), and this formulism provides information about the host–guest interaction.[11] A plot obtained for **1**, displays characteristic sorption behavior associated with a true host–guest sensing response.

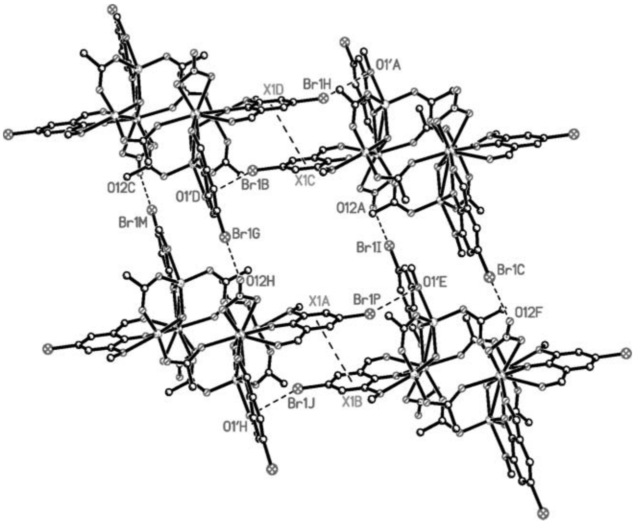

Fig. 2 View of a 2-D layer in **1** generated by intermolecular Br···O and aryl π–π interactions.

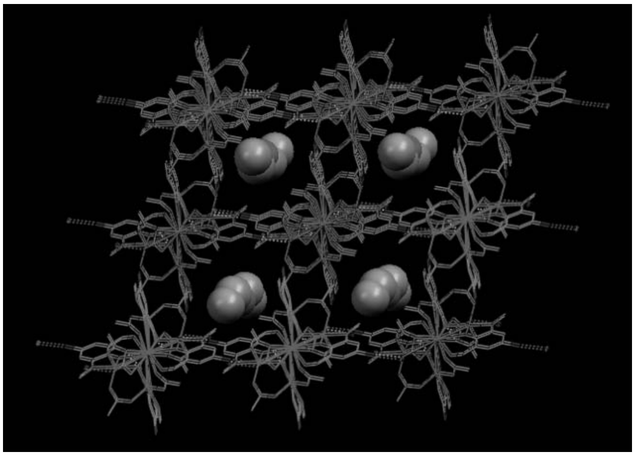

Fig. 3 View of **1** along the *b*-axis showing the 3-D network with incorporation of diethyl ether molecules.

Compound **1** is stable in MeCN solution at room temperature for up to one week and molar conductivity studies indicate that dissociation into ions does not occur. ^1H NMR data for **1** in CD_3CN is consistent with the presence of a discrete Eu_2Zn_4 species composed of two equivalent $EuZn_2$ halves as found in the solid state (See S7 ESI†). Thus at 298 K a total of 12 signals are observed, of which 8 can be assigned to the four deprotonated salicylaldehyde (L) ligands. Three signals are assigned to the six OAc^- groups and one to the two μ-OH units. The Et_2O molecules are also observed (δ 1.120 (t), 3.415 (q) ppm).

The photophysical properties of **1** have been studied in CH_3CN and the UV-vis absorption spectra of HL and **1** are shown in Fig. 5. The free ligand (HL) exhibits absorption bands at 250, 301 and 409 nm, which become red-shifted to 283, 363 and 495 nm, respectively, upon formation of **1**. The excitation and emission

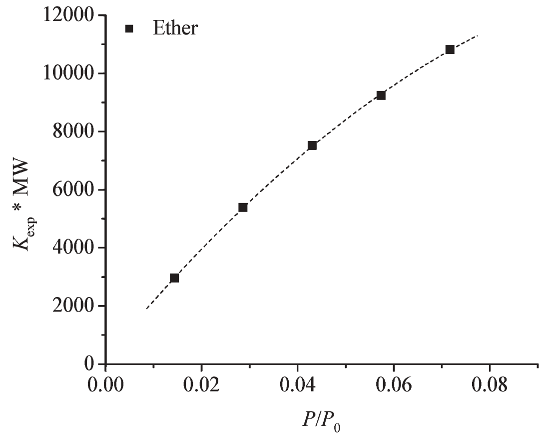

Fig. 4 Sorption isotherm of the guest VOC Et_2O with host complex **1**.

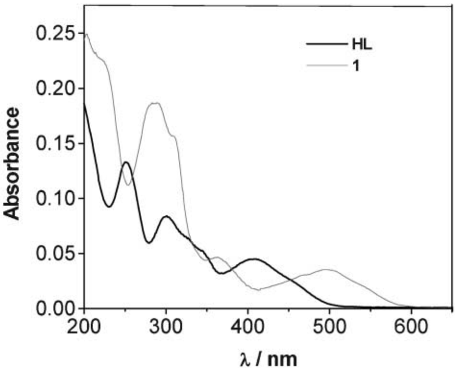

Fig. 5 UV-Vis spectra of free HL and **1** in CH_3CN.

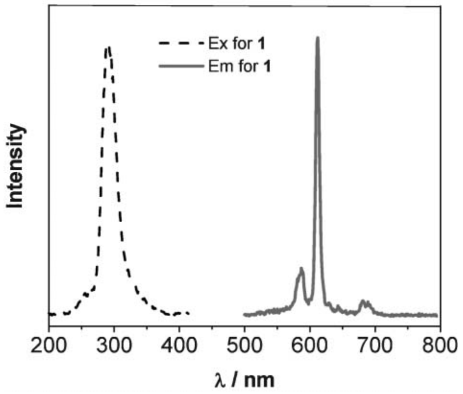

Fig. 6 Excitation and emission spectra of **1** in CH_3CN.

spectra of **1** are shown in Fig. 6. Upon excitation of the ligand centered (L) absorption band, **1** shows visible emission bands typical of the Eu^{3+} ($^5D_0 \rightarrow {}^7F_j$ transitions, j = 1, 2, 3 and 4). The typical Eu^{3+} excitation bands were not present in the excitation spectrum of **1** indicating that the energy transfer from the deprotonated salicylaldehyde ligands (antenna) to the Eu^{3+} ions takes place.[12] There are relatively few reports on the luminescent properties of heteropolynuclear lanthanide complexes.[2,4] For **1** the fluorescence quantum yield (Φ_{em}) in CH_3CN is 0.009.[13]

We thank the Robert A. Welch Foundation (Grants F-816 and F-1529) for support.

Notes and references

§ *Experimental procedure*: a solution of HL (0.046 g, 0.20 mmol) in CH_3CN (5 ml) was added to a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.044 g, 0.20 mmol) and $Eu(NO_3)_3 \cdot 5H_2O$ (0.086 g, 0.20 mmol) in ethanol (5 ml). The mixture was stirred, heated under reflux (30 min) and then allowed to cool to room temperature. Diethyl ether was allowed to diffuse slowly into the solution in a closed vessel at room temperature. Yellow single crystals of **1** were collected after one month. Yield 0.070 g (65%, based on HL). Elemental analysis (after 2 h under vacuum): found: C, 26.69; H, 2.19; N, 1.42%. Calc. for $C_{44}H_{44}Br_4N_2O_{32}Eu_2Zn_4(Et_2O)_{0.2}$: C, 26.73; H, 2.30; N, 1.39%. ESI-MS (CH_3CN) *m*/*z*: 1938 $[M–2Et_2O–OAc^-]^+$. ^1H NMR (500 MHz, CD_3CN): δ (ppm) 1.120 (t, Et_2O), 1.801 (6H), 3.415 (q, Et_2O), 3.864 (6H), 4.063 (2H), 4.512 (6H), 5.676 (6H), 7.307 (2H), 7.416 (2H), 7.575 (6H), 7.768 (2H), 8.949 (2H), 9.922 (2H), 10.420 (2H). IR (CH_3CN, cm^{-1}): 3444.5, 1652.6, 1558.8, 1540.3, 1506.5, 1456.1, 1395.0, 1236.8, 1203.7, 955.9, 708.0 cm^{-1}.

¶ *Crystal data* for **1**: $C_{52}H_{64}Br_4N_2O_{34}Eu_2Zn_4$, M = 2146.09, triclinic, space group $P\bar{1}$, a = 11.390(2), b = 13.007(3), c = 13.194(3) Å, α = 102.47(3), β = 101.11(3), γ = 104.01(3)°, V = 1788.8(6) $Å^3$, Z = 1, Dc = 1.992 g cm^{-3}, μ = 5.368, θ from 3.27 to 27.52°, F(000) = 1048, T = 153 K. R_1 = 0.0398, wR_2 = 0.0894 (strongest data) for 8137 independent reflections with a goodness-of-fit of 1.050. All data were collected on a Nonius Kappa CCD diffractometer and structures solved using the program SHELXL-97. CCDC 265078. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607183j

1 For a recent review see (*a*) N. R. Champness, *Dalton Trans.*, 2006, 877; (*b*) H. Li, M. Eddaoudi, M. O'Keefe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (*c*) M. J. Zaworotko, *Nature*, 1999, **402**, 242; (*d*) E. Y. Lee, S. Y. Jang and M. P. Suh, *J. Am. Chem. Soc.*, 2005, **127**, 6374; (*e*) A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Côté, J. Kim and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 7110; (*f*) A. V. Davis and K. N. Raymond, *J. Am. Chem. Soc.*, 2005, **127**, 7912.

2 (*a*) R. E. P. Winpenny, *Chem. Soc. Rev.*, 1998, **27**, 447; (*b*) G. Blasse, *Mater. Chem. Phys.*, 1992, **31**, 3.

3 B.-Q. Ma, D.-S. Zhang, S. Gao, T.-Z. Jin, C.-H. Yan and G.-X. Xu, *Angew. Chem., Int. Ed.*, 2000, **39**, 3644.

4 See, for example, refs. 103–106 in: M. Sakamoto, K. Manseki and H. Ōkawa, *Coord. Chem. Rev.*, 2001, **219–221**, 379.

5 (*a*) A. Caneschi, A. Cornia, A. C. Fabretti and D. Gatteschi, *Angew. Chem., Int. Ed.*, 1999, **38**, 1295; (*b*) R. Bhula and D. C. Weatherburn, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 688; (*c*) M. Cavalluzzo, Q. Chen and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1993, 131; (*d*) N. Steunou, C. Bonhomme, C. Sanchez, J. Vaissermann and L. G. Hubert-Pfalzgraf, *Inorg. Chem.*, 1998, **37**, 901; (*e*) R. C. Mehrotra, A. Singh and S. Sogani, *Chem. Soc. Rev.*, 1994, **23**, 215.

6 J.-P. Costes, F. Dahan and F. Nicodème, *Inorg. Chem.*, 2001, **40**, 5285.

7 (*a*) X.-P. Yang, R. A. Jones and M. J. Wiester, *Dalton Trans.*, 2004, 1787, see also ; (*b*) X.-P. Yang and R. A. Jones, *J. Am. Chem. Soc.*, 2005, **127**, 7686; (*c*) X.-P. Yang, R. A. Jones, W.-K. Wong, V. Lynch, M. M. Oye and A. L. Holmes, *Chem. Commun.*, 2006, 1836.

8 (*a*) H. A. Bent, *Chem. Rev.*, 1968, **68**, 587; (*b*) A. D. Bond, J. Griffiths, J. M. Rawson and J. Hulliger, *Chem. Commun.*, 2001, 2488; (*c*) M. C. Aragoni, M. Arca, F. A. Devillanova, F. Isaia, V. Lippolis, A. Mancini, L. Pala, A. M. Z. Slawin and J. D. Woollins, *Chem. Commun.*, 2003, 2226.

9 For C–H···Y (Y = N, O, P, Cl or Br) interaction see, for example: (*a*) R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063; (*b*) G. A. Jeffrey and H. Maluszynska, *Int. J. Biol. Macromol.*, 1982, **4**, 173.

10 (*a*) M. H. Keefe, R. V. Slone, J. T. Hupp, K. F. Czaplewski, R. Q. Snurr and C. L. Stern, *Langmuir*, 2000, **16**, 3964.

11 (*a*) J. W. Grate, A. Snow, D. S. Ballantine, Jr., H. Wohltjen, M. H. Abraham, R. A. McGill and P. Sasson, *Anal. Chem.*, 1988, **60**, 869; (*b*) J. W. Grate, M. H. Abraham, C. M. Du, R. A. McGill and W. J. Shuely, *Langmuir*, 1995, **11**, 2125.

12 (*a*) N. Sabbatini, M. Guardigli and J. M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201; (*b*) C. Piguet, G. Hopfgartner, A. F. Williams and J.-C. G. Bünzli, *J. Chem. Soc., Chem. Commun.*, 1995, 491.

13 Quantum yield was determined relative to $[Ru(bipy)_3]Cl_2$ in water (bipy = 2,2′-bipyridine; Φ_{em} = 0.028): K. Nakamaru, *Bull. Chem. Soc. Jpn.*, 1982, **5**, 2697.