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Novel three-dimensional network generated from the reaction of $Eu(NO_3)_3$ with an amide type tripodal ligand†

Jian Zhang,[a] Yu Tang,[a] Ning Tang,[a] Min-Yu Tan,*[a] Wei-Sheng Liu[a] and Kai-Bei Yu[b]

[a] *College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, P.R. China. E-mail: tangyu@lzu.edu.cn*
[b] *Analysis Center, Chengdu Branch of Chinese Academy of Science, Chengdu, 610041, P.R. China*

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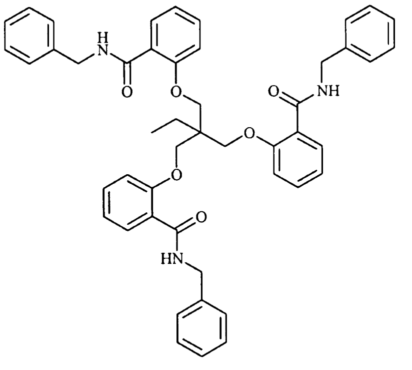
The reaction of $Eu(NO_3)_3·6H_2O$ with amide type tripodal ligand L produces an unexpected three-dimensional network, which is directed by both coordinate and hydrogen bonds.

Tripodal ligands have been widely used in both coordination and organometallic chemistry.[1] Recently, some rigid tripodal ligands have been synthesized for the construction of various novel cage- or box-like complexes and have demonstrated their potential use in supramolecular chemistry.[2] Amide type tripodal ligands have been used as the active materials in ion-selective electrodes,[3] but their lanthanide complexes have not yet attracted great attention, in spite of their high tendency to coordinate Ln^{3+}. Our group is interested in the supramolecular coordination chemistry of amide type tripodal ligands with lanthanide(III) ions, and recently we synthesized 1,1,1-tris-{[(2′-benzylaminoformyl)phenoxyl]methyl} propane (L) and investigated the reaction of L with lanthanide nitrates. To our surprise, the reaction of L with $Eu(NO_3)_3·6H_2O$ does not yield the cage- or box-like structure, but a one-dimensional chain-like coordination polymer $[Eu(NO_3)_3L(CH_3CO_2C_2H_5)]_\infty$ (**1**). It is more interesting that hydrogen bonding between the polymer chains generates a three-dimensional network.



L

Coordination and hydrogen bonding interactions are regarded as the most important driving forces in crystal engineering.[4] Up to now most of the supramolecular structures incorporating these two interactions have been based on transition metals.[5] The analogous chemistry of the lanthanide metals remains undeveloped,[6] despite the potential utility of the complexes as luminescent and sensory materials.[7] This is attributed to the preference of the lanthanide(III) ions for high coordination numbers, which favors the formation of condensed structures,[8] especially when using tripodal ligands as hosts. To the best of our knowledge, compound **1** represents the first 3-D network of lanthanide ions which contain amide type tripodal ligands as building blocks, assembled by both coordination and hydrogen bonds. Herein we report the synthesis, crystal structure and fluorescence properties of compound **1**.

The relatively flexible ligand L was prepared by the replacement reaction of 1,1,1-tris(*p*-tosyloxymethyl)propane and *N*-benzylsalicylamide. Compound **1** was prepared by the reaction of $Eu(NO_3)_3·6H_2O$ with ligand L in a molar ratio of 1 : 1 in ethyl acetate. ‡

Recrystallisation of **1** from methanol and ethyl acetate afforded crystals suitable for X-ray analysis. § The single-crystal X-ray analysis of complex **1** revealed that each Eu center binds to nine oxygen donor atoms, six of which belong to three bidentate nitrate groups, two to carbonyl groups from two tripodal ligands and the remaining one to the carbonyl group of ethyl acetate (Fig. 1 and Fig. 1S, ESI). The coordination geometry around the Eu atom is a one-capped distorted square antiprism. This type of coordination mode for a tripodal ligand is rare. In fact, tripodal ligands have been employed as hosts for 3d or 4f ions, leading to mononuclear (3d or 4f) and homodinuclear (4f, 4f) complexes.[9] Compound L was synthesized as a hexadentate or tridentate ligand, which has three carbonyl oxygen and three ether oxygen donor atoms, and we hoped that it could be used as a good chelator. Due to the steric problems involved with six oxygen atoms coordinating to the same Eu(III) ion, L acts as a bidentate bridging spacer in complex **1**. Two arms of each ligand bind two neighboring Eu atoms; another arm remains uncoordinated, forming the 1-D polymer along the *a* axis, directed by coordination bonding.

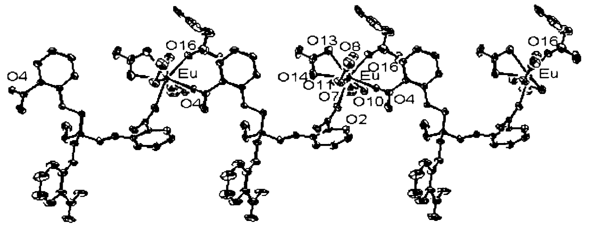


Fig. 1 Molecular structure of $[Eu(NO_3)_3L(CH_3CO_2C_2H_5)]_\infty$, showing the 1-D polymeric structure. All the benzyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Eu–O (2) 2.312(3), Eu–O(16) 2.388(3), Eu–O (4) 2.330(3), Eu–O (11) 2.458(4), Eu–O (13) 2.473(4), Eu–O (14) 2.476(4), Eu–O (8) 2.492(4), Eu–O (7) 2.498(4), Eu–O (10) 2.541(4); O(2)–Eu–O(16) 152.93(13), O(4A)–Eu–O(16) 81.31(12), O (2)–Eu–O (4) 86.55(12), O (2)–Eu–O (11) 82.87(15), O(16)–Eu–O(8) 74.10(13), O(16)–Eu–O(7) 124.10(13), O (4)–Eu–O (11) 130.81(16), O (4)–Eu–O (13) 146.12(12), O (2)–Eu–O (14) 76.16(14), O (2)–Eu–O (10) 80.76(13).

As shown in Fig. 2, the polymer chains are further packed into a three-dimensional network through two types of inter-chain hydrogen bonding interaction along two different directions. Firstly, "amide–amide" type double hydrogen bonds along the *c* axis link pairs of ligands from two adjacent polymer

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† Electronic supplementary information (ESI) available: views of: the 1-D polymeric structure of **1**, amide–amide hydrogen bonding interactions between ligands from adjacent polymer chains, 3-D framework assembly *via* amide–nitrate hydrogen bonding and the crystal packing in **1**. See http://www.rsc.org/suppdata/dt/b1/b111116g/

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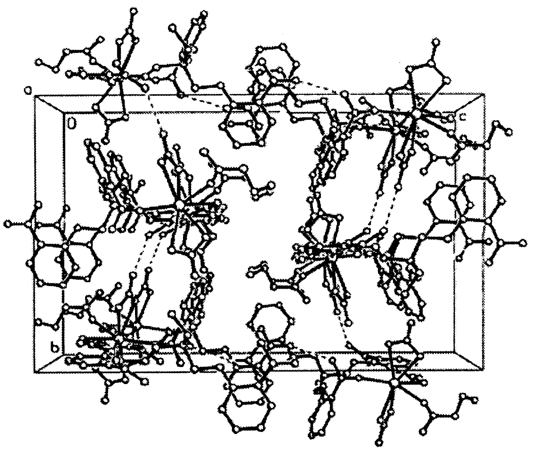

Fig. 2 Crystal packing of **1** (viewed along the *a* axis). All the benzyl groups are omitted for clarity. The dashed lines represent hydrogen bonds (see ESI for a complete crystal packing plot).

chains (denoted as A and B, Fig. 2S, ESI). One uncoordinated carbonyl group of a ligand in chain A forms a hydrogen bond with one H–N group of the other ligand in chain B. Meanwhile, one uncoordinated carbonyl group in chain B and one H–N group in chain A form a hydrogen bond in the same pattern, both with an N ··· O distance of 2.901 Å. The interlocking mode of the double hydrogen bonding between the two polymer chains makes the structure very rigid. It has been established that amide–amide interaction typically involves "head-to-head" or catemer hydrogen bonds in metal complexes.[10] Our work provides a new example of hydrogen bonds existing between N-substituted amides in metal complexes.

Furthermore, the double-chain assemblies are joined into a 3-D framework through inter-assembly amide–nitrate hydrogen bonds with an N ··· O distance of 2.884 Å (Fig. 3S, ESI). This type of hydrogen bonding linkage system is comprised of one coordinated nitrate and one amide group, and can be formulated as Eu–O_2NO ··· HN(R)C=O–Eu. Such a hydrogen bonding linkage extends periodically along the *b* axis in a zig-zag fashion. With the formation of the hydrogen bonding interactions described above, one-dimensional polymer chains are developed into a three-dimensional network, producing channels along the *a* axis.

In general, tripodal ligands are able to shield the encapsulated Ln^{3+} from interaction with the surroundings,[11] especially solvent molecules, such as water or alcohol. It is noteworthy that although the tripodal ligand L does not shield Eu^{3+} using all three arms, compound **1** is still highly luminescent. The emissions resulting from excitation at 350 nm are all characteristic of the Eu^{3+} ion, and the broad emission band around 450 nm observed for the free ligand is significantly reduced, indicating an efficient ligand-to-metal energy-transfer process (antenna effect),[12] as shown in Fig. 3. A detailed luminescence study is in progress.

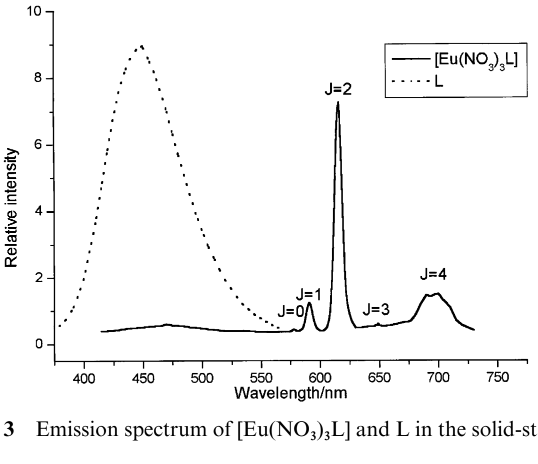

Fig. 3 Emission spectrum of $[Eu(NO_3)_3L]$ and L in the solid-state.

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Notes and references

‡ Preparation of **1**: To an ethyl acetate solution (10 mL) of europium nitrate (0.045 g, 0.1 mmol) was added an ethyl acetate solution (10 mL) of L (0.076 g, 0.1 mmol) and the mixture was stirred for 4 h at room temperature. The precipitated solid was filtered, washed with ethyl acetate and dried *in vacuo* over P_2O_5 for 48 h (Found: C, 51.33; H, 3.89; N, 7.79. $C_{48}H_{49}EuN_6O_{16}$ requires C, 51.57; H, 4.42; N, 7.52%). The solid Eu(III) complex was recrystallized from $CH_3OH–CH_3CO_2CH_2CH_3$ (1 : 1 v/v) by slow evaporation to give transparent colorless crystals of $[Eu(NO_3)_3L(CH_3CO_2C_2H_5)]_\infty$. Yield 0.062 g. IR (KBr/cm^{-1}): 3373(m), 2974(w), 1726(w), 1807(vs), 1564(s), 1491(s), 1382(w), 1299(s), 1227(m), 1165(w),1110(m), 1027(m), 825(w), 755(m), 702(m), 600(w), 524(w).

§ Crystal data for **1**: $C_{52}H_{55}EuN_6O_{17}$, $M_r = 1187.98$, monoclinic, space group $P2_1/c$, $a = 13.314(3)$, $b = 16.009(2)$, $c = 25.310(5)$ Å, $\beta = 90.41(2)°$, $U = 5394.5(18)$ Å^3, $Z = 4$, $\rho_{calc} = 1.463$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71073$ Å), $T = 295(2)$ K. $\mu = 1.238$ mm^{-1}. Final R_1 and $wR2$ are 0.0424 and 0.0976 respectively, GOF = 0.955. CCDC reference number 166868. See http://www.rsc.org/suppdata/dt/b1/b111116g/ for crystallographic data in CIF or other electronic format.

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