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Note

Mononuclear single helices of lanthanum(III) and europium(III). Metal dependent diastereomeric excess

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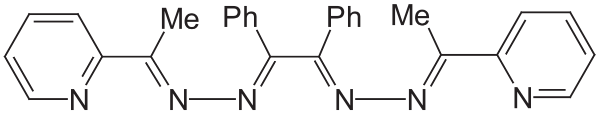
ABSTRACT

Using the 1:2 condensate of benzildihydrazone and 2-acetylpyridine as a tetradentate N donor ligand L, $LaL(NO_3)_3$ (**1**) and $EuL(NO_3)_3$ (**2**), which are pale yellow in colour, are synthesized. While single crystals of **1** could not be obtained, **2** crystallises as a monodichloromethane solvate, **2**·CH_2Cl_2 in the space group *Cc* with $a = 11.7099(5)$ Å, $b = 16.4872(5)$ Å, $c = 17.9224(6)$ Å and $\beta = 104.048(4)°$. From the X-ray crystal structure, **2** is found to be a rare example of monohelical complex of Eu(III). Complex **1** is diamagnetic. The magnetic moment of **2** at room temperature is 3.32 BM. Comparing the FT-IR spectra of **1** and **2**, it is concluded that **1** also is a mononuclear single helix. ^1H NMR reveals that both **1** and **2** are mixtures of two diastereomers. In the case of the La(III) complex (**1**), the diastereomeric excess is only 10% but in the Eu(III) complex **2** it is 80%. The occurrence of diastereomerism is explained by the chiralities of the helical motif and the type of pentakis chelates present in **1** and **2**.

1. Introduction

There are ample examples of helical motifs in biology. These are self-assembled. These prompted the syntheses of artificial helices initially. But now synthetic helical molecules find applications in different fields like stereoselective catalysis, chemical sensing, DNA binding etc. [1–5]. Syntheses of purely organic helical molecules are more difficult than metallo-organic helices. This is because the directive coordination behaviour of the metal ions facilitates generation of metallo helices. A variety of inorganic single, double and triple stranded helices have been constructed in the past using non-helical organic ligands [6–8]. For the past few years we have been engaged in synthesizing metal complexes of ligands which themselves are helical. One such ligand is L. Our synthetic strategy has generated a number of helical and möbius molecules [9–15]. Metals used are Ni, Cu, Ag, Zn, Cd and Hg. In the present report, the metal ions involved are the lanthanides La(III) and Eu(III).



ligand L

2. Results and discussion

The ligand L is the 1:2 condensate of benzildihydrazone and 2-acetylpyridine [12]. The N═C(Ph)–C(Ph)═N torsion angle of 85.9(5)° brings about its helicity.

Reaction of $La(NO_3)_3{\cdot}xH_2O$ and $Eu(NO_3)_3{\cdot}xH_2O$ with L in equimolar ratio in acetonitrile at room temperature gives $LaL(NO_3)_3$ (**1**) and $EuL(NO_3)_3$ (**2**) respectively in moderate yield. We have not been able to grow single crystals of **1**. But direct diffusion of *n*-hexane into a dichloromethane solution of **2** yields single crystals of its mono dichloromethane solvate.

The X-ray crystal structure of **2**·CH_2Cl_2 contains the metal complex $EuL(NO_3)_3$ together with solvent dichloromethane. The complex is shown in Fig. 1 along with the numbering scheme in the metal coordination sphere. Selected bond distances and angles are given in Table 1. The metal complex adopts an approximate C2 conformation as is apparent from Fig. 1. The europium atom is ten-coordinate. All the three nitrate ligands are bonded to the metal centre in a bidentate fashion with Eu–O distances ranging from 2.463(7) to 2.523(6) Å. The four nitrogen atoms of the ligand L are bonded to the metal with distances to the imino nitrogen atoms N(48), N(53) of 2.566(7), 2.589(7) Å and to the pyridine nitrogen atoms N(60) and N(41) of 2.623(7), 2.679(7) Å. The ligand adopts a conformation in which the central torsion angles are C(54)–N(53)–N(52)–C(51) 112.8(3), N(53)–N(52)–C(51)–C(50) −5.1(3), N(52)–C(51)–C(50)–N(49) 76.4(3), C(51)–C(50)–N(49)–

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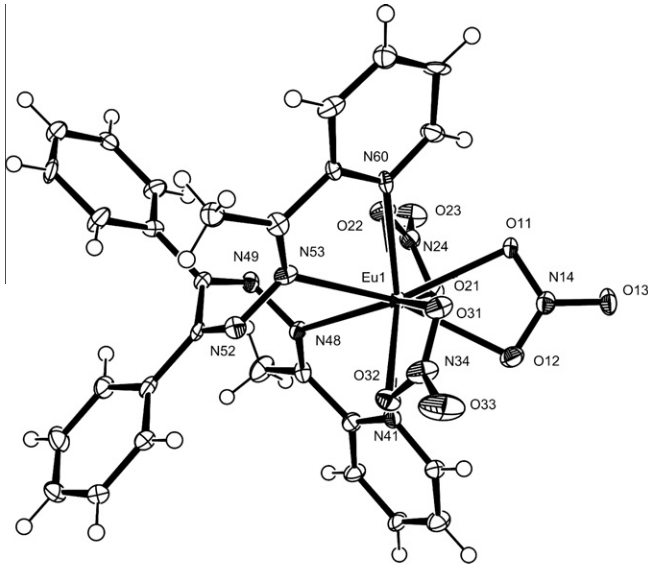

Fig. 1. The structure of **2** in **2**·CH_2Cl_2 with ellipsoids at 25% probability.

N(48) −2.0(3), C(50)–N(49)–N(48)–C(47) 118.5(3)°. The angle between the planes containing pyridine rings is 77.36°.

The topology of **2** is helical. This is evident from its space-filling model shown in Fig. 2. Complex **2** is a mononuclear single helix. Though there are many literature reports of double and triple helices [16,17] but till date only two examples of mononuclear single helix of Eu(III) are known [18,19]. The FT-IR spectra of **1** and **2** are virtually identical. Further, as revealed in molar conductance measurements, complex **1** is non-electrolyte like **2** in methanol indicating that the nitrate groups are bound to the metal in **1** as well. Hence it is reasonable to assume that our La(III) complex also has a structure similar to that of the Eu(III) complex **2**.

Complexes **1** and **2**, being single helical, can have two optical isomers – P (plus; right handed) and M (minus; left handed) [20]. The configuration shown in Figs. 1 and 2 is M. Now the sort of pentakis chelate encountered in **2** (and in **1**) is schematically shown in Fig. 3. It can have two absolute configurations. This type of chelate is identified for the first time. So a convention has to be developed to determine their absolute configurations. In structure I of Fig. 3, if one traces the chelate rings from the top in a sequence indicated in the figure (1 → 2 → 3 → 4 → 5), then a left handed screw is generated. In keeping with the convention used for octahedral tris chelates [20], we assign Λ to I. Configuration II in Fig. 3 can then be assigned as Δ. Consequently we can have four enantiomers for each of **1** and **2** – PΛ, MΛ, PΔ and MΔ, i.e. two diastereomers are possible for **1** and **2**. In the chemistry of helicates diastereomeric selectivity/excess has often been observed [21–25]. In order to find out whether there is any diastereomeric selectivity in our case, we have examined the ^{1}H NMR spectra of **1** and **2** in $CDCl_3$ (Fig. 4). Since complexes **1** and **2** have a C_2 axis (revealed from Fig. 1), the two methyl groups in them are expected to give rise to only one singlet in the absence of any diastereomeric problem. In reality, both for **1** and **2**, two methyl signals are observed with different intensity. In the case of **1**, the methyl signals appear at 2.28 and 2.40 ppm (reference: TMS) with an intensity ratio of 0.83:1 indicative of 45:55% population of the two diastereomers [26]. In the case of **2**, the proton NMR spectrum is paramagnetically shifted. The two methyl signals appear at 7.48 and 8.87 ppm (reference: TMS) with an intensity ratio of 1:0.24 which means that in **2** the population of the two diastereomers is 10:90% [26]. Thus in **1** and **2** we have metal dependent diastereomeric excess. Earlier Perrett-Aebi et al. [24] have observed such metal dependent

Table 1
Selected bond distances (Å) and angles (°) in **2**·CH_2Cl_2. For atom labeling scheme, see Fig. 1.

Eu(1)–O(11)	2.463(7)	Eu(1)–O(12)	2.523(6)
Eu(1)–O(21)	2.480(6)	Eu(1)–O(23)	2.440(6)
Eu(1)–O(31)	2.513(6)	Eu(1)–O(32)	2.503(6)
Eu(1)–N(48)	2.566(7)	Eu(1)–N(53)	2.589(7)
Eu(1)–N(60)	2.623(7)	Eu(1)–N(41)	2.679(7)
O(21)–Eu(1)–O(11)	77.9(2)	O(22)–Eu(1)–O(21)	51.6(2)
O(11)–Eu(1)–O(21)	72.5(2)	O(21)–Eu(1)–O(32)	169.0(2)
O(11)–Eu(1)–O(32)	112.8(2)	O(21)–Eu(1)–O(32)	132.7(2)
O(21)–Eu(1)–O(31)	133.7(2)	O(11)–Eu(1)–O(31)	75.1(2)
O(21)–Eu(1)–O(31)	144.3(2)	O(32)–Eu(1)–O(31)	51.0(2)
O(21)–Eu(1)–O(12)	117.8(2)	O(11)–Eu(1)–O(12)	51.5(2)
O(21)–Eu(1)–O(12)	77.7(2)	O(32)–Eu(1)–O(12)	72.7(2)
O(31)–Eu(1)–O(12)	70.5(2)	O(21)–Eu(1)–N(48)	73.8(2)
O(11)–Eu(1)–N(48)	144.9(2)	O(21)–Eu(1)–N(48)	73.8(2)
O(32)–Eu(1)–N(48)	97.1(2)	O(31)–Eu(1)–N(48)	139.9(2)
O(12)–Eu(1)–N(48)	128.5(2)	O(21)–Eu(1)–N(53)	95.4(2)
O(11)–Eu(1)–N(53)	132.0(2)	O(21)–Eu(1)–N(53)	137.9(2)
O(32)–Eu(1)–N(53)	75.5(2)	O(31)–Eu(1)–N(53)	76.4(2)
O(12)–Eu(1)–N(53)	143.9(2)	N(48)–Eu(1)–N(53)	71.8(2)
O(21)–Eu(1)–N(60)	69.2(2)	O(11)–Eu(1)–N(60)	73.0(2)
O(21)–Eu(1)–N(60)	115.8(2)	O(32)–Eu(1)–N(60)	110.4(2)
O(31)–Eu(1)–N(60)	67.2(2)	O(12)–Eu(1)–N(60)	116.5(2)
N(48)–Eu(1)–N(60)	114.4(2)	N(53)–Eu(1)–N(60)	60.5(2)
O(21)–Eu(1)–N(41)	112.6(2)	O(11)–Eu(1)–N(41)	114.5(2)
O(21)–Eu(1)–N(41)	69.2(3)	O(32)–Eu(1)–N(41)	66.4(2)
O(31)–Eu(1)–N(41)	112.6(2)	O(12)–Eu(1)–N(41)	69.7(2)
N(48)–Eu(1)–N(41)	60.3(2)	N(53)–Eu(1)–N(41)	111.9(2)
N(60)–Eu(1)–N(41)	172.3(2)		

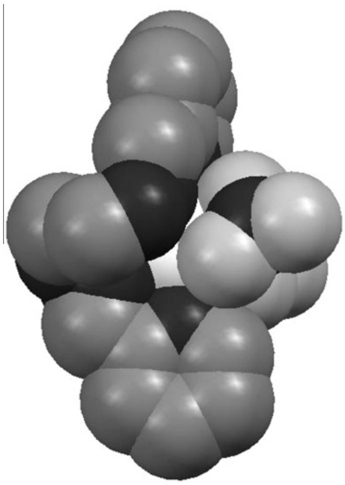

Fig. 2. A space-filling model of **2** showing its helical nature. Colour code: Eu, white; N, black; C, dark gray; O, light gray.

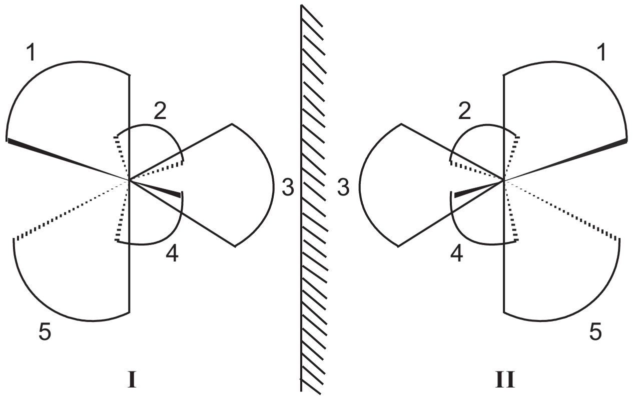

Fig. 3. Schematic representation of the type of pentakis chelate observed in Fig. 2 (I) and its non-superimposable mirror image (II).

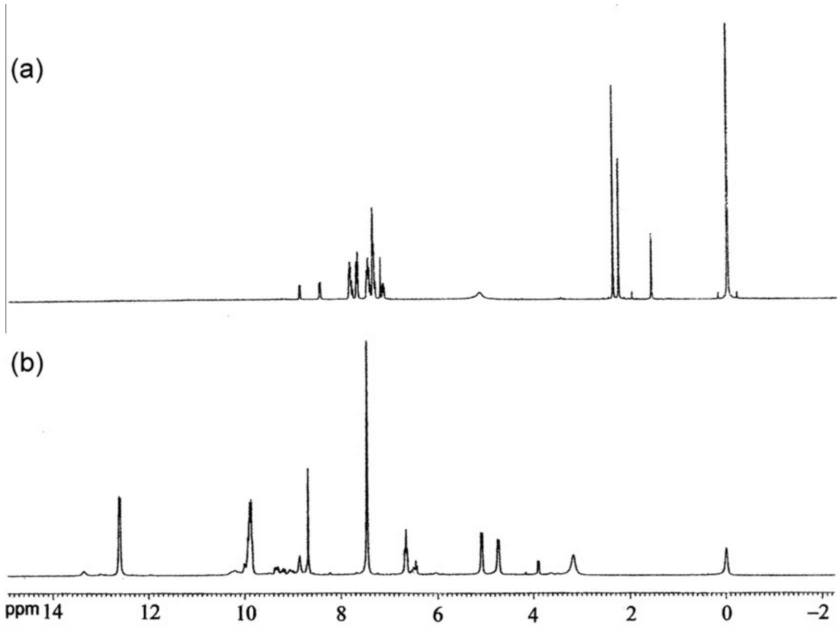

Fig. 4. 300 MHz ^1H NMR spectra of **1** (a) and **2** (b) in $CDCl_3$ where TMS is the reference. The sharp peaks at 7.26 ppm in (a) and at 7.69 ppm in (b) are due to the residual protons in the solvent. The peaks at 1.60 ppm in (a) and at 3.19 ppm in (b) are due to water present in the solvent.

diastereomeric excess in the helicates of Cu(I) and Ag(I) of the same ligand.

3. Experimental

3.1. Materials and physical measurements

The ligand was prepared by a procedure reported earlier by us [12]. Micro-analyses were performed by a Perkin–Elmer 2400II elemental analyser. Molar conductances were measured in methanol by a Systronics (India) conductivity bridge (model 306). FT-IR spectra (KBr) were recorded on a Shimadzu FT-IR-8400S spectrophotometer, UV–Vis spectra in acetonitrile on a Perkin–Elmer Lambda 950 spectrophotometer and 300 MHz ^1H NMR spectra in $CDCl_3$ on a Bruker DPX300 spectrometer. Magnetic moments were measured at room temperature by a magnetic susceptibility balance procured from Sherwood Scientific, UK. Pascal's constants were used for diamagnetic corrections.

3.2. Syntheses of LaL$(NO_3)_3$ (**1**)

L (0.089 g, 0.2 mmol) dissolved in 10 ml of acetonitrile was added to an acetonitrile solution (10 ml) of $La(NO_3)_3 \cdot xH_2O$ (0.065 g) dropwise with stirring. The yellow colour of the solution faded and compound started appearing within 5 min of stirring. After stirring for 1 h the precipitated compound was filtered off, washed with few drops of petroleum ether and dried in air. Yield: 0.100 g (65%). *Anal.* Calc. for $C_{28}H_{24}N_9LaO_9$: C, 43.71; H, 3.14; N, 16.38. Found: C, 43.59; H, 3.15; N, 16.29%. Main FT-IR bands (KBr) ν/cm^{-1}: 3404 (br,s), 1614 (m), 1591 (w), 1566 (w), 1517 (sh), 1497 (sh), 1466 (m), 1441 (sh), 1385 (vs), 1275 (m), 1028 (w), 1005 (w), 785 (m), 739 (m) and 692 (m). Λ_M/mho cm^2 mol^{-1}: 17. UV–Vis λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 263 (4 200), 298(5 300).

3.3. Synthesis of EuL$(NO_3)_3$ (**2**)

It was prepared exactly the same way as **1** by starting with $Eu(NO_3)_3 \cdot xH_2O$ (0.068 g) and L (0.089 g, 0.2 mmol). Yield: 78 mg (50%). *Anal.* Calc. for $C_{28}H_{24}N_9EuO_9$: C, 42.98; H, 3.09; N, 16.11. Found: C, 42.80; H, 3.04; N, 16.29%. Main FT-IR bands (KBr) ν/cm^{-1}: 3398 (br,s), 1612 (w), 1591 (m), 1568 (w), 1527 (sh), 1500 (m), 1471 (sh), 1445 (sh), 1385 (vs), 1279 (m), 1030 (m), 1009 (w), 785 (m), 741 (m) and 692 (m). Λ_M/mho cm^2 mol^{-1}: 21.μ/μ_B: 3.32 (at 297 K). UV–Vis: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 263 (4 040), 298 (4 840).

3.4. X-ray crystallography

Crystal data for $\mathbf{2} \cdot CH_2Cl_2$ are given in Table 2. These were collected at 150(2) K with Mo Kα radiation using the Oxford Diffraction X-Calibur CCD System. The crystal was positioned at 50 mm from the CCD. Three hundred and twenty one frames were measured with a counting time of 2 s. Data analysis was carried out with the CRYSALIS program [27]. The structure was solved using direct methods with the SHELX97 program [28]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric

Table 2
Crystallographic data for $EuL(NO_3)_3 \cdot CH_2Cl_2$ ($\mathbf{2} \cdot CH_2Cl_2$).

Formula	$C_{29}H_{26}N_9EuCl_2O_9$
M	867.45
Space group	monoclinic, *Cc*
Cell dimensions (Å, °)	
a	11.7099(5)
b	16.4872(5)
c	17.9224(6)
β	104.048(4)
U (Å^3)	3356.7(2)
Z, D_{calc} (g cm^{-3})	4, 1.716
μ (mm^{-1})	2.094
F(0 0 0)	1728
Number of reflections unique	4864
Observed [$I > 2\sigma(I)$]	4649
Parameters	453
R indices (observed data)	R_1, 0.0518; wR_2, 0.1358
R indices (all data)	R_1, 0.0534; wR_2, 0.1378
Largest difference in peak and hole (e Å^{-3})	2.375 and 2.506

positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An absorption correction was carried out using the ABSPACK program [29]. The structure was refined on F^2 using SHELX97 [28].

Acknowledgments

We thank EPSRC and the University of Reading for funds for the X-Calibur system. Discussions with Dr. T.K. Paine are gratefully acknowledged.

Appendix A. Supplementary material

CCDC 706293 contains 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.05.016.

References

[1] C.T. Yeung, H.L. Yeung, C.S. Tsang, W.Y. Wong, H.L. Kwong, Chem. Commun. (2007) 5203.
[2] H.L. Kwong, H.L. Yeung, W.S. Lee, W.T. Wong, Chem. Commun. (2006) 4841.
[3] M. Elhabiri, R. Scopelliti, J.G. Binzli, C. Piguet, J. Am. Chem. Soc. 121 (1999) 10747.
[4] C. Dolain, H. Jiang, J.M. Leger, P. Guionneau, I. Huc, J. Am. Chem. Soc. 127 (2005) 12943.
[5] M.J. Hannon, Chem. Soc. Rev. 36 (2007) 280.
[6] Y. Wang, H. Fu, F. Shen, X. Sheng, A. Peng, Z. Gu, H. Ma, J.S. Ma, J. Yao, Inorg. Chem. 46 (2007) 3548.
[7] M. Vazquez, M.R. Bermejo, M. Fondo, A. Garcia-Deibe, A.M. Gonzalez, R. Pedrido, Eur. J. Inorg. Chem. (2002) 465.
[8] T. Riss-Johannessen, N. Dupont, G. Canard, G. Bernardinelli, A. Hauser, C. Piguet, Dalton Trans. (2008) 3661.
[9] M. Zimmer, D.A. Tocher, G.K. Patra, J.P. Naskar, D. Datta, Indian J. Chem., Sect. A 38 (1999) 1087.
[10] S. Chowdhury, P.B. Iveson, M.G.B. Drew, D.A. Tocher, D. Datta, New J. Chem. 27 (2003) 193.
[11] S. Chowdhury, M.G.B. Drew, D. Datta, New J. Chem. 27 (2003) 831.
[12] M.G.B. Drew, D. Parui, S. De, S. Chowdhury, D. Datta, New J. Chem. 31 (2007) 1763.
[13] M.G.B. Drew, S. De, D. Datta, Inorg. Chim. Acta 360 (2007) 3448.
[14] M.G.B. Drew, S. De, D. Datta, Inorg. Chim. Acta 362 (2009) 2487.
[15] S. De, M.G.B. Drew, H.S. Rzepa, D. Datta, New J. Chem. 32 (2008) 1831.
[16] Y.Q. Sun, J. Zhang, Y.M. Chen, G.Y. Yang, Angew. Chem., Int. Ed. 44 (2005) 5814.
[17] C. Piguet, G. Hopfgartner, A.F. Williams, J.C.G. Buenzli, Chem. Commun. (1995) 491.
[18] E.C. Constable, R. Chotalia, D.A. Tocher, J. Chem. Soc., Chem. Commun. (1992) 771.
[19] M.H.W. Lam, D.Y.K. Lee, S.S.M. Chiu, K.W. Man, W.T. Wong, Eur. J. Inorg. Chem. (2000) 1483.
[20] C. Piguet, G. Bernardinelli, G. Hopfgartner, Chem. Rev. 97 (1997) 2005.
[21] G. Baum, E.C. Constable, D. Fenske, C.E. Housecroft, T. Kulke, Chem. Eur. J. 5 (1999) 1862.
[22] A. Lutzen, M. Hapke, J. Griep-Raming, D. Hasse, W. Saak, Angew. Chem., Int. Ed. 41 (2002) 2086.
[23] M. Albrecht, S. Schmid, S. Dehn, C. Wickleder, S. Zhang, A.P. Bassett, Z. Pikramenon, R. Frohlich, New J. Chem. 31 (2007) 1755.
[24] L. Perrett-Aebi, A.V. Zelewsky, A. Neels, New J. Chem. 33 (2009) 462.
[25] C.S. Tsang, H.L. Yeung, W.T. Wong, H.L. Kwong, Chem. Commun. (2009) 1999.
[26] The assignments of the methyl groups are rather straightforward, as all other signals appear structured.
[27] CRYSALIS Program, Version 1, Oxford Diffraction, 2005.
[28] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
[29] ABSPACK, Oxford Diffraction, 2005.