

# Gelation of La(III) cations promoted by 5-(2-pyridyl)tetrazolate and water†

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Received (in Cambridge, UK) 6th April 2006, Accepted 31st May 2006

First published as an Advance Article on the web 3rd July 2006

DOI: 10.1039/b605006a

Addition of water to the product formed when LaCl<sub>3</sub> and 1*H*-5-(2-pyridyl)tetrazole (LH) were treated with an excess of triethylamine in ethanol, resulted in the reversible formation of a hydrogel, which when further treated with EtOH-<sup>1</sup>PrOH produced crystals of [LaL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>](H<sub>2</sub>O)<sub>4</sub>, as determined by X-ray crystallography.

Due to their unique properties, lanthanides have found applications in a wide range of fields, *e.g.* medicinal chemistry,<sup>1,2</sup> the design of novel luminescent<sup>3</sup> or magnetic materials,<sup>4</sup> anti-corrosion coatings<sup>5</sup> and precursors for the deposition of ultra-pure lanthanide oxides as high- $\kappa$  gate dielectrics in Si-based field effect transistors.<sup>6</sup> Special attention has recently focussed on forming gel-like systems containing lanthanide cations or complexes, with the intent of improving the thermal stability and the mechanical properties of the material.<sup>7</sup> The advantage of such gels is that as “soft materials” they offer facile processability by means of cheap fabrication techniques such as microfluidics, micromolding in capillaries (MIMICS), and soft lithography.<sup>8</sup> The citrate gel process has been extensively employed for the preparation of ceramic materials based on ultrapure lanthanide chromites, LnCrO<sub>3</sub>, and for the deposition of luminescent Ln<sub>2</sub>O<sub>3</sub>-Eu (Ln = Gd, Lu) thin films.<sup>9</sup> Moreover, nanostructured hydrogels have proven to be optimal candidates as responsive materials in biological applications such as biomaterials and biosensors.<sup>10</sup> Although a rigorous definition of “gel” is not straightforward, these systems can be roughly described as either physically (*i.e.* by means of hydrophobic interaction or hydrogen bonds) or covalently cross-linked polymeric architectures which swell in contact with a solvent.<sup>10</sup> Cross-linking is essential in preventing the complete dissolution of the material, and thus formation of a “liquid” solution.

Three main strategies have been followed for the preparation of lanthanide containing gels: (i) lanthanide salts or complexes are simply added to a gelating matrix, which can be a polymer or a silica glass precursor;<sup>11</sup> (ii) the ligands of the lanthanide complex are endowed with chemical groups able to covalently graft to the framework;<sup>7</sup> (iii) the lanthanide cations are anchored to specific chemical functionalities of the matrix.<sup>12</sup>

We report here the first example of gelation of a La complex in water without the need for an additional gelating polymer. The

hydrogel is obtained by the addition of water to a La(III) complex in which the metal cation is coordinated by 5-(2-pyridyl)tetrazolate anions. In this case, gel formation was completely unexpected since the tetrazolate ligand was not specifically designed to form a cross-linked architecture with the ability to swell in contact with water.

We are currently studying the formation of Ln complexes with N donor chelating heterocycles to assess the possibility of using them as “protecting” ligands in the formation of Ln clusters.<sup>13</sup> In the course of these studies we reacted LaCl<sub>3</sub> with 1*H*-5-(2-pyridyl)tetrazole (LH) using a modification of the synthetic procedure recently described by Roesky *et al.*<sup>14</sup> LH was synthesized by nucleophilic addition of NaN<sub>3</sub> to the cyano group of 2-pyridinecarbonitrile in water, catalysed by ZnBr<sub>2</sub>.<sup>15</sup> The capacity of L<sup>-</sup> to form mononuclear Ln complexes of the type LnL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> has been reported for Ln = Gd, Eu, and Dy.<sup>16</sup> In attempting the synthesis of the clusters, an excess of triethylamine was added to an ethanolic solution containing both LaCl<sub>3</sub> and LH in a 1 : 3 stoichiometric ratio.‡ Because of its relative thermodynamic acidity (p*K*<sub>a</sub> = 4.8), the tetrazole ring is readily deprotonated by triethylamine. Upon addition of the base a white precipitate is formed which is insoluble in both apolar and polar organic solvents, even after prolonged heating and/or sonication. However, when mixed with hot water (80 °C), gelation occurs within a few minutes (Fig. 1).

To gain some understanding of the structure of the gel we analyzed the dry material by means of IR and NMR spectroscopy. The presence of a strong broad band around 3300 cm<sup>-1</sup> in the IR spectrum, even after several days of drying at 50 °C under reduced pressure, suggested the presence of a hydrated compound. The absorptions at 1606 and 1571 cm<sup>-1</sup>, which we ascribe to the C=N and N=N stretches of the ligand, are typical of the tetrazole ring. <sup>1</sup>H-NMR on the sample (dispersed in carefully dried DMSO after several hours of sonication) showed four broad signals at 8.75,

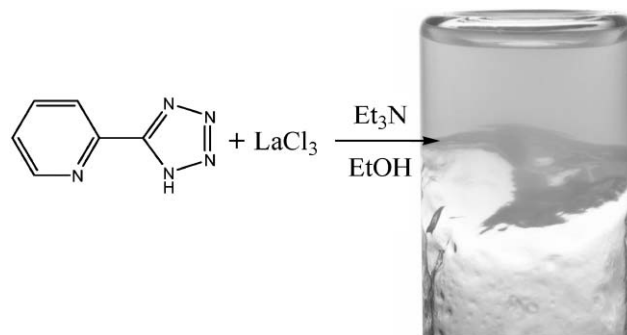


Fig. 1 Synthesis and formation of the La pyridyltetrazolate hydrogel.

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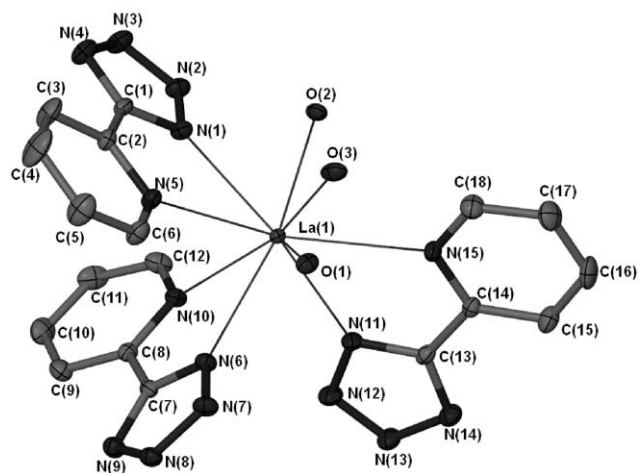
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† Electronic supplementary information (ESI) available: Crystal structures of LaL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>. See DOI: 10.1039/b605006a

8.08, 7.95 and 7.24 ppm, corresponding to the four hydrogen atoms of the pyridine ring, confirming the presence of **L**.<sup>15</sup> The resonance at 3.33 ppm indicated the presence of water, in accordance with the IR spectrum. The NMR analysis also showed the presence of a small amount of triethylamine. The two triplets at 1.05 and 0.98 ppm along with the quartet signal at 2.41 ppm suggest that Et<sub>3</sub>N is present both as base and conjugate acid. The second quartet, which should be around 3.2 ppm, is almost completely masked by the strong absorption. From integration of the NMR signals we have estimated the dry product to be composed of tetrazolate anions, amine (as Et<sub>3</sub>N and [Et<sub>3</sub>NH]OH) and water in the ratio of 1 : 0.1 : 3. Moreover, the total amine content is present as 50% base and 50% conjugate acid. On the basis of these spectroscopical data, we conclude that the core of the gel, is mainly composed of hydrated La<sup>3+</sup> cations coordinated by **L** ligands. The exact role of the base (NEt<sub>3</sub>) is not yet clear and is being further investigated. However, we believe that the presence of a mixture of triethylamine and triethylammonium results from the reversible protonation of the amine by the acidic water molecules coordinated to the La centre, with concomitant formation of a hydroxy anionic complex of the type [LaL<sub>3</sub>(H<sub>2</sub>O)<sub>x</sub>(OH)][HNEt<sub>3</sub>].<sup>§</sup> The addition of an excess of water thus promotes the formation of a three dimensional hydrogen-bonded architecture, which also explains the reversible behaviour of the gel upon mechanical and thermal stimulation, upon which it becomes temporarily less viscous.

In attempting to fully understand the role of **L** and triethylamine in the gelation process we repeated the synthetic procedure replacing **LH** with picolinic acid. However, we have seen no evidence of gel formation for this system. In addition, to assess whether triethylamine is necessary for gel formation, we synthesized the neutral LaL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> complex by metathesis of LaCl<sub>3</sub> with **LNa** in water. Heating and/or sonicating these crystals in water, even for several hours, has never led to gel formation. We therefore conclude that both **L**, and the presence of a small amount of triethylamine, are necessary for the formation of the gel.

Dilution of the hydrogel in a 1 : 1 mixture of EtOH-<sup>i</sup>PrOH results in the formation, after a few days, of colourless block-shaped crystals.<sup>¶</sup> The structure was analyzed by single crystal X-ray diffraction and determined to be the neutral [LaL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>](H<sub>2</sub>O)<sub>4</sub> complex (Fig. 2),<sup>||</sup> in which each La<sup>3+</sup> is nonacoordinated by three bidentate ligands **L** and three molecules of water. Four more shared lattice water molecules are present in the second coordination sphere. This supports our predicted structure of the complex in the gel core, [LaL<sub>3</sub>(H<sub>2</sub>O)<sub>x</sub>(OH)][HNEt<sub>3</sub>], in that the IR spectra of the dry material and of the crystals, [LaL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>](H<sub>2</sub>O)<sub>4</sub>, are very similar. Given this, and inferring that the crystals result from the breakdown of the gel structure, we further analysed the intermolecular bonding in the solid state packing of the crystals. Although pyridyltetrazoles tend to maximize π-stacking interactions between the aromatic systems,<sup>17</sup> in this case this is hampered by the three coordinated water molecules which are bound to each La cation. However, for each metal, one of the ligands arranges itself in an offset face-to-face π-stacking configuration with the ligand of a neighbouring complex (C···C 3.7 Å; N···C 3.4 Å), forming at the same time a vertex-to-face arrangement between the pyridine ring and another tetrazole (C···N 3.4 Å). More extensive non-covalent interactions between the complex molecules is further offset by the competitive



**Fig. 2** Crystal structure of LaL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>. Hydrogen atoms and lattice water molecules are not shown for clarity. Selected bond distances (Å): La1–O1 2.486(2); La1–O2 2.5252(19); La1–O3 2.539(2); La1–N1 2.675(2); La1–N5 2.763(2); La1–N6 2.654(2); La1–N10 2.743(2); La1–N11 2.662(2); La1–N15 2.763(2).

inclusion of four water molecules in the cavities between them. The extensive hydrogen bonding which then forms between all the water molecules, and which also involves the nitrogen atoms of the tetrazole rings, establishes the three dimensional network in the solid state, and is most likely the key factor in determining the formation of the hydrogel structure. This conclusion is supported by the fact that adding EtOH or <sup>i</sup>PrOH (which do not possess the same capacity for creating three dimensional hydrogen-bonded structures as H<sub>2</sub>O does) to the hydrogel disrupts the hydrogen bonding and results in the crystallization of LaL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>, with only water incorporated in the lattice. Moreover, no other solvent other than water is able to provide for gel formation.

Importantly, and rather surprisingly, gelation is a completely reversible process, and the dry starting material can be recovered intact on evaporation of the water from the hydrogel at 70 °C (IR spectra before and after the gelation are identical). In addition, the gel structure has proven to be stable over periods of months and there is no evidence for hydrolysis of the complex with subsequent release of the tetrazolate ligand from the starting material, even when treated with hot water over sustained periods of time. This stability most likely results from the relatively low basicity of the tetrazolate ligand.

We are currently exploring the possibility of forming pyridyltetrazolate based hydrogels using other lanthanide cations. Preliminary results indicate that Eu does not seem to support gelation, perhaps due to the lower Brønsted acidity of the heavier elements. However, we have been able to form a stable mixed La–Eu pyridyltetrazolate based gel containing a metal : metal ratio of up to 1 : 1 suggesting that the La complex is capable of being used as a matrix for other Ln cations. This work is still in progress.

In summary, we have described the preparation of a hydrogel using a La complex and triethylamine. On the basis of the spectroscopic evidence we have determined that the gel is formed when the complex, in which La is coordinated to 5-(2-pyridyl)tetrazolate, undergoes deprotonation caused by the presence of the base, triethylamine. The resulting complex is then trapped in a hydrogen-bonded three dimensional network formed

by the addition of water. We have also demonstrated that for gelation to occur both the ligand LH, and the base are required. To the best of our knowledge this is the first time in which direct gelation of a lanthanide complex in water is presented without the need of a specifically designed self-assembling ligand or a polymeric gelating matrix.

## Notes and references

‡ *Synthetic details.* All materials were used as received without further purification. 1H-5-(2-pyridyl)tetrazole was synthesized from the corresponding 2-pyridinecarbonitrile and NaN<sub>3</sub> in H<sub>2</sub>O following the literature procedure.<sup>15</sup> LaCl<sub>3</sub> was prepared by dissolution of La<sub>2</sub>O<sub>3</sub> in 33% HCl.

§ *Gel formation.* ([LaL<sub>3</sub>(H<sub>2</sub>O)<sub>x</sub>(OH)]/[HNEt<sub>3</sub>]): LaCl<sub>3</sub> (1 mmol) and 5-(2-pyridyl)tetrazole (3 mmol) were added to 20 ml of ethanol. Triethylamine (4.5 mmol) was added dropwise to the solution under vigorous stirring. After 24 h the white precipitate which formed was filtered off and washed with 30 ml ethanol, 15 ml diethyl ether, and 15 ml hexane, before being dried for 3 h under reduced pressure. Yield 0.24 g, mp >330 °C (decomp.). <sup>1</sup>H-NMR (300.13 MHz, 30 °C d<sub>6</sub>-DMSO) δ 8.75 (1H, br s, H<sup>6</sup>); 8.32 (1H, br s, H<sup>2</sup>); 8.08 (1H, br s, H<sup>4</sup>); 7.40 (1H, br s, H<sup>5</sup>); 3.33 (5H, s, H<sub>2</sub>O); 2.41 (0.3H, q, *J* = 7.2 Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 1.05 (0.4H, t, *J* = 7.0 Hz, HN(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); 0.98 (0.4H, t, *J* = 7.2 Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>). IR (diamond ATR) ν<sub>max</sub> (cm<sup>-1</sup>): 3310br, 1606s, 1571w, 1462s, 1424s, 1287s, 1159w, 1058w, 1002w, 801w, 733w and 718w. Gelation occurred on heating to 80 °C, the solid (0.2 g) dispersed in 10 ml H<sub>2</sub>O.

¶ *Synthesis of [LaL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>](H<sub>2</sub>O)<sub>4</sub>.* Addition of a 1 : 1 mixture of ethanol-isopropanol to the gel (formed as above) resulted in the formation of large colourless block-shaped crystals which were analysed as [LaL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>](H<sub>2</sub>O)<sub>4</sub>. Yield (not maximised) 0.046 g, mp > 312 °C (decomp.). <sup>1</sup>H-NMR (300.13 MHz, 30 °C d<sub>6</sub>-DMSO) δ 8.75 (1H, br s, H<sup>6</sup>); 8.10 (1H, d, *J* 7.7, H<sup>3</sup>); 7.94 (1H, t, *J* 7.7, H<sup>4</sup>); 7.38 (1H, t, *J* 5.8 H<sup>5</sup>); 3.33 (~7H, s, H<sub>2</sub>O). <sup>13</sup>C-NMR (75 MHz, 30 °C, d<sub>6</sub>-DMSO) δ 161.25 (CN<sub>4</sub>); 149.52 (C<sup>2</sup>); 149.37 (C<sup>6</sup>); 138.15 (C<sup>4</sup>); 122.97 (C<sup>3</sup>); 120.98 (C<sup>5</sup>). Anal. calc. for [LaL<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>].1.5(H<sub>2</sub>O): C 32.8, H 3.2, N 32.0; found: C 33.0, H 3.7, N 32.3. IR (diamond ATR) ν<sub>max</sub> (cm<sup>-1</sup>): 3300br, 1636w, 1605s, 1570w, 1461w, 1427s, 1386s, 1284s, 1248w, 1156w, 1099w, 1059w, 1035w, 1002w, 796w, 750w and 728w.

|| *Crystal structure analysis.* Crystal data analysed using X-Seed: C<sub>18</sub>H<sub>24</sub>LaN<sub>15</sub>O<sub>6.50</sub>, *M* = 693.43, 0.16 × 0.12 × 0.10 mm<sup>3</sup>, monoclinic, space group *P2<sub>1</sub>/n* (No. 14), *a* = 9.1993(18), *b* = 17.748(4), *c* = 16.947(3) Å, β = 99.54(3)°, *V* = 2728.7(9) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.688 g cm<sup>-3</sup>, *F*<sub>000</sub> = 1384, Nonius Kappa CCD, MoKα radiation, λ = 0.71073 Å, *T* = 123(2) K,

2θ<sub>max</sub> = 56.6°, 30874 reflections collected, 6653 unique (*R*<sub>int</sub> = 0.0478). Final *Goof* = 1.055, *R*1 = 0.0317, *wR*2 = 0.0573, *R* indices based on 5280 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 467 parameters, 18 restraints. Lp and absorption corrections applied, μ = 1.631 mm<sup>-1</sup>. CCDC 604028. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605006a

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