Polyhedron xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Structural diversity of lanthanoid salicylate hydrates

Thomas Behrsing [a], Glen B. Deacon [a,*], Jenny Luu [a], Peter C. Junk [b,*], Brian W. Skelton [c,1], Allan H. White [c,2]

[a] School of Chemistry and Centre for Green Chemistry, Monash University, Clayton, Victoria 3800, Australia
[b] College of Science & Engineering, James Cook University, Townsville, Queensland 4811, Australia
[c] School of Chemistry and Biochemistry M313, The University of Western Australia, Crawley, Western Australia 6009, Australia

ARTICLE INFO

Article history:
Received 20 April 2016
Accepted 24 May 2016
Available online xxxx

Dedicated to Professor Martin Bennett, honouring him on the occasion of his 80th birthday and for his outstanding contribution in the field of Inorganic Chemistry.

Keywords:
Lanthanoid
Carboxylate
Salicylate
Crystal structure
Monomer

ABSTRACT

From metathesis reactions between lanthanoid salts and sodium salicylate (Na(salH)) in water, four classes of lanthanoid salicylate hydrates have been identified. Single crystal X-ray studies established a new monomeric class $[Ln(salH)_3(H_2O)_3]\cdot 3H_2O$ (**6Ln**). This new rhombohedral *R*3*c*, *Z* = 6 form '**6Ln**' has the nine coordinate metal atom on a crystallographic 3-axis, for Ln = Sm–Gd, Ho, Er, Yb, Lu, Y. We also have augmented or defined the previously known different forms, consolidating or extending their putative 'domains of existence'. The monohydrate, Ln = '**1Ce**', monoclinic, $P2_1/n$, has been re-examined at low-temperature suggesting further elasticity in its formulation beyond the recently proposed '$[Ln(H_2sal)(Hsal)(sal)H_2O)]_{(\infty|\infty)}$' for the Ln = Gd complex, '**1Gd**', one of the protonic hydrogen atoms being associated with a very short phenoxyl–O···carboxylate–O distance (2.427(3) Å). With refinement and the insights from a previous Ln = Eu study, suggest the protonic disposition to be around the O···O median. The 'domain of existence' for this form embraces Ln = La (dependent on a powder diffraction study) – Gd. The tetrahydrate is manifested in two forms: triclinic, centrosymmetric binuclear $[Ln_2(salH)_6(H_2O)_4]\cdot 4H_2O$, $P\bar{1}$, *Z* = 1, '**4Ln**' recorded here in a 153 K determination, for Ln = Ho, consolidating the assignment of its domain of existence to be Ho–Er, Y, and 'polymeric mononuclear' $[Ln(salH)_3(H_2O)_2]_{(\infty|\infty)}\cdot 2H_2O$, '**4Ln,**' recorded here for Ln = Tb–Er, Yb, Lu, Y. The **6Gd** hexahydrate shows paramagnetic f^7 magnetic behaviour. The reaction conditions leading to the isolation of a particular structural type of lanthanoid salicylate could not be reliably identified, indicating that a fine balance exists in the preferential crystallization of the lanthanoid salicylate hydrate phases. The discovery of the monomeric class has applications for the species acting as a corrosion inhibitor in dilute aqueous solution.

1. Introduction

Lanthanoid complexes with aromatic carboxylate ligands are known to form a wide range of structural archetypes [1–5], such as honeycomb, diamond, and open frameworks [6–11], many of which have potential applications in areas such as gas adsorption, light conversion devices, luminescence probes [12–18], and corrosion inhibitors [19–28]. The structural diversity possibly arises in part because of the presence of a conjugated π-electron system [29], and because of the various carboxylate coordination modes available, such as monodentate, chelating, bidentate bridging and tridentate bridging [2,3]. Polymeric structures are by far the most widely described [1–5,30–32].

The salicylate ligand (LH^- = $salH^-$; 2-$HOC_6H_4COO^-$) has additionally an *ortho*-phenol substituent as a further potential donor, one which can be further deprotonated to L^{2-} [33]. This arrangement permits diverse coordination modes with the electropositive lanthanoid metals. Several structural studies have been reported on lanthanoid salicylate complexes [33–43] more recently stemming from a magnetic or luminescence focus [33–35], but no comprehensive or systematic account of the published structural types has been reported. There are also complications with the syntheses with two structurally different holmium complexes isolated under essentially the same conditions [41]. Three structural classes of lanthanoid salicylates have been identified, namely polymeric monohydrates $[Ln(salH)_3(H_2O)]_{(\infty|\infty)}$ [33–39], polymeric tetrahydrates $[Ln(salH)_3(H_2O)_2]_{(\infty|\infty)}\cdot 2H_2O$ [41–43], and dimeric species $[Ln_2(salH)_6(H_2O)_4]\cdot 4H_2O$ [35,40,41]. Reported structures are included in Table 1.

The major contribution in the current work is the preparation and characterisation of a new structural class viz. the monomeric hexahydrates $[Ln(salH)_3(H_2O)_3]\cdot 3H_2O$. Besides intrinsic importance, these complexes plausibly relate to the species present in

* Corresponding authors. Fax: +61 3 9905 4597.
E-mail addresses: glen.deacon@monash.edu (G.B. Deacon), peter.junk@jcu.edu.au (P.C. Junk).
[1] Present address: Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, Crawley, Western Australia 6009, Australia.
[2] Deceased 26/3/2016.

http://dx.doi.org/10.1016/j.poly.2016.05.047
0277-5387/

Table 1
Structurally defined classes of hydrated lanthanoid(III) salicylates.

Crystal form	Formulation	Members [Refs]
Monohydrate (1Ln)		
Monoclinic, $P2_1/x$, $Z = 4$ ($x = n$ or c)	$[Ln(salH)_3(H_2O)]$	La–Gd [36],[a] Ce [37], this work, Sm [38], Eu [33,39], Gd [34]
Tetrahydrate (4Ln)		
Monoclinic, $C2/c$ (Cc), $Z = 8$	$[Ln(salH)_3(H_2O)_2]_{(\infty\|\infty)}\cdot 2H_2O$	Dy [43], Tb, Ho [41,42], Tb–Er, Yb, Lu, Y, this work
Tetrahydrate (4Ln′)		
Triclinic, $P\bar{1}$, $Z = 1$	$[Ln_2(salH)_6(H_2O)_4]\cdot 4H_2O$	Ho [41], this work, Er [35], Y [40]
Hexahydrate (6Ln)		
Rhombohedral, $R3c$, $Z = 6$ (hex)	$[Ln(salH)_3(H_2O)_3]\cdot 3H_2O$	Sm–Gd, Ho, Er, Yb, Lu, Y, this work Tb[b]
Trihydrate		
Monoclinic, $P2_1/n$, $Z = 4$	$[\{Fe(sal)_2(bpy)\}_2Ln(NO_3)(H_2O)_3]\cdot EtOH$	Ce [23]
Triclinic, $P\bar{1}$, $Z = 2$	$[\{Fe(sal)_2(bpy)\}_4Ln_2(H_2O)_{11}][salH]_2\cdot EtOH\cdot 3H_2O$	Ce [23]

[a] These structures were defined by powder diffraction results [36] and have been confirmed in present XRPD measurements.
[b] XRPD identification. All other structural assignments in the table pertain to single crystal studies.

dilute aqueous solution, the conditions under which the complexes are utilised as corrosion inhibitors [19–22]. In addition, members of the other three structural classes have been prepared and structurally characterised, illuminating the domains of existence of each form.

2. Results and discussion

2.1. Syntheses

An aqueous solution of a lanthanoid chloride (or, less commonly, the nitrate salt) was treated with sodium salicylate (Na(salH)) in a 1–3 mole ratio in water, resulting in the formation of a precipitate, which was normally microcrystalline as indicated by X-ray powder diffractograms. Slow evaporation of the filtrate often gave crystalline deposits amenable to study by single crystal X-ray diffraction.

In the synthesis of the polymeric monohydrates **1Ln** (Ln = La, Ce, Nd, Eu, Gd), the yield of precipitate was high (57–95%), but the crystalline solid was obtained in <10% yield and was unsuitable for single crystal structure determination. Eventually suitable crystals for synchrotron structure determination were obtained from a synthesis of **1Ce** in aqueous ethanol in an H-tube assembly (see Experimental).

Mid-way through this study, the reaction of $EuCl_3$ with Na(salH) gave a precipitate of **1Eu** in high yield and then produced the first well-characterised example of a new structural class $[Eu(salH)_3(H_2O)_3]\cdot 3H_2O$ (**6Eu**), a mononuclear hexahydrate, which crystallised from the filtrate in low yield. This result is both surprising and significant as it indicates that *different* mechanisms of assembly were present during the spontaneous formation of the monohydrate precipitate (**1Eu**) and the slow crystallisation of the hexahydrate (**6Eu**) from the filtrate. The same distribution between a precipitate (**1Sm**) and crystals (**6Sm**) was also observed for the slightly larger Sm^{3+} ion. For Gd, Tb, Y, Ho, Er, Yb and Lu, only the monomeric hexahydrate (**6Ln**) was obtained for **both** the precipitate (60–90%) and deposited crystals (4–28%) (Eq. (1)). Thus, the 'domain of existence' of the hexahydrate complex was found to span the extensive range of Sm–Tb, Y, Ho, Er, Yb and Lu.

$$Ln^{3+} + 3\ salH^- + 6\ H_2O \rightarrow [Ln(salH)_3(H_2O)_3]\cdot 3H_2O\downarrow \quad (\mathbf{6Ln}) \tag{1}$$

The polymeric tetrahydrate complexes $[Ln(salH)_3(H_2O)_2]_{(\infty|\infty)}\cdot 2H_2O$ (**4Ln**) (Ln = Tb–Er, Y, Yb, Lu) crystallized from aqueous filtrates (Eq. (2)), in 6–28% yield. More variable behaviour was observed with the precipitates with unidentified amorphous products obtained for Ln = Tb and Ho and yields of **4Ln** precipitates of 0% (Ln = Lu) and 80% in other cases.

$$Ln^{3+} + 3\,salH^- + 4H_2O \rightarrow [Ln(salH)_3(H_2O)_2]_{(\infty|\infty)}\cdot 2H_2O\downarrow \quad (\mathbf{4Ln}) \tag{2}$$

In one preparation, dimeric $[Ho_2(salH)_6(H_2O)_4]\cdot 4H_2O$ (**4Ho′**) crystallized under seemingly identical reaction conditions (Eq. (3)) after formation of an amorphous precipitate (see also **4Ho**) but this could not be repeated, and only polymeric $[Ho(salH)_3(H_2O)_2]_{(\infty|\infty)}\cdot 2H_2O$ crystallised in subsequent reactions. The result is consistent with an earlier report whereby both forms **4Ho** and **4Ho′** were obtained under apparently similar conditions [41]. Because the synthesis of **4Y′** has also been reported, an extensive set of variation of conditions (pH, crystallization temperature) were examined for crystallization of Ln = Ho, Er, Y, Yb (similar size Ln^{3+} ions), but **4Ln′** products were not obtained.

$$Ho^{3+} + 3\,salH^- + 4H_2O \rightarrow 1/2[Ho_2(salH)_6(H_2O)_4]\cdot 4H_2O \quad (\mathbf{4Ln'}) \tag{3}$$

The present structurally defined (see below) classes of lanthanoid salicylate hydrates are presented in Table 1, together with those previously reported. An "Existence Diagram" summarising these is given in Table S1 (Supplementary Data).

2.2. Characterization

The new class of monomeric hexahydrates **6Ln** was established by X-ray crystal structures of all eight complexes. Bulk products gave satisfactory C, H, Ln analyses, except for **6Tb** which only had a metal analysis. All eight sets of bulk crystals and six corresponding precipitates (Eu, Sm gave **1Ln** precipitates) had near identical IR spectra and X-ray powder patterns (Supplementary Data). The XRPD of the bulk precipitate of **6Gd** agreed well with that simulated from the structure of **6Gd** except for some displacement of lines owing to the temperature differential (RT vs. 100 K) for the two measurements (Fig. S6). In the case of the known class **1Ln**, analytical characterization was by metal analysis, but the bulk precipitate of **1Ce** gave satisfactory C, H, Ce analysis. Precipitates and crystalline residues all gave similar IR spectra and similar X-ray powder patterns (Supplementary Data), and the XRPD pattern of **1Ce** correlated well with patterns simulated from reported structural data for **1Sm** [38] and **1Gd** [34]. For **4Ln** representative bulk crystals (**4Er**, **4Tb**, **4Yb**, **4Lu**, **4Y**) were characterized by C, H, Ln analyses as was dimeric **4Ho′**, with the other crystals and