

Structural diversity of lanthanum saccharinates induced by 1,10-phenanthroline: A synthetic and X-ray crystallographic study



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ABSTRACT

Four new lanthanum(III) complexes of formulae $[\text{La}(\text{sac})_3(\text{phen})_2(\text{H}_2\text{O})_2] \cdot (\text{phen})(\text{H}_2\text{O})_2$ (**1**), $[\text{La}(\text{sac})_3(\text{phen})_2(\text{H}_2\text{O})_2] \cdot (\text{phen})$ (**2**), $[\text{La}(\text{sac})_2(\text{phen})(\text{H}_2\text{O})_4] \cdot (\text{sac})$ (**3**) and $[\text{La}(\text{sac})_2(\text{phen})_2(\text{H}_2\text{O})_3] \cdot (\text{sac})(\text{phen})(\text{H}_2\text{O})$ (**4**) (phen = 1,10 phenanthroline, sac = saccharinate) have been synthesised and characterised by single crystal X-ray diffraction, IR, elemental analysis and thermogravimetric analysis. The binding mode of the sac anion was manipulated through the use of phen as structure inducer. In all four complexes the La(III) ion is in a nine-coordinate environment. The structures of **1** and **2** are similar, comprising of three sac anions coordinating in a monodentate fashion through the carbonyl O-atom, two bidentate phen and two water molecules coordinating directly to the same La(III) ion; a third, uncoordinated phen moiety also forms part of the unit cell. In addition, **1** is characterized by the presence of two crystallization water molecules which are absent in **2**. In compound **3** the coordination sphere of La(III) is completed by a bidentate chelating sac through the N- and carbonyl O-atoms, a monodentate sac, a bidentate phen and four water ligands; a third, uncoordinated sac is also present in the crystal lattice. Compound **4** contains two bidentate phen, three water ligands and two monodentate O(carbonyl) sac ligands. The presence of three sac anions coordinating to the same lanthanide ion as well as a bidentate N–Ln–O chelating sac, confirmed by single crystal X-ray crystallography, is unprecedented for rare-earth saccharinates.

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1. Introduction

Saccharin (o-sulfobenzimide) is a very interesting and versatile ligand in coordination chemistry. Although structurally rigid, the saccharinate anion (sac) offers flexible coordination sites to metallic centres through an amide nitrogen, a carbonyl oxygen and two sulfonyl oxygen atoms [1]. Saccharin has been in use for more than 100 years as a non-caloric artificial sweetener and it was briefly linked to some stomach and bladder cancers [2], but has since regained its status of being non-harmful to humans [3]. Early suggestions of possible use for saccharin in chelation therapy [4] were followed by recent reports of silver(I), bismuth(III) and palladium(II) saccharinate complexes being investigated for their antibacterial and anticancer properties [5–8].

Metal saccharinates are interesting for the crystal chemistry of the metals because of the versatile ligation properties of saccharin and a vast library of transition metal complexes has been published to date which show the ligand coordinating in a

mono-, bi- or tridentate fashion. In these examples interaction through the deprotonated nitrogen atom is the most common [1]. Although there are examples of M–O(carbonyl) bonds [9], monodentate coordination via the carbonyl O-atom is generally less common [10] and is encountered when branched or bulky co-ligands are present [1]. O bonding is also characteristic of the interactions with the s- and p-block metals. There are numerous examples of bidentate modes of coordination, in a bridging fashion, through N and O (sulfonyl) [8] or N and O (carbonyl) atoms [11]. Tridentate interactions [12] and complexes in which the coordination mode involves all donor sites of sac anion [13] are extremely rare. Bi- and tridentate coordination modes were observed more frequently with Pb(II) and Ag(I) [1]. Much less common are examples where the sac ligand coordinates in a bidentate chelating fashion to the central metal [14]. The only known examples to date are the complexes of Pb(II) [15], Ba(II) [13], Tl(I) [12] and Cu(II) [16].

By contrast, rare-earth metal saccharinate complexes are still fairly unexplored. To our knowledge, fifteen such complexes have been reported to date of which only six have been fully characterised via single crystal X-ray diffractometry [17–19]. All reported complexes are mixed aqua-saccharinato species, where the sac

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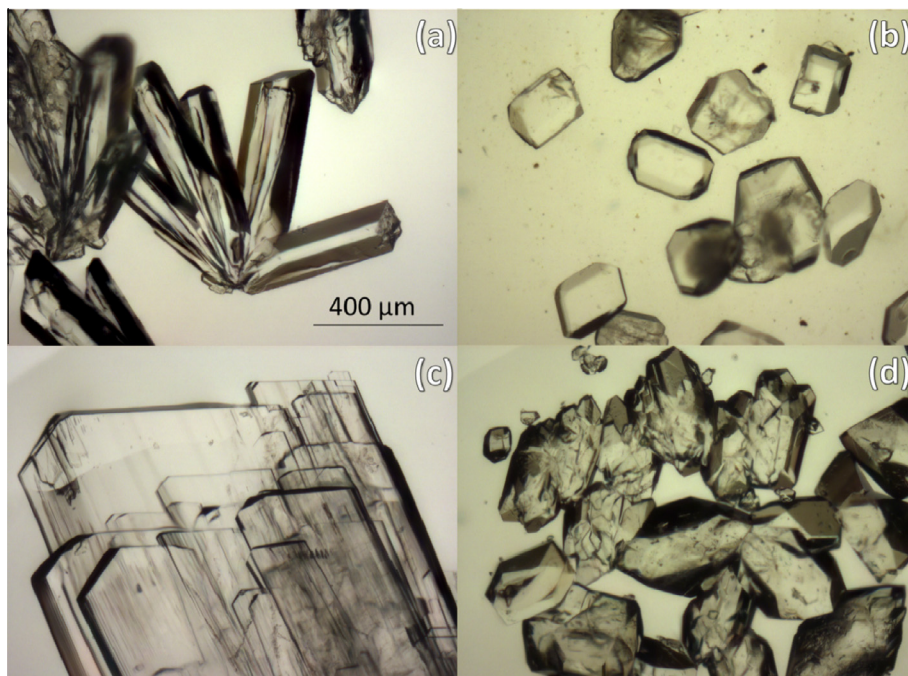


Fig. 1. Photographs of crystals of compounds 1–4 (a–d respectively).

Table 1
Summary of crystal data and structure refinement parameters for 1–4.

	1	2	3	4
	[La(sac) ₃ (phen) ₂ (H ₂ O) ₂](phen)·(H ₂ O) ₂	[La(sac) ₃ (phen) ₂ (H ₂ O) ₂](phen)	[La(sac) ₂ (phen)(H ₂ O) ₄](sac)	[La(sac) ₂ (phen) ₂ (H ₂ O) ₃](sac)·(phen)·(H ₂ O)
Empirical formula	C ₅₇ H ₄₄ LaN ₉ O ₁₃ S ₃	C ₅₇ H ₄₀ LaN ₉ O ₁₁ S ₃	C ₃₃ H ₂₈ LaN ₅ O ₁₃ S ₃	C ₅₇ H ₄₄ LaN ₉ O ₁₃ S ₃
Formula weight	1298.10	1262.07	937.69	1298.10
T (K)	303.15	293.15	293.15	293.15
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>c</i>
<i>a</i> (Å)	13.677(5)	12.0636(8)	7.3938(7)	18.0733(14)
<i>b</i> (Å)	13.994(5)	14.0892(10)	15.0874(15)	15.3141(11)
<i>c</i> (Å)	17.694(5)	18.3259(12)	16.0771(16)	20.5461(16)
α (°)	83.704(5)	70.6330(10)	87.042(2)	90.00
β (°)	74.147(5)	81.3870(10)	88.982(2)	99.883(2)
γ (°)	62.021(5)	65.3210(10)	85.580(2)	90.00
Volume (Å ³)	2876.3(17)	2669.9(3)	1785.6(3)	5602.3(7)
<i>Z</i>	2	2	2	4
ρ_{calc} (g/cm ³)	1.499	1.570	1.744	1.539
μ (mm ⁻¹)	0.923	0.990	1.446	0.948
<i>F</i> (000)	1316.0	1276.0	940.0	2632.0
Crystal size (mm)	0.3 × 0.3 × 0.2	0.3 × 0.3 × 0.2	0.4 × 0.2 × 0.2	0.4 × 0.2 × 0.2
Radiation	Mo K α (λ = 0.71069)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
2 θ range for data collection (°)	5.76–56.78	4.72–56.62	2.54–56.64	5.3–56.7
Index ranges	–18 ≤ <i>h</i> ≤ 14 –18 ≤ <i>k</i> ≤ 18 –23 ≤ <i>l</i> ≤ 21	–16 ≤ <i>h</i> ≤ 14 –18 ≤ <i>k</i> ≤ 12 –24 ≤ <i>l</i> ≤ 21	–9 ≤ <i>h</i> ≤ 9 –20 ≤ <i>k</i> ≤ 19 –21 ≤ <i>l</i> ≤ 14	–20 ≤ <i>h</i> ≤ 24 –20 ≤ <i>k</i> ≤ 13 –25 ≤ <i>l</i> ≤ 27
Reflections collected	19185	17851	12025	37303
Independent reflections	13294 [<i>R</i> _{int} = 0.0407, <i>R</i> _{sigma} = 0.1210]	12356 [<i>R</i> _{int} = 0.0190, <i>R</i> _{sigma} = 0.0449]	8361 [<i>R</i> _{int} = 0.0216, <i>R</i> _{sigma} = 0.0449]	13676 [<i>R</i> _{int} = 0.0637, <i>R</i> _{sigma} = 0.0925]
Data/restraints/parameters	13294/0/681	12356/0/732	8361/0/499	13676/0/754
Goodness-of-fit (GOF) on <i>F</i> ²	0.991	1.156	1.105	1.017
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0880, <i>wR</i> ₂ = 0.2243	<i>R</i> ₁ = 0.0426, <i>wR</i> ₂ = 0.1245	<i>R</i> ₁ = 0.0520, <i>wR</i> ₂ = 0.1811	<i>R</i> ₁ = 0.0615, <i>wR</i> ₂ = 0.1195
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1398, <i>wR</i> ₂ = 0.2544	<i>R</i> ₁ = 0.0548, <i>wR</i> ₂ = 0.1483	<i>R</i> ₁ = 0.0673, <i>wR</i> ₂ = 0.2478	<i>R</i> ₁ = 0.1023, <i>wR</i> ₂ = 0.1362
Largest difference in peak/hole (e Å ⁻³)	2.31/–4.42	0.93/–0.95	1.82/–2.46	1.53/–1.02

anion behaves exclusively as a monodentate ligand, coordinating to the metal centre through the carbonyl oxygen atom, (consistent with the preference of lanthanoid cations to bind oxygen). These complexes are characterised by the presence of saccharin and its

anion (in two forms, bonded and non-bonded to the metal centre) in the crystal lattice [1a]. In these examples up to a maximum of two sac ligands bind directly to the metal centres, with aqua ligands completing the coordination sphere. Given the sometimes

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