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Synthesis and X-ray crystallographic studies of complexes involving H_2acacen with the early lanthanoids (H_2acacen = N,N'-ethylenebis(acetylacetoneimine))

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Abstract

The coordination properties of the Schiff base ligand N,N'-ethylenebis(acetylacetoneimine) (H_2acacen), were investigated with a range of lanthanoid nitrate hexahydrate salts yielding $[Ln(NO_3)_3(H_2acacen)_2][C_6H_{12}]_n$ (Ln = La, Pr, Nd and Sm), and X-ray crystallographic characterisation revealed that the early lanthanoids all adopt the same polymeric structure with a single, bidentate H_2acacen ligand attached to each metal centre and two monodentate H_2acacen ligands bridging between successive metal centres resulting in a polymeric array. In a similar reaction, $Yb(NO_3)_3 \cdot 6H_2O$ induced decomposition of H_2acacen resulting in isolation of the new complex $[Yb(H_2O)_2(NO_3)_2(\mu\text{-}NO_3)(acac)]_2$.

1. Introduction

Studies involving the Schiff base ligand N,N-ethylenebis(acetylacetoneimine), (H_2acacen) with the lanthanoids have been relatively few, and little is known about the structural properties of these complexes. This ligand is closely related to the ubiquitous salen (= N,N'-ethylenebis(salicylideneimine)) ligands in its coordinating ability, containing two oxygen and two nitrogen donor sites, however additional flexibility can result in a more diverse number of coordination modes. While these ligands have been examined with the transition metals to some extent [1–5], the number of lanthanoid complexes is very limited. In this context, there exists only one fully structurally characterised example involving a fluorinated derivative of acacen, and this was synthesised in situ by the addition of $Ce(NO_3)_3 \cdot 6H_2O$ to an ethanolic solution of 5,5,5-trifluoro-4-hydroxy-4-trifluoromethyl-pentanone and ethylenediamine. The resulting complex, $[Ce\{F_{12}(acacen)\}_2]$, possesses roughly square anti-prismatic geometry with each ligand bound to the eight coordinate metal centre via both nitrogen and oxygen donor atoms [6]. A heteroleptic example involving this ligand has also been synthesised by treating $Ln(Cp)_3$ (Cp^- = cyclopentadienide) with an equimolar amount of H_2acacen, yielding the tetranuclear cluster complex $[\eta^5\text{-}CpLn_2(acacen)_2)(\mu\text{-}OH)]_2 \cdot n$thf (Ln = Pr and Nd) [7]. Curiously, a salen analogue is also synthesised in this way, and adopts similar morphology. Examples of binary complexes which also incorporate transition metals into the ligand are also known [3].

The present work involves an investigation into the isomorphous series of complexes $[Ln(NO_3)_3(H_2acacen)_2][C_6H_{12}]_n$ (Ln = La, Pr, Nd and Sm) (**1**–**4**). The analogous ytterbium reaction in this series resulted in decomposition of the ligand and yielded $[Yb(H_2O)_2(NO_3)_2(\mu\text{-}NO_3)(acac)]_2$ (**5**) (acac = acetylacetonate).

2. Experimental

All metal salts ($La(NO_3)_3 \cdot 6H_2O$, $Pr(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$, $Yb(NO_3)_3 \cdot 6H_2O$) were purchased from Aldrich and used without purification. H_2acacen was synthesised according to literature

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methods [5,8–10]. All solvents were distilled before use. The Campbell Microanalytical Laboratory of the University of Otago, New Zealand, performed the microanalyses. It was found that for most compounds, the C, H, N analyses were variable and this is presumably due to loss of solvent (C_6H_{12}) since they were generally low in carbon. Infrared spectra were performed as Nujol mulls on a Perkin–Elmer 1600 FTIR spectrometer for the region 4000–650 cm^{-1}.

2.1. General synthetic method

A sample of $Ln(NO_3)_3 \cdot 6H_2O$ (0.05 g) was dissolved in THF, then to this was added an equimolar amount (0.0257 g) of H_2acacen dissolved in thf–cyclohexane. The solution was stirred vigorously for 30 min with heating to affect dissolution. The solution was then left open to atmosphere, upon X-ray quality crystals formed after several days. Individual details are given below.

2.2. $[La(NO_3)_3(H_2acacen)_2][C_6H_{12}]$ (**1**)

Crystallised as light pink, cubic X-ray quality crystals. *Anal.* Calc. for $C_{27}H_{50}N_7O_{13}La$: C, 39.57; H, 6.15; N, 11.96; Found: C, 32.91; H, 5.39; N, 11.65%; IR (Nujol): 3200w, 2358w, 1211w, 1029m, 943s, 818m, 722m, 655w, 630w, 549s cm^{-1}.

2.3. $[Pr(NO_3)_3(H_2acacen)_2][C_6H_{12}]$ (**2**)

Crystallised as light green, cubic, X-ray quality crystals. *Anal.* Calc. for $C_{27}H_{50}N_7PrO_{13}$: C, 39.47; H, 6.13; N, 11.93; Found: C, 38.63; H, 5.62; N, 11.94%; IR (Nujol): 2359w, 1210w, 1029m, 940s, 816m, 720m, 655w, 630w, 551s cm^{-1}.

2.4. $[Nd(NO_3)_3(H_2acacen)_2][C_6H_{12}]$ (**3**)

Crystallised as light pink, cubic X-ray quality. *Anal.* Calc for $C_{27}H_{50}N_7NdO_{13}$: C, 39.31; H, 6.11; N, 11.88; Found: C, 34.84; H, 5.62; N, 11.65%; IR (Nujol): 3348w, 2364w, 1215w, 1029m, 943s, 819m, 722m, 655w, 630w, 551s cm^{-1}.

2.5. $[Sm(NO_3)_3(H_2acacen)_2][C_6H_{12}]$ (**4**)

Crystallised as colourless, cubic, X-ray quality crystals. *Anal.* Calc. for $C_{27}H_{50}N_7SmO_{13}$: C, 39.02; H, 6.06; N, 11.80; Found: C, 37.33; H, 5.35; N, 11.87%; IR (Nujol): 3344w, 1208w, 1029m, 941s, 820m, 722m, 655w, 630w, 548s cm^{-1}.

2.6. $[Yb(H_2O)_2(NO_3)_2(\mu\text{-}NO_3)(acac)]_2$ (**5**)

A sample of $Yb(NO_3)_3 \cdot 6H_2O$ (0.05 g) was dissolved in water, then to this an equimolar amount (0.0258 g) of H_2acacen dissolved in water was slowly added. The solution was left for several days, after which decomposition became evident upon formation of an oily residue. Only a small amount of crystalline material was isolable, and this was only characterised by X-ray crystallography.

2.7. X-ray crystallographic studies

Crystallographic measurements were made on a capillary mounted specimen for compound **1** at room temperature and in highly viscous oil at 223 K for compounds **2** to **5**, using a Siemens SMART CCD diffractometer (graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), exposure 30 s per frame, empirical absorption correction using SADABS) [11]. The experimental conditions and crystal data are given below. The structures were solved by Patterson and Fourier methods and refined against F^2 using SHELXS and SHELXL-97 [12], with the aid of the interface program X-SEED [13]. All heavy atoms were refined anisotropically, hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride, except for acidic protons which were located on the final difference Fourier map and refined isotropically. The cyclohexane molecules of lattice solvation in **1**–**4** were disordered, but this disorder was successfully refined. Selected bond lengths and hydrogen bonding parameters are listed in Tables 1–5.

2.8. $[La(NO_3)_3(H_2acacen)_2][C_6H_{12}]$ (**1**)

$C_{27}H_{50}N_7O_{13}La$, $M = 819.65$, monoclinic, $P2_1/n$, $a = 11.629(3)$, $b = 15.547(3)$, $c = 20.513(4)$ Å, $\beta = 102.539(4)°$, $V = 3620.1(13)$ Å^3, $Z = 4$, calculated density = 1.504 g cm^{-3}, $\mu_{Mo} = 1.249$ mm^{-1}, crystal

Table 1
Selected (i) bond distances (Å) and (ii) hydrogen bonding distances (Å) and angles (°) for $([La(H_2acacen)_2][C_6H_{12}])_n$ (**1**)

Atoms	Distances	Atoms	Distances
(i)			
La(1)–O(1)	2.666(6)	La(1)–O(8)	2.680(6)
La(1)–O(2)	2.675(7)	La(1)–O(10)	2.474(5)
La(1)–O(4)	2.689(6)	La(1)–O(11)	2.579(6)
La(1)–O(5)	2.641(6)	La(1)–O(21)	2.489(5)
La(1)–O(7)	2.680(7)	La(1)–O(13)	2.499(6)

D–H···A	d(D–H)	d(H···A)	d(D···A)	(D–H–A)
(ii)				
N(5)–H(5N)···O(11)	0.997(10)	1.901(10)	2.716(9)	136.8(19)
N(6)–H(6N)···O(5)	0.999(10)	2.27(8)	2.977(10)	127.0(7)
N(6)–H(6N)···O(12)	0.999(10)	1.86(6)	2.698(8)	139.0(8)
N(7)–H(7N)···O(8)	1.000(10)	2.45(7)	3.056(11)	119.0(6)
N(7)–H(7N)···O(13)	1.000(10)	1.94(6)	2.688(9)	130.0(6)

Table 2
Selected (i) bond distances (Å) and (ii) hydrogen bonding distances (Å) and angles (°) for ([Pr(H_2acacen)$_2$][C_6H_{12}])$_n$ (**2**)

Atoms	Distances	Atoms	Distances
(i)			
Pr(1)–O(1)	2.621(3)	Pr(1)–O(8)	2.642(3)
Pr(1)–O(2)	2.621(4)	Pr(1)–O(10)	2.552(3)
Pr(1)–O(4)	2.596(3)	Pr(1)–O(11)	2.436(3)
Pr(1)–O(5)	2.672(3)	Pr(1)–O(12)	2.445(3)
Pr(1)–O(7)	2.649(3)	Pr(1)–O(13)	2.448(3)

D–H···A	d(D–H)	d(H···A)	d(D···A)	(D–H–A)
(ii)				
N(4)–H(4N)···O(10)	0.989(10)	1.94(4)	2.707(5)	133(4)
N(6)–H(6N)···O(4)	0.993(10)	2.32(4)	2.973(5)	122(3)
N(6)–H(6N)···O(12)	0.993(10)	1.89(3)	2.709(4)	137(4)
N(7)–H(7N)···O(8)	0.995(10)	2.37(3)	3.046(5)	125(3)
N(7)–H(7N)···O(13)	0.995(10)	1.89(3)	2.668(5)	133(3)

Table 3
Selected (i) bond distances (Å) and (ii) hydrogen bonding distances (Å) and angles (°) for ([Nd(H_2acacen)$_2$][C_6H_{12}])$_n$ (**3**)

Atoms	Distances	Atoms	Distances
(i)			
Nd(1)–O(1)	2.6062(18)	Nd(1)–O(8)	2.6320(19)
Nd(1)–O(2)	2.6007(19)	Nd(1)–O(10)	2.4145(17)
Nd(1)–O(4)	2.6565(17)	Nd(1)–O(11)	2.5340(16)
Nd(1)–O(5)	2.5804(18)	Nd(1)–O(12)	2.4236(16)

D–H···A	d(D–H)	d(H···A)	d(D···A)	(D–H–A)
(ii)				
N(4)–H(4N)···O(4)	0.997(10)	2.25(3)	2.955(3)	126(2)
N(4)–H(4N)···O(10)	0.997(10)	1.81(2)	2.674(3)	144(3)
N(5)–H(5N)···O(11)	0.983(10)	1.95(2)	2.708(3)	132(2)
N(6)–H(6N)···O(5)	0.985(10)	2.23(3)	2.938(3)	128(3)
N(6)–H(6N)···O(12)	0.985(10)	1.92(3)	2.702(3)	134(3)
N(7)–H(7N)···O(8)	1.000(10)	2.35(3)	3.029(3)	124(3)
N(7)–H(7N)···O(13)	1.000(10)	1.84(3)	2.667(3)	138(3)

Table 4
Selected (i) bond distances (Å) and (ii) hydrogen bonding distances (Å) and angles (°) for ([Sm(H_2acacen)$_2$][C_6H_{12}])$_n$ (**4**)

Atoms	Distances	Atoms	Distances
(i)			
Sm(1)–O(1)	2.656(4)	Sm(1)–O(8)	2.579(4)
Sm(1)–O(2)	2.540(4)	Sm(1)–O(10)	2.511(4)
Sm(1)–O(4)	2.614(4)	Sm(1)–O(11)	2.396(3)
Sm(1)–O(5)	2.611(4)	Sm(1)–O(12)	2.397(3)
Sm(1)–O(7)	2.588(4)	Sm(1)–O(13)	2.399(4)

D–H···A	d(D–H)	d(H···A)	d(D···A)	(D–H–A)
(ii)				
N(4)–H(4N)···O(10)	0.73(4)	2.13(4)	2.730(6)	140.0(5)
N(5)–H(5N)···O(1)	0.987(10)	2.20(2)	2.990(6)	135.4(16)
N(5)–H(5N)···O(11)	0.987(10)	1.896(10)	2.688(6)	135.2(16)
N(6)–H(6N)···O(2)	0.75(6)	2.46(6)	2.964(7)	126.0(6)
N(6)–H(6N)···O(12)	0.75(6)	2.08(6)	2.714(6)	143.0(6)
N(7)–H(7N)...O(5)	0.88(5)	2.46(5)	3.039(7)	124.0(4)
N(7)–H(7N)···O(13)	0.88(5)	1.94(5)	2.684(6)	141.0(4)

Table 5
Selected (i) bond distances (Å) and (ii) hydrogen bonding distances (Å) and angles (°) for [Yb(H_2O)$_2$(NO_3)(μ-NO_3)(acac)]$_2$ (**5**)

Atoms	Distances	Atoms	Distances
(i)			
Yb(1)–O(1)	2.274(7)	Yb(1)–O(8)	2.368(8)
Yb(1)–O(2)	2.248(7)	Yb(1)–O(1S)	2.305(7)
Yb(1)–O(3)	2.478(9)	Yb(1)–O(2S)	2.401(9)
Yb(1)–O(5)	2.413(8)	Yb(1)–O(6)	2.332(6)
Yb(1)–O(6)	2.577(7)		

D–H···A	d(D–H)	d(H···A)	d(D···A)	(D–H–A)
(ii)				
O(1S)–H(1SB)···O(5)	1.0000(11)	2.44(10)	3.051(11)	119(8)
O(2S)–H(2SA)···O(5)	1.000(6)	2.2(5)	2.910(14)	130(45)
O(1S)–H(1SA)···O(1)#1	1.0000(14)	1.73(5)	2.665(10)	154(9)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+2$.

size 0.30 × 0.20 × 0.18 mm, reflections collected = 23 869, unique reflections = 8460 (R_{int} = 0.1095), R_1 [$I > 2\sigma(I)$] = 0.0680, wR_2 (all data) = 0.2015.

2.9. [Nd(NO_3)$_3$(H_2acacen)$_2$][C_6H_{12}] (2)

$C_{27}H_{50}N_7O_{13}Nd$, $M = 824.98$, monoclinic, $P2_1/n$, $a = 11.5549(18)$, $b = 15.386(2)$, $c = 20.339(3)$ Å, $\beta = 102.792(2)°$, $V = 3526.2(9)$ Å^3, $Z = 4$, calculated density = 1.554 g cm^{-3}, $\mu_{Mo} = 1.543$ mm^{-1}, crystal size 0.40 × 0.40 × 0.40 mm, reflections collected = 22 219, unique reflections = 8277 (R_{int} = 0.0209), R_1 [$I > 2\sigma(I)$] = 0.0272, wR_2 (all data) = 0.0772.

2.10. [Pr(NO_3)$_3$(H_2acacen)$_2$][C_6H_{12}] (3)

$C_{27}H_{50}N_7O_{13}Pr$, $M = 821.65$, monoclinic, $P2_1/n$, $a = 11.6368(11)$, $b = 15.4286(14)$, $c = 20.4259(19)$ Å, $\beta = 102.241(2)°$, $V = 3583.9(6)$ Å^3, $Z = 4$, calculated density = 1.523 g cm^{-3}, $\mu_{Mo} = 1.429$ mm^{-1}, crystal size 0.40 × 0.35 × 0.20 mm, reflections collected = 22 762, unique reflections = 8397 (R_{int} = 0.0658), R_1 [$I > 2\sigma(I)$] = 0.0447, wR_2 (all data) = 0.1007.

2.11. [Sm(NO_3)$_3$(H_2acacen)$_2$][C_6H_{12}] (4)

$C_{27}H_{50}N_7O_{13}Sm$, $M = 831.09$, monoclinic, $P2_1/n$, $a = 11.6730(11)$, $b = 15.3454(14)$, $c = 20.3911(19)$ Å, $\beta = 102.130(2)°$, $V = 3571.0(6)$ Å^3, $Z = 4$, calculated density = 1.546 g cm^{-3}, $\mu_{Mo} = 1.714$ mm^{-1}, crystal size 0.30 × 0.25 × 0.25 mm, reflections collected =

23 058, unique reflections = 8470 ($R_{int} = 0.0767$), R_1 [$I > 2\sigma(I)$] = 0.0490, wR_2 (all data) = 0.1267.

2.12. *[Yb(H$_2$O)$_2$(NO$_3$)$_2$(μ-NO$_3$)(acac)]$_2$ (**5**)*

$C_5H_{11}N_2O_{10}Yb$, $M = 432.20$, triclinic, $P\bar{1}$, $a = 8.2798(17)$, $b = 8.8703(18)$, $c = 10.702(2)$ Å, $\alpha = 107.41(3)°$, $\beta = 93.33(3)°$, $\gamma = 116.41(3)°$, $V = 654.7(2)$ Å^3, $Z = 2$, calculated density = 2.192 g cm^{-3}, $\mu_{Mo} = 7.188$ mm^{-1}, crystal size 0.20 × 0.25 × 0.15 mm, reflections collected = 4203, unique reflections = 2953 ($R_{int} = 0.0358$), R_1 [$I > 2\sigma(I)$] = 0.0618, wR_2 (all data) = 0.1641.

3. Results and discussion

Complexes $\{[Ln(NO_3)_3(H_2acacen)_2][C_6H_{12}]\}_n$ (Ln = La, Pr, Nd and Sm) (**1**–**4**) were synthesised by dissolving the lanthanoid nitrate in thf, then adding a thf–cyclohexane solution of H$_2$acacen with gentle stirring. Problems with solubility arose if the two solids were combined before solvent was added. The use of water as a solvent proved to be unsuitable as the product obtained was usually a viscous oily residue. It is evident that decomposition of H$_2$acacen occurs when combined with the heavier lanthanoid nitrates in H$_2$O (and to a lesser extent thf), since the only isolable complex from this reaction for Ln = Yb was $[Yb(H_2O)_2(NO_3)_2(\mu\text{-}NO_3)(acac)]_2$ (see later). Composition of all complexes was confirmed by microanalysis.

Complexes **1**–**4** are isomorphous and crystallise in the monoclinic space group $P2_1/n$. The metal centre is 10 coordinate, and contains three bidentate nitrate anions in a planar fashion about the metal center. The remaining coordination sites are occupied by oxygen atoms of H$_2$acacen. The first mode of coordination involves a single bidentate H$_2$acacen ligand coordinated via the two oxygen donor atoms, resulting in an unusual 14-membered chelate ring (Fig. 1). This chelate ring is remarkably reminiscent to that in $[UO_2(NO_3)_2)(salpn)]$ (salpn = *N*,*N*′-propylenebis(salicylideneimine)) where the nitrogen atoms of the Schiff base are not involved in metal binding [14]. The second mode of attachment involves two separate H$_2$acacen ligands, each coordinated in a monodentate fashion. These ligands then extend away laterally from the central metal atom and coordinate to additional metal centers, thus forming an infinite, zigzag polymeric array (Fig. 1). This dual conformation demonstrates the flexibility of the H$_2$acacen ligand relative to the salen ligand. The Ln–O$_{(H_2acacen)}$ bonds from the bidentate ligand are highly unsymmetrical in all four examples (range of 2.396(3)–2.581(4) Å), which is presumably a result of buttressing by the nitrate anions. The two Ln–O$_{(H_2acacen)}$ bond lengths arising from the monodentate bridging ligands are however, almost identical, since these two groups are spatially distant from the nitrate ions.

The fact that the metal centre is the neutral metal salt means that the ligands must be protonated to retain electrostatic neutrality. These protons were located on the nitrogen atoms, and hydrogen bond to the oxygen atoms of the Schiff base and the nitrate oxygens via intramolecular hydrogen bonding in both the bidentate and monodentate ligands (see Tables 1–4). This may explain the conformational twist of the ligand, since these interactions ‘anchor’ the ligands into their respective positions.

The four examples recorded here only contain the lighter lanthanoid elements. Repeated attempts to obtain examples of the heavier species (Eu–Yb) failed to yield crystals of suitable quality for X-ray analysis, and the products tended to be either insoluble precipitates or oily residues. An exception to this was the gadolinium species, the microanalysis of which suggested the empirical formula $[Gd(NO_3)_3\cdot thf][H_2acacen]$, however the poor quality of the crystals, and their slow decomposition prevented further analysis being obtained. This apparent deviation in morphology remains unclear, but is not surprising that structural changes may take place taking into account the lanthanoid contraction and therefore different coordinative requirements. The persistent presence of oily residues may be attributed to decomposition, promoted by the presence of the lanthanoid ion. Hydrolysis of Schiff bases in the presence of such ions is not totally surprising considering cleavage-type reactions have been observed in the study of DNA scission by cerium compounds [15]. Thus, interaction of $Yb(NO_3)_3\cdot 6H_2O$ and H$_2$acacen in water, yielded the dimeric complex $[Yb(H_2O)_2(NO_3)_2(\mu\text{-}NO_3)(acac)]_2$ (acac = 2,4-pentanedione). Bidentate acac species are well known ligands [16,17], and its presence in this complex indicates that cleavage of the Schiff base linkage in the parent H$_2$acacen ligand has occurred. Repeated recrystallisation of the H$_2$acacen starting material from thf, in addition to the clean NMR exclude the possibility of the acac originating as a contaminant in the starting material. Interestingly, this complex has not been previously observed. Compound **5**. which was hand-picked from the oily residue of the reaction mixture crystallises in the triclinic space group $P\bar{1}$, and exists as a nitrate bridged dimer. Only one metal centre resides in the asymmetric unit, with the second being generated by symmetry. Each metal centre is nine coordinate and contains two water molecules, a bidentate acac ligand, and two bidentate nitrate anions one of which is also bridging via O6 between the two metal centres (Fig. 2). Interestingly, the M–O$_{(nitrate)}$ bridging bond length (2.332(6) Å is significantly shorter than the corresponding M–O$_{(nitrate)}$ terminal bond lengths (2.577(7) and 2.367(8) Å). This dual coordination of the nitrate anion is unusual, and has only been observed

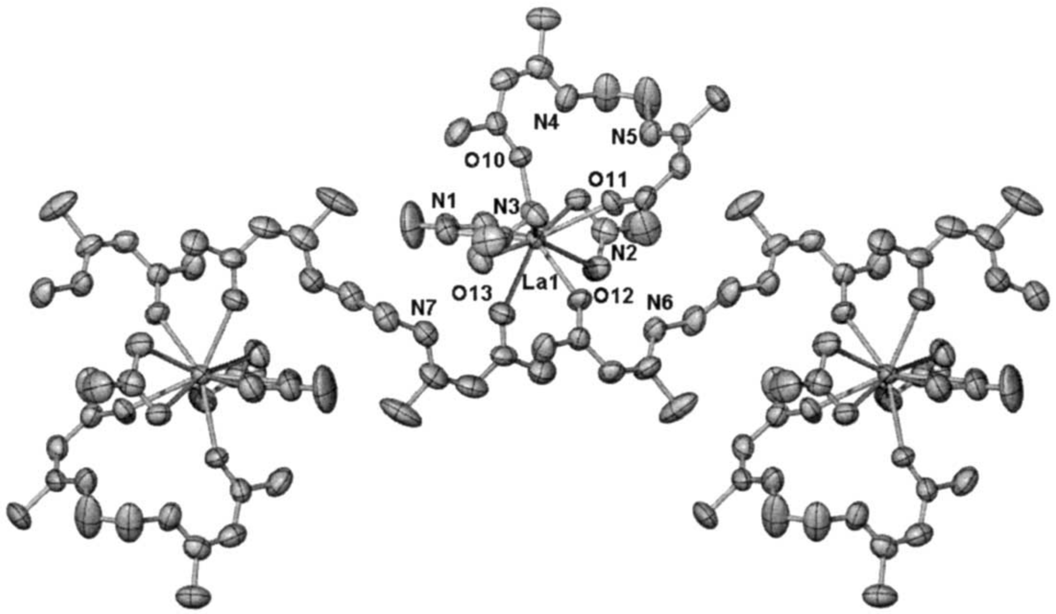

Fig. 1. The extended polymeric array of $\{[Ln(NO_3)_3(H_2acacen)_2][C_6H_{12}]\}_n$ (Ln = La, Ce, Pr and Sm) (**1**–**4**). Hydrogen atoms have been omitted for clarity.

in three previous lanthanoid species [18–20]. As in compounds **1**–**4**, intramolecular hydrogen bonding is evident, this time between the H atoms on water molecules and the O atoms of the acac ligand (see Table 5).

4. Conclusions

This investigation involved the Schiff base ligand *N*,*N*-ethylenebis(acetylacetoneimine) (H_2acacen) and the early lanthanoid nitrates (Ln = La, Pr, Nd and Sm). The four complexes were isostructural and the asymmetric unit contained a single, neutral lanthanoid nitrate centre, to which were coordinated three separate H_2acacen ligands, each in a different fashion. One entire ligand was bound in a bidentate fashion through the oxygen donor atoms leading to a 14-membered chelate ring which is the first structurally characterised example observed for this ligand with any metal. The remaining two ligands were each bound in a monodentate fashion via the oxygen donor atoms, and extended out away

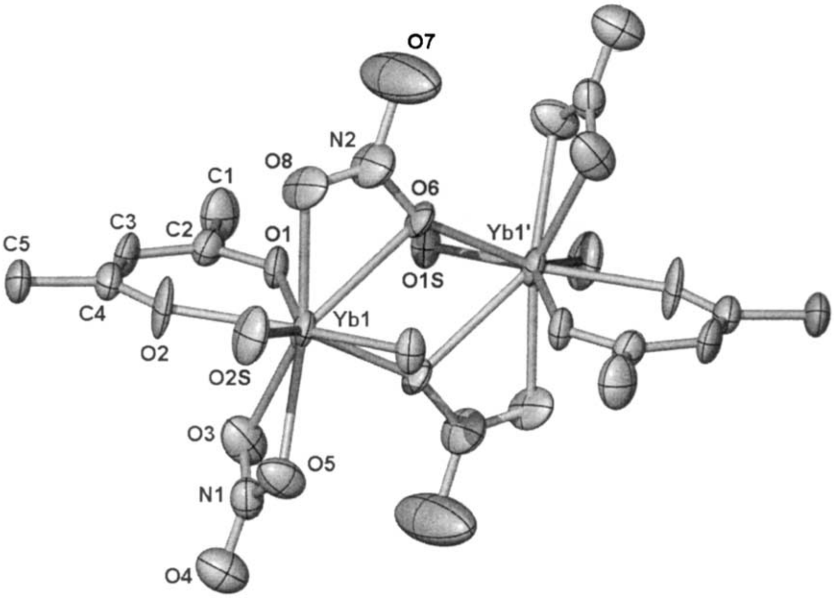

Fig. 2. X-ray crystal structure of the dimeric $[Yb(H_2O)_2(NO_3)_2(\mu\text{-}NO_3)(acac)]_2$ (**5**).

from the metal centre to afford a polymeric array. In an analogous reaction involving ytterbium a small number of crystals resulted which were analysed as the new heteroleptic complex $[Yb(H_2O)_2(\mu\text{-}NO_3)_2(acac)]_2$. The isolation of an acac complex suggests that significant metal catalysed decomposition of the H_2acacen ligand occurred.

5. Supplementary material

All other pertinent crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 190930, 190927, 190928, 190929, 190926 for compounds **1**, **2**, **3**, **4** and **5**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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