

The sodium salt of a tris(tridentate anion)gadolinium(III) complex: pentasodium bis[chelidamato(3-)]-[chelidamato(2-)]gadolate(III) hexadecahydrate

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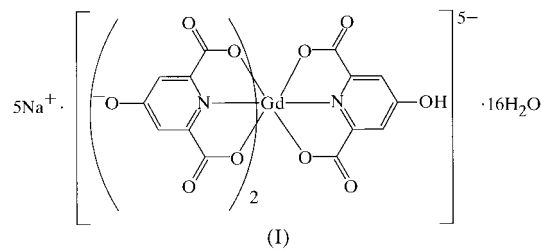
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The sodium salt of a complex anion formed between gadolinium(III) and three variously deprotonated chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid) ligand moieties, assigned as $\text{Na}_5[\text{Gd}(\text{C}_7\text{H}_2\text{NO}_5)_2(\text{C}_7\text{H}_3\text{NO}_5)] \cdot 16\text{H}_2\text{O}$, *i.e.* pentasodium (4-hydroxypyridine-2,6-dicarboxylate)bis(4-oxidopyridine-2,6-dicarboxylate)gadolinium(III) hexadecahydrate, forms as colourless monoclinic crystals upon vapour diffusion of ethanol into its aqueous solution. The ligand moieties, assigned as two trianionic and one dianionic chelidamate species, are all tridentate in the complex anion of tricapped trigonal prismatic donor-atom geometry. The geometry of the ligands and that of the primary coordination sphere is very similar to that of the analogous anionic tris(ligand)-rare earth complexes of the pyridine-2,6-dicarboxylate (dipicolinate) dianion.

Comment

The dianion of pyridine-2,6-dicarboxylic acid (dipicolinic acid) is well known to form stable complexes of the rare earth elements, which in the cases of Eu^{III} and Tb^{III} are strongly luminescent (Riehl & Richardson, 1986; Dong & Flint, 1992). Substituted dipicolinic acid, 4-hydroxypyridine-2,6-dicarboxylic acid or chelidamic acid (H_3chel ; Hall *et al.*, 2000), which may bind in forms up to the trianionic (Bag *et al.*, 1962), has been of interest because of the possibility of using the additional functional group to introduce substituents which may, amongst other things, modify the electronic properties of complexes subsequently formed (Metcalf *et al.*, 1990, 1993). It is necessary to be sure that apparent modifications to such properties are not consequences of changes in the gross physical structure of the complexes and, for this reason, we

have conducted a synthetic and structural study of a tris(chelidamate)-rare earth(III) complex, as its sodium salt, to confirm both that tris(chelidamate) complex anions may be isolated as solids and to establish in detail their tris(tridentate) structure. The potential interest in derived materials of the form $M_x[\text{Ln}(\text{chelidamate})_3]$, where both M and Ln could be photoactive (Brayshaw *et al.*, 1995), was another driving force for this study. In the event, in early trials with a number of Ln and group I elements as counter-cations, small crystals only were obtained for the combination $M = \text{Na}$ and $\text{Ln} = \text{Gd}$; as it happens, this is a rather unfortunate combination leading to difficulties, in the context of accessible data of modest quality, in assigning sodium cations *versus* water molecules of solvation, both Na^+ and H_2O being isoelectronic, and the absolute Na content is difficult of access by other analytical means given a material which desolvates rapidly. Thus, although it has been generally assumed that the species present in solution near neutral pH are hexa-anionic $[\text{Ln}(\text{chel})_3]^{6-}$ (Metcalf *et al.*, 1990, 1993; Pike *et al.*, 1983), elemental analyses of the material presently isolated were consistent with an Na:Gd ratio of 5:1 and the final structural model adopted, in which H atoms were not resolved, was consistent in stoichiometry and connectivity with a formulation of $\text{Na}_5[\text{Gd}(\text{chel})_2(\text{Hchel})] \cdot 16\text{H}_2\text{O}$, (I), where chel^{3-} is chelidamate, indicative of the triply deprotonated anion of the parent acid, H_3chel .



The numbering scheme adopted within the ligand is as follows (there is insufficient space to label all atoms in the figures): atom numbers are of the form $Xlmn$, where l identifies the ligand (1–3), m the position in the ring and n is used only for the substituent carboxyl groups. Na atoms are numbered 1–5 and water O-atom numbering runs from 1 to 17 (omitting 14 because of its use in a ligand). The O/21 ($l = 1$ –3) atoms lie at the vertices of one triangular face of the Gd coordination environment and O/61 are at the other.

Relative to dipicolinic acid, a diprotic acid H_2dipic , chelidamic acid offers a further degree of acidity by way of dissociation of the phenolic functionality, which, at least in the free acid, might be expected to be facilitated by the formation of the N-protonated keto/pyridine (pyridone) form. Despite studies of its dissociation (Bag *et al.*, 1962), the priority order of deprotonation of the carboxylic and phenolic groups has not been established with any certainty, and the extent of any pyridone formation remains an unknown factor. We have described some rather marked differences between the solid-state forms of dipicolinic and chelidamic acids relating to the distribution of the acidic protons (Hall *et al.*, 2000). Nonetheless, it comes as no surprise to find, in the present structure, in which one formula unit is the asymmetric unit, a complex

species in which, as in the tris(dipicolinate)–rare earth(III) arrays, three *O,N,O*-tridentate ligands are disposed about the central metal atom in an array of putative 32 symmetry.

The complex anions are disposed in the structure in layers normal to c^* . The projection of a single layer down that axis (Fig. 1) clearly shows the putative 32 symmetry of the anion, with its 3-axis lying quasi-parallel to c^* , the angle between being $2.1(1)^\circ$. To date, no tris(dipicolinato)gadolinate(III) arrays have been reported in the literature structurally characterized to the point of providing detailed geometry of the metal-atom environment, although the species has been generically defined by inference from the fact that the series $[\text{Cr}\{(\text{NH}_2)_2\text{sar}\}][\text{Ln}(\text{dipic})_3]\cdot 8\text{H}_2\text{O}$ (sar = 3,6,10,12,16,19-hexaazabicyclo[6.6.6]icosane) is, by implication, an isomorphous array following detailed structure determinations for Ln = La, Ce and Lu (Harrowfield *et al.*, 1995). Interestingly, that structure also exhibits layering similar to the present compound, the cell being shown in that reference in a counterpart projection to the present Fig. 1. This motif sheet appears to be a common feature in structures of $[\text{Ln}(\text{dipic})_3]^{3-}$ derivatives, being evident similarly in $\text{Cs}_3[\text{Eu}(\text{dipic})_3]\cdot 9\text{H}_2\text{O}$ and $[\text{Co}(\text{sar})][\text{Eu}(\text{dipic})_3]\cdot 8\text{H}_2\text{O}$ (Brayshaw *et al.*, 1995), and is similar to that observed in many chelating heteroaromatic base complexes wherein vertex-to-face heterocycle interactions (the ‘sextuple aryl embrace’) have been proposed as an important factor influencing the lattice assembly (Dance & Scudder, 1998).

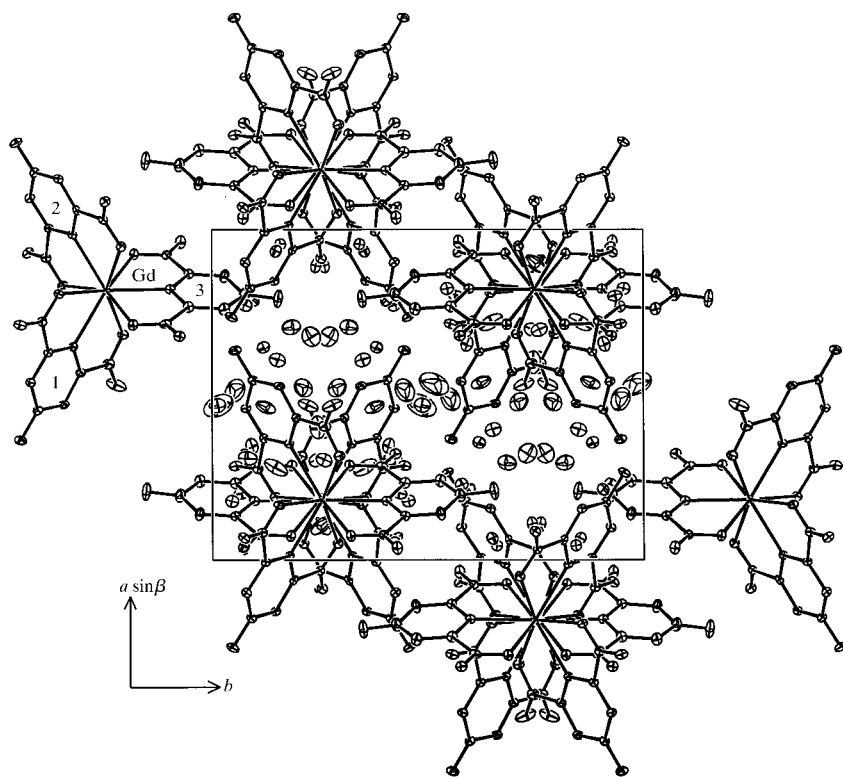


Figure 1

Unit-cell contents with 30% amplitude displacement ellipsoids projected down c . The quasi-32 symmetry of the anions is clearly seen.

For consideration and comparison of the metal-atom environment in the context of related species, the parameters of the present array may be compared with those of the dipicolinate counterpart complex ion as found in $[\text{Co}(\text{NH}_3)_6][\text{Gd}(\text{dipic})_3]\cdot 11\text{H}_2\text{O}$ (Table 2; Brayshaw *et al.*, 2000), but with credibility enhanced by their close similarity to those of the Ln = Eu counterpart arrays (wherein the metal radius should differ by only *ca* 0.01 Å), as recorded recently (Brayshaw *et al.*, 1995). Ligand parameters may also be compared with those for other chelidamate species previously structurally characterized in $[(\text{chelH})M(\text{OH})(\text{OH}_2)]_2\cdot 4\text{H}_2\text{O}$ ($M = \text{Fe}, \text{Cr}$), in which the metal ions are progressively much smaller species ($M = \text{Fe}$: Thich *et al.*, 1976; $M = \text{Cr}$: Cline *et al.*, 1979), and in various macrocyclic ether esters and associated derivatives (Nakatsuji *et al.*, 1985; Bradshaw *et al.*, 1985). Comparison of the $[\text{GdL}_3]^{n-}$ ($L = \text{dipic}$ and chelH_x) data of Table 2 shows that, although the two complex species in general are quite similar, the incorporation of the aryloxy in the ring *para* to the metal atom is not totally without consequence for the geometry about the metal as well as within the ring. The latter changes are largely as expected. At the metal, however, it is clear that in the chelidamate, the metal is more tightly bound to the nitrogen than in the dipicolinate, with consequent perturbation in nearby associated ring geometries. Extension of the comparison to consideration of the chelidamate dianion in association with smaller trivalent high-spin iron and chromium species shows that the metal–nitrogen and

metal–oxygen distances remain broadly equivalent, the *N,O*-chelate components closing around the metal with concomitant substantial changes in the associated angular geometries, the organic esters offering a relaxed paradigm. In respect of the 4-hydroxy/oxido substituents in the present ligand rings, the intra-ring angles are diminished in keeping with a pronounced keto contribution to the C–O bond. With values of 1.329 (9), 1.334 (9) and 1.30 (1) Å for the three ligands, these values hardly differ significantly; it is of interest to note that calculations from the data for the cyclic chelidamate ester derivative $\text{ROH}\cdot\text{RO}^- (\text{benzylammonium})^+\cdot\text{CH}_2\text{Cl}_2$ ($\text{ROH} = 19\text{-hydroxy-3,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1]heneicosa-1(21),17,19-triene-2,16-dione}$; Bradshaw *et al.*, 1985) show that the distance is 1.29 Å in the anionic form and 1.34 Å in the protonated form. However, in these latter and related species (Thich *et al.*, 1976; Cline *et al.*, 1979; Hall *et al.*, 2000), the angular parameters of the ring C atoms are usefully diagnostic of protonation or otherwise at the oxygen, the intra-ring angle being more greatly diminished (to 113.7° in this case) from 120° in the deprotonated form with symmetrical exocyclic angles, while in the protonated form the

intra-ring angle rises to 117.8° with the exocyclic angles unsymmetrical (118.6 and 123.4°), as is also consistently the case in both of the Fe^{III} and Cr^{III} $[(\text{chelH})M(\text{OH})(\text{OH}_2)]_2 \cdot 4\text{H}_2\text{O}$ arrays. These data (consistent with the above distance) generally suggest that in the present complex ligand two of the three ligands are protonated at O4. Rather remarkably perhaps, we find no involvement of any of the deprotonated O14 atoms in the coordination sphere of any of the assigned Na atoms. The nature of the O14 interactions are of interest; whereas O34 interacts with a pair of nearby water molecules (O9,17), the only interactions evinced by O14,24 are between themselves in adjacent moieties: $\text{O14} \cdots \text{O24}(x-1, y, z) = 2.470(8) \text{ \AA}$, with a more distant approach to O14 by O5($1-x, y-\frac{1}{2}, \frac{1}{2}-z$) at $2.697(8) \text{ \AA}$, the $\text{O14} \cdots \text{O24}$ interaction presumably consequent on a shared protonic hydrogen. The carboxylate planes are reasonably coplanar with the central C_5N plane; in the present array, divergences are rather greater than in tris-(dipicolinate)-rare earth(III) species, and, concomitantly, the divergences of the Gd atom from the relevant planes are significant and substantial.

Assignment of the protonic and cationic complement of the rest of the structure is fraught with difficulty in consequence of our inability to resolve and refine H atoms, and in the presence of disorder beyond the complex species. Sodium ions and water, being isoelectronic, in their present forms present difficulties in assignment; nevertheless, their behaviour in crystal lattices is such as to inspire some confidence in the present assignment, water oxygen rarely having a coordination environment of other O atoms greater than four, while the

coordination number of sodium is rarely as low as that, with, despite its generally higher coordination number, shorter $X \cdots \text{O}$ distances. Such is the case here, Na1–5 all having coordination numbers greater than five, with most associated $\text{Na} \cdots \text{O}$ distances less than 2.5 \AA , while O1–17 have coordination numbers of four or less, with $\text{O} \cdots \text{O}$ contact distances as assigned being greater, generally, than 2.4 \AA (exceptions: O13,15,16, modelled as disordered, where the situation is less clearcut). Inspection of the sodium environments shows that all of Na1–4 interact with an (uncoordinated) $\text{O}1m2$ of the complex anion and a further similar oxygen of the glide-generated image. At either pole of the principal axis of the quasi-32 coordination environment, we find O122 and O162, these poles confronting each other in successive units of the one-dimensional polymer strand so generated. In accommodating four sodium ions, O122 are disposed with Na1 pendant from O122, Na2,3 bifurcating from O222 and Na4 pendant from O322 (bifurcating with Na5 which plays no part in constructing the polymer in this dimension). At the other pole of the next glide-generated member of the polymer strand, O162 interact with Na3,4, bifurcating O262 and Na1,2, bifurcating at O362, *i.e.* O162 being void of sodium interactions.

The above, we believe, constitutes a *prima facie* case for the assignment of Na1–4; Na5 plays a different role, but has an environment typically that of a sodium cation, and is also eminently plausible as such. As such, the stoichiometry requires triple deprotonation of two of the chelidamate ligands, the other being doubly deprotonated, consistent with

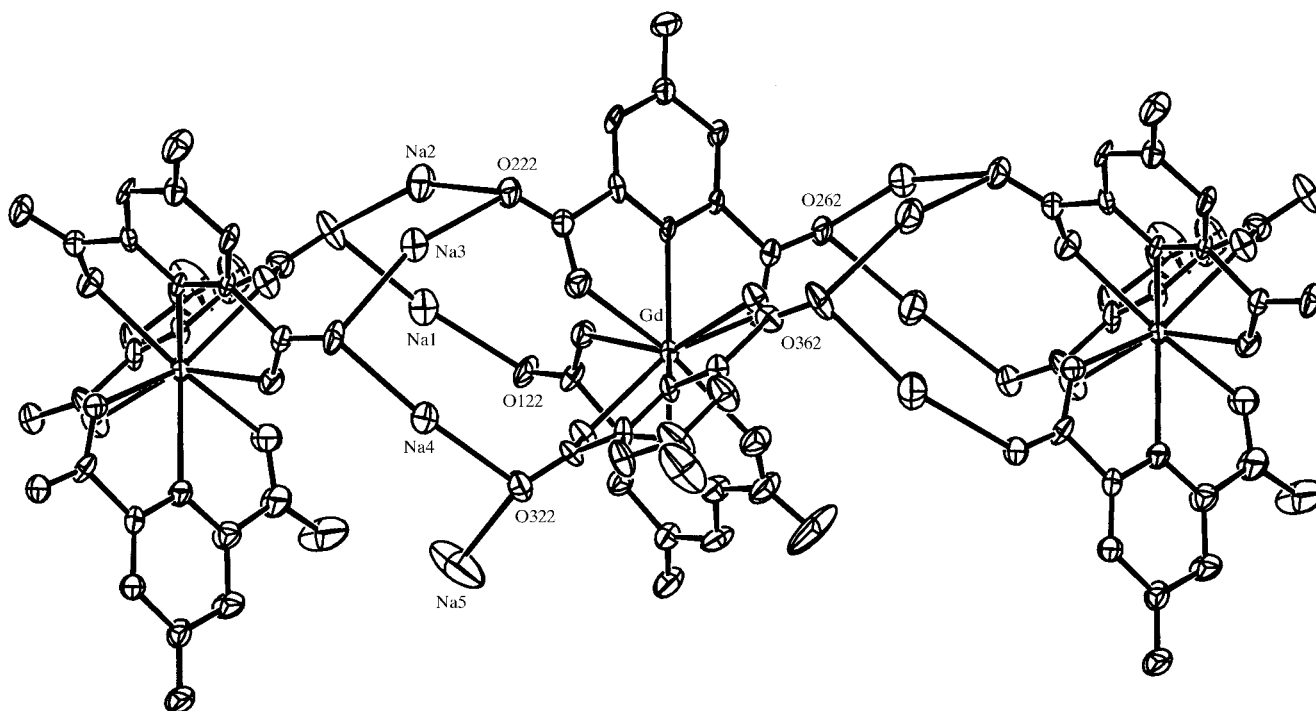


Figure 2

View of the $\dots[\text{GdL}_3]\text{Na}_4[\text{GdL}_3]\text{Na}_4\dots$ polymer strand generated by the glide plane, normal to its propagation axis (c), which lies horizontal in the page.

the model proposed above. We note that the asymmetry may not be unambiguous in the context of the modelling of three of the water molecules as disordered over pairs of sites, possibly concerted, and conforming to different configurations of protonic soup. Difference-map residues, rather larger than desirable, are found in the regions of the heavy atom and disorder. A more definitive description of this aspect requires access to crystals and instrumentation capable of yielding more extensive and better quality data. In respect of the aqueous hydrogen-bonding array, there is little to be said, the environs of the undisordered species being plausible.

While we have commented above on the layering of the structure normal to *c*, in terms of the array of complex anions, the interspersing cationic/aqueous layer is not without interest either. We have drawn attention to the manner in which successive complex anion carboxylates at either pole of the complex cation are linked up the *c* axis in a manner which incorporates interactions with all Na atoms (Fig. 2). However, all sodium ions are also linked by water molecules O1–5,10 into continuous strands along the *b* axis, O6,7,11–13,16 being pendant, albeit hydrogen bonded to neighbouring strands, so that a web is formed of cations, anions and associated water molecules in the *bc* plane.

Experimental

The title compound was prepared by a method similar to that used for the synthesis of the Dy and Tm analogues (Pike *et al.*, 1983), with sodium carbonate replacing the lithium hydroxide used in the earlier procedure. Crystals suitable for X-ray analysis were grown by diffusion of ethanol into an aqueous solution of the complex.

Crystal data

Na ₅ [Gd(C ₇ H ₂ NO ₅) ₂ ·(C ₇ H ₃ NO ₅)]·16H ₂ O	$D_x = 1.828 \text{ Mg m}^{-3}$
$M_r = 1101.74$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 12 reflections
$a = 12.748 (3) \text{ \AA}$	$\theta = 12.97\text{--}15.38^\circ$
$b = 16.508 (9) \text{ \AA}$	$\mu = 1.819 \text{ mm}^{-1}$
$c = 19.190 (16) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 97.50 (5)^\circ$	Hexagonal prism, colourless
$V = 4004 (4) \text{ \AA}^3$	$0.35 \times 0.32 \times 0.18 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.06$
θ – 2θ scans	$\theta_{\text{max}} = 24.99^\circ$
Absorption correction: Gaussian (Busing & Levy, 1957)	$h = -15 \rightarrow 15$
$T_{\text{min}} = 0.567$, $T_{\text{max}} = 0.756$	$k = -19 \rightarrow 15$
18 620 measured reflections	$l = -22 \rightarrow 16$
7023 independent reflections	12 standard reflections
6441 reflections with $F > 4\sigma(F)$	frequency: 60 min
	intensity decay: none

Refinement

Refinement on F	H-atom parameters not refined
$R = 0.072$	$w = 1/[\sigma^2(F) + 0.004F^2]$
$wR = 0.068$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.606$	$\Delta\rho_{\text{max}} = 1.663 \text{ e \AA}^{-3}$
6441 reflections	$\Delta\rho_{\text{min}} = -1.729 \text{ e \AA}^{-3}$
577 parameters	

Table 1
Selected geometries (\AA , $^\circ$).

	$l = 1$	$l = 2$	$l = 3$	Average
<i>(a)</i> Gadolinium and associated ligand parameters				
Gd–N1	2.496 (6)	2.482 (6)	2.475 (6)	2.484
Gd–O121	2.469 (5)	2.449 (5)	2.415 (5)	
Gd–O161	2.434 (6)	2.447 (5)	2.470 (5)	2.45
N1–Gd–N($l+1$)	118.5 (2)	120.4 (2)	121.2 (2)	120.0
O121–Gd–O($l+1$)21	75.0 (2)	76.6 (2)	78.5 (2)	
O161–Gd–O($l+1$)61	75.6 (2)	74.8 (2)	78.4 (2)	76.5
N1–Gd–O121	63.7 (2)	64.1 (2)	64.8 (2)	
N1–Gd–O161	64.0 (2)	64.2 (2)	63.5 (2)	64.0
N1–Gd–O($l+1$)21	132.7 (2)	135.3 (2)	137.1 (2)	
N1–Gd–O($l-1$)61	136.7 (2)	136.0 (2)	132.6 (2)	135.1
N1–Gd–O($l+1$)61	75.7 (2)	74.7 (2)	74.7 (2)	
N1–Gd–O($l-1$)21	73.7 (2)	71.6 (2)	75.4 (2)	74.3
O121–Gd–O161	127.7 (2)	128.3 (2)	128.3 (2)	128.1
O121–Gd–O($l+1$)61	90.3 (3)	90.6 (2)	88.7 (2)	89.9
O121–Gd–O($l-1$)61	146.2 (2)	150.2 (2)	149.2 (2)	148.5
Gd–O121–C121	124.0 (5)	124.0 (5)	122.7 (4)	
Gd–O161–C161	124.7 (5)	123.8 (5)	124.2 (4)	123.9
Intra-ligand interplanar angles				
(CSN)1//CCO212	3.8 (3)	10.6 (3)	12.2 (3)	
(CSN)1//CCO216	4.1 (3)	7.1 (3)	4.2 (3)	
Gadolinium deviations from planes				
(CSN)1	0.05 (1)	0.02 (1)	0.24 (1)	
CCO212	0.26 (1)	0.60 (1)	0.49 (1)	
CCO216	0.18 (1)	0.39 (1)	0.47 (1)	
<i>(b)</i> Intra-ligand geometries				
N1–C12	1.345 (9)	1.34 (1)	1.341 (9)	
N1–C16	1.35 (1)	1.345 (9)	1.338 (9)	1.34
C12–C13	1.35 (1)	1.38 (1)	1.37 (1)	
C15–C16	1.39 (1)	1.38 (1)	1.37 (1)	1.36
C13–C14	1.41 (1)	1.38 (1)	1.43 (1)	
C14–C15	1.42 (1)	1.41 (1)	1.41 (1)	1.41
C14–O14	1.329 (9)	1.334 (9)	1.30 (1)	1.32
C12–C121	1.52 (1)	1.53 (1)	1.50 (1)	
C16–C161	1.48 (1)	1.52 (1)	1.52 (1)	1.51
C121–O121	1.269 (9)	1.270 (9)	1.273 (9)	
C161–O161	1.27 (1)	1.263 (8)	1.287 (9)	1.27
C121–O122	1.249 (9)	1.24 (1)	1.257 (9)	
C161–O162	1.24 (1)	1.255 (9)	1.239 (9)	1.25
Gd–N11–C12	121.8 (5)	121.2 (4)	120.9 (4)	
Gd–N11–C16	120.0 (4)	121.5 (5)	122.5 (4)	121.3
C12–N11–C16	118.2 (6)	117.3 (6)	116.2 (6)	117.2
N11–C12–C13	123.1 (7)	123.2 (6)	124.3 (7)	
N11–C16–C15	122.5 (7)	123.8 (7)	124.0 (7)	123.5
N111–C12–C121	113.6 (6)	114.1 (6)	112.9 (6)	
N11–C16–C161	115.1 (7)	113.4 (6)	114.2 (6)	113.9
C13–C12–C121	123.3 (7)	122.7 (7)	122.8 (7)	
C15–C16–C161	122.4 (8)	122.8 (6)	121.7 (7)	122.6
C12–C121–O121	116.3 (7)	114.7 (7)	117.3 (6)	
C16–C161–O161	116.1 (8)	116.6 (6)	114.2 (6)	115.9
C12–C121–O122	118.4 (6)	119.3 (6)	119.0 (7)	
C16–C161–O152	121.2 (8)	118.5 (6)	120.9 (6)	119.6
O121–C121–O122	125.3 (7)	126.0 (7)	123.7 (7)	
O161–C161–C162	122.6 (8)	124.9 (7)	124.9 (7)	124.6
C12–C13–C14	120.8 (7)	119.1 (7)	119.6 (7)	
C14–C15–C16	119.0 (8)	117.8 (6)	120.4 (7)	119.5
C13–C14–O14	122.2 (7)	123.4 (7)	122.7 (8)	
C15–C14–O14	121.5 (7)	117.8 (6)	122.3 (8)	121.7
C13–C14–C15	116.3 (7)	118.7 (7)	115.0 (7)	116.7

Available material comprised rather small specimens, giving rise to extensive albeit weak data. In order to optimize the available data, more than a hemisphere was measured, yielding a limited amount of merged data. Solution of the structure was straightforward, with the complication described above of assignment of sodium cations *vis-à-vis* water molecules, compounded by inability to resolve H atoms, and

Table 2

Comparative metal–chelidamate geometries (Å, °).

Mean parameters are compared for the *M*(tridentate ligand) arrays in [Gd(dipic)₃]^{3−} as found in its [Co(NH₃)₆]³⁺ salt (Brayshaw *et al.*, 2000) and the present array.

	[Gd(dipic) ₃] ^{3−}	[Gd(chel) ₃] ^{3−}
<i>M</i> –N1	2.512	2.484
<i>M</i> –O21,61	2.436	2.45
N1–O2,6	1.34	1.34
C2,6–C3,5	1.39	1.36
C4–C3,5	1.37	1.41
C4–O4	–	1.32
C21,61–O21,61	1.26	1.27
C21,61–O22,62	1.23	1.25
<i>M</i> –N1–C2,6	120.3	121.3
<i>C</i> 2–N1–C6	119.4	117.2
N1–C2,6–C3,5	121.8	123.5
N1–C2,6–C21,61	114.4	113.9
C3,5–C2,6–C21,61	123.8	122.6
C2,6–C21,61–O22,62	118.1	119.6
O21,61–C21,61–O22,62	126.4	124.6
C2,6–C21,61–O21,61	115.5	115.9
<i>M</i> –O21,61–C21,61	125.3	123.9
C2,6–C3,5–C4	118.5	119.5
C3–C4–C5	120.0	116.7
C3,5–C4–O4	–	121.6

disorder among certain water molecules, resolved by consideration of cation environments and refinement behaviour at the level described. The possibility of an ethanolic component or slightly different water stoichiometry among the disordered components cannot be ruled out.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *Xtal3.5 GENTAN* (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal3.5*; program(s) used to refine structure: *Xtal3.5 CRYLSQ*; molecular graphics: *Xtal3.5 PIG ORTEP*; software used to prepare material for publication: *Xtal3.5 BONDLA CIFIO*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1323). Services for accessing these data are described at the back of the journal.

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