Three isomorphous Ln complexes: {[Ln$_2$(bt)$_6$(bno)(H$_2$O)$_4$]·bno}$_n$ (bt is but-2-enoate and bno is 4,4′-bipyridyl N,N′-dioxide), with Ln = Nd, Er and Y

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The polymeric title compounds, namely *catena*-poly[[[di-μ-but-2-enoato-$\kappa^3 O{:}O,O'{;}\kappa^3 O,O'{:}O'$-bis[diaquadibut-2-enoato-$\kappa O{;}\kappa^2 O,O'$-neodymium(III)]]-μ-4,4′-bipyridyl N,N′-dioxide-$\kappa^2 O{:}O'$] 4,4′-bipyridyl N,N′-dioxide solvate] and the erbium(III) and yttrium(III) analogues, {[Ln$_2$(C$_4$H$_5$O$_2$)$_6$(C$_{10}$H$_8$N$_2$O$_2$)(H$_2$O)$_4$]·C$_{10}$H$_8$N$_2$O$_2$}$_n$ (Ln = Nd, Er and Y), form from [Ln$_2$(bt)$_6$(H$_2$O)$_4$] dimers (bt is but-2-enoate) bridged by 4,4′-bipyridyl dioxide (bno) spacers into sets of parallel chains; these linear arrays are interconnected by aqua-mediated hydrogen bonds into broad two-dimensional structures, which in turn interact with each other though the hydrogen-bonded bridged bno solvent units. Both independent bno units in the structures are bisected by symmetry centres.

Comment

The construction of extended frameworks containing *f* elements bridged by carboxylate groups has attracted a great deal of interest because of the large variety of architectures that might result from the high and variable coordination numbers of the metal centres as well as the coordination versatility of the carboxylate ligands. In this respect, butenoic (crotonic) acid has proved to be highly efficient in coupling Ln^{III} ions (Rizzi *et al.*, 2003; Baggio *et al.*, 2005). In addition, we have observed that the incorporation of diimines during the synthetic procedure might favour crystallization, either through their inclusion as neutral ligands or counter-ions or even as external crystallization agents (Atria *et al.*, 2006). In particular, 4,4′-bipyridine and its derivatives appear to be quite suitable – owing to their well known spacer properties – for generating grid or cluster structures, which are interesting not only from a structural point of view but also for their potential application in ion exchange, catalysis, molecular absorption, optical, electronic and magnetic areas.

In this context, we have recently reported (Muñoz *et al.*, 2005) the synthesis and full characterization of an Ln[1] series formulated as {[Ln(bt)$_3$(bpy)$_{1/2}$(H$_2$O)]$_2$}$_n$ (bt is butenoate, bpy is 4,4′-bipyridine, and Ln = Nd, Gd, Ho, Er and Y); these structures will be referred to as (IV).

Complementing the former, we report here the syntheses and crystal structures of a related isomorphous series of general formula {[Ln(bt)$_3$(bno)$_{1/2}$(H$_2$O)$_2$]$_2$·(bno)}$_n$ [bno is 4,4′-bipyridyl dioxide, and Ln = Nd, (I), Er, (II), and Y, (III)], which exhibit close similarities to as well as interesting differences from the above-mentioned series (IV).

(I)   Ln=Nd
(II) Ln=Er
(III) Ln=Y
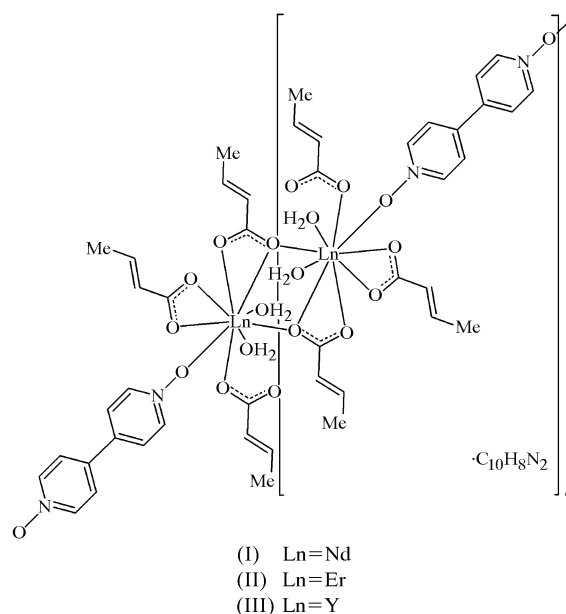
The title compounds crystallize in the triclinic space group $P\bar{1}$, and their asymmetric unit is composed of a nine-coordinate Ln cation, three butenoate ligands, two aqua ligands and one independent half of a whole bno unit, bisected by a symmetry centre. In what follows, we shall describe (I), the Nd compound, as representative of the whole series, pointing out any significant difference with the rest when pertinent. Fig. 1 shows a molecular plot of (I), and Tables 1, 3 and 5 give selected bond distances for all three isostructural compounds.

The cation coordination sites are provided by five carboxylate O atoms from one monocoordinated and two chelating butenoate units, one of which also acts in a bridging mode linking to a neighbouring Ln cation and thus providing a sixth site. The independent bno O atom and two aqua ligands complete the ninefold coordination.

Coordination distances span the range 2.377 (3)–2.671 (3) Å in (I), 2.262 (4)–2.773 (4) Å in (II) and 2.277 (2)–2.761 (3) Å in (III), which can be considered normal for this kind of complex. The carboxylate groups bite in rather dissimilar ways. That at C21 does so in a rather symmetric way, with bond differences in the range of 1–3% (percentages refer to the lower value in the pair). That at C11, instead, presents a pronounced asymmetry due to the involvement of atom O12

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[1] In this paper, we shall give the term 'Ln' a broader sense than normal, so as to include the whole lanthanide family plus the 'outlier' yttrium species.
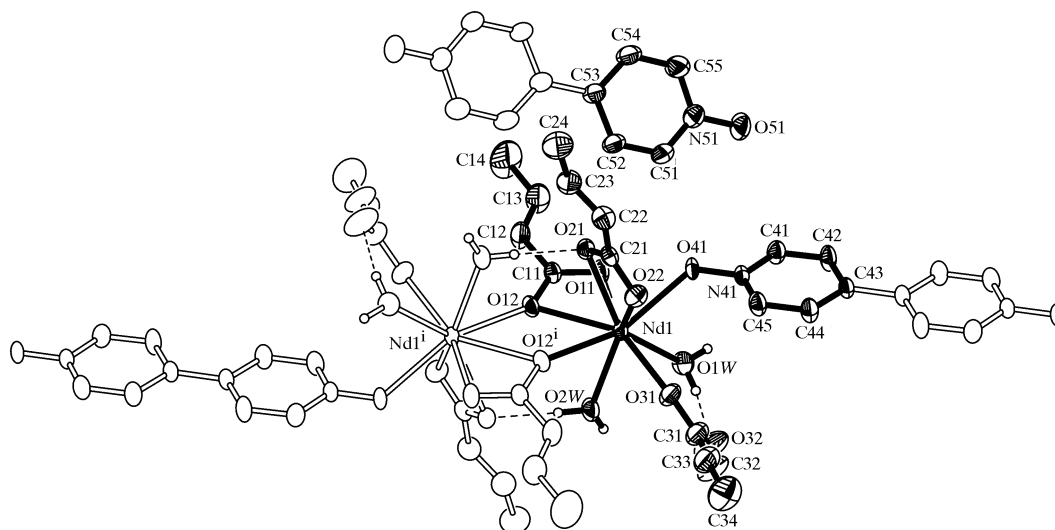
Figure 1
A molecular ellipsoid plot of (I). The independent part is shown with full 30% probability displacement ellipsoids (and bonds); the symmetry-related part is shown with open ellipsoids (and bonds). Note the way in which dimers and, in a second instance, chains are formed. Broken lines represent intramolecular hydrogen bonds. The symmetry codes are as in Table 1.
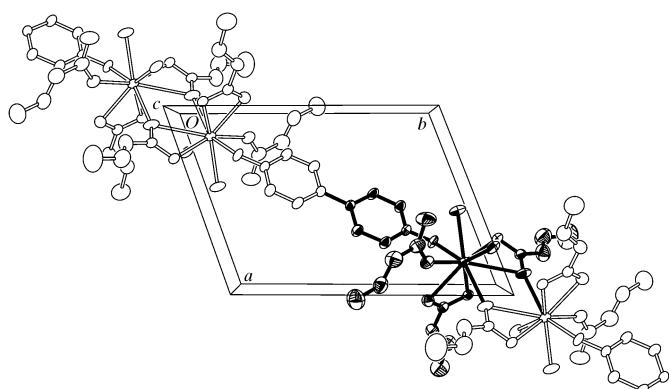

Figure 2
A linear chain in (I), running along [110].

in bridging; the resulting differences in the chelating distances are 5.7, 16.2 and 15.1% in (I)–(III), respectively. Still larger are the differences between chelating (long) *versus* bridging (short) distances for atom O12, which amount to 7.7, 18.3 and 17.5%, respectively.

The $[Ln(bt)_3(bno)_{1/2}(H_2O)_2]$ group already described acts as the elemental motif of a linear array, through the combined effects of two independent symmetry centres in the structure. That at $(1, 1, \frac{1}{2})$ generates dimeric units by joining neighbouring coordination polyhedra through an $[Ln-O]_2$ loop; these loops are characterized by Ln···Ln distances (Å)/O—Ln—O angles (°) of 4.373 (1)/63.9 (1), 4.369 (1)/63.0 (1) and 4.361 (1)/63.1 (1), respectively. The centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, which duplicates the independent pyridyl oxide group into a complete bno molecule, acts as the linkage between dimeric units, thus generating a linear chain that runs parallel to [110] and which is a distinctive feature in the structure (Fig. 2).

As expected from the existence of strong chelation restraints, the coordination polyhedron (Fig. 1) is rather difficult to describe within the limits of conventional geometries. However, it presents a good example of the applicability of the vector bond-valence approach recently presented by Harvey *et al.* (2006). An extremely simplified idea of what is presented therein is that if ligands are considered as 'a whole' and their collective coordinative interaction represented by a unique coordination vector joining the ligands to the metal centre, in addition to some other surprising results, substantial simplifications in the geometry description can be achieved. A detailed application of the procedure is beyond the scope of this paper, but if in the case of the chelating carboxylates the direction of the 'resultant interaction' is approximated by the $Nd-C_{carboxylate}$ vector (a very reasonable guess), the geometry ends up being described by a quite regular pentagonal bipyramid with the base defined by atoms C21, O41, O1W, O2W and O12^i [internal angle sequence: 71.0 (2), 72.2 (2), 67.3 (2), 72.7 (2) and 77.0 (2)°; mean deviation from the least-squares plane: 0.087 (1) Å], with atoms C11 and O31 at the apices, deviating by 5.3 (1) and 11.9 (1)°, respectively, from the plane normal.

Tables 2, 4 and 6 give information on the strong hydrogen bonds having the aqua H atoms as donors; those corresponding to entries 1 and 2 are intrachain and shown in Fig. 1. Interchain interactions (entries 3 and 4) can be envisaged as a two-step process, leading first to the formation of two-dimensional structures parallel to (001), by way of the hydrogen bond involving atom H1*WA* (third entry). These two-dimensional structures, in turn, are interconnected by the bno ligand, acting as a hydrogen-bonded bridge between planar arrays, into a final hydrogen-bonded three-dimensional structure.

A second type of nonbonding interaction providing packing stability is the C31—O32···Cg^{ii} contact [Cg is the centroid of the N51/C51–C55 ring; symmetry code: (ii) $-x + 1$, $-y + 2$, $-z + 2$; Fig. 3], weaker in structure (I) and more important in the remaining two, whose parameters are summarized in Table 7.

The similarities with the series of structures (IV) reported by Muñoz *et al.* (2005) are many and evident by inspection of both molecular diagrams; however, there are important differences as well, such as those derived from the presence of the solvent unit in (I), defining completely different packing patterns, or those resulting from the greater amount of open space left to coordination when the –ONC_5 group binds to the cation as in (I) instead of the –NC_5 group as in (IV). In the latter case, the three carboxylate groups chelate the cation; in the former, instead, one of them 'opens' by freeing O32, thus leaving room for the coordination of an extra aqua ligand, to which the same O32 atom makes a very strong intramolecular hydrogen bond, closing a wider Ln—O—H···O—C—O—Ln loop.
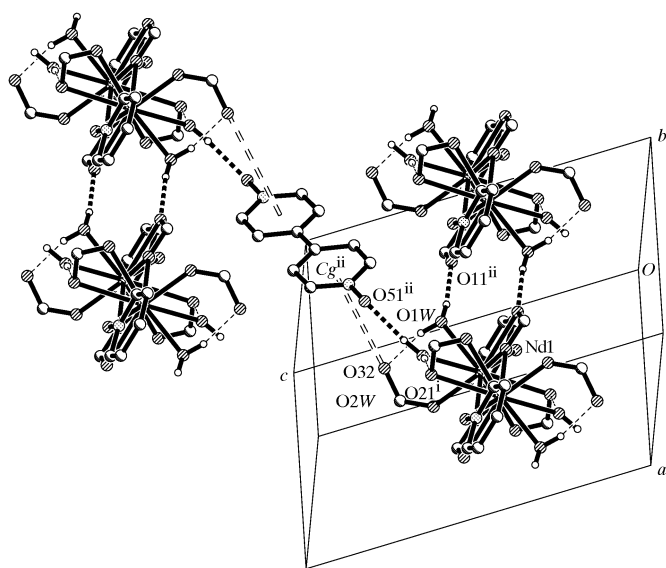

Figure 3
The packing of (I), projected on to the (110) plane, showing the packing interactions. Note in projection the chains, binding each other into planes parallel to (001) by way of the interchain hydrogen bond involving O11^{ii}. Note also the bridging function of the bno solvent molecule, through the interplanar hydrogen bond involving atom O51^{ii}. Single fine broken lines represent intramolecular hydrogen bonds, heavy broken lines intermolecular hydrogen bonds, and double broken lines the C—O···π bonds. The symmetry codes are as in Table 2.

Experimental

The three complexes were prepared using the same general method. A solution of 4,4′-dipyridyl N,N'-dioxide hydrate (1 mmol) in ethanol was added to an aqueous solution containing Ln_2O_3 (1 mmol) and crotonic acid (6 mmol). The resulting mixture was refluxed for 24 h, filtered while hot and then concentrated to 25 ml. The filtrate was left at room temperature. On standing, crystals suitable for single-crystal X-ray diffraction appeared and were used without further processing.

Compound (I)

Crystal data

[Nd$_2$(C$_4$H$_5$O$_2$)$_6$(C$_{10}$H$_8$N$_2$O$_2$)-(H$_2$O)$_4$]·C$_{10}$H$_8$N$_2$O$_2$	$\beta = 70.535 (2)°$
	$\gamma = 68.632 (2)°$
$M_r = 1247.40$	$V = 1267.3 (2)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 9.3495 (10)$ Å	Mo $K\alpha$ radiation
$b = 12.0160 (13)$ Å	$\mu = 2.10$ mm^{-1}
$c = 12.8534 (14)$ Å	$T = 298 (2)$ K
$\alpha = 84.498 (2)°$	$0.21 \times 0.18 \times 0.13$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	10743 measured reflections
	5490 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	4882 reflections with $I > 2\sigma(I)$
$T_{min} = 0.64$, $T_{max} = 0.77$	$R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.081$	
$S = 0.86$	
5490 reflections	$\Delta\rho_{max} = 0.99$ e Å^{-3}
331 parameters	$\Delta\rho_{min} = -0.57$ e Å^{-3}
6 restraints	

Table 1
Selected bond lengths (Å) for (I).

Nd1—O31	2.377 (3)	Nd1—O11	2.528 (3)
Nd1—O2W	2.466 (3)	Nd1—O21	2.533 (3)
Nd1—O41	2.461 (2)	Nd1—O22	2.546 (3)
Nd1—O1W	2.471 (3)	Nd1—O12	2.671 (3)
Nd1—O12^i	2.480 (2)		

Symmetry code: (i) $-x + 2$, $-y + 2$, $-z + 1$.

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O2W—H2WA···O21^i	0.85 (4)	1.87 (4)	2.703 (4)	168 (4)
O1W—H1WB···O32	0.85 (4)	1.80 (4)	2.625 (5)	164 (4)
O1W—H1WA···O11^{ii}	0.85 (4)	1.94 (4)	2.779 (4)	172 (5)
O2W—H2WB···O51^{ii}	0.85 (4)	1.91 (4)	2.753 (4)	171 (4)

Symmetry codes: (i) $-x + 2$, $-y + 2$, $-z + 1$; (ii) $-x + 1$, $-y + 2$, $-z + 1$.

Compound (II)

Crystal data

[Er$_2$(C$_4$H$_5$O$_2$)$_6$(C$_{10}$H$_8$N$_2$O$_2$)-(H$_2$O)$_4$]·C$_{10}$H$_8$N$_2$O$_2$	$\beta = 71.181 (1)°$
	$\gamma = 69.099 (1)°$
$M_r = 1293.44$	$V = 1240.7 (2)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 9.1731 (9)$ Å	Mo $K\alpha$ radiation
$b = 12.0358 (12)$ Å	$\mu = 3.44$ mm^{-1}
$c = 12.7221 (13)$ Å	$T = 298 (2)$ K
$\alpha = 85.728 (2)°$	$0.18 \times 0.14 \times 0.12$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	9217 measured reflections
	5394 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	4772 reflections with $I > 2\sigma(I)$
$T_{min} = 0.56$, $T_{max} = 0.67$	$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.095$
$S = 1.06$
5394 reflections
331 parameters
6 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 1.09$ e Å^{-3}
$\Delta\rho_{min} = -1.61$ e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

Er1—O31	2.262 (4)	Er1—O11	2.387 (4)
Er1—O12^i	2.344 (3)	Er1—O21	2.423 (3)
Er1—O2W	2.350 (3)	Er1—O22	2.465 (3)
Er1—O41	2.361 (3)	Er1—O12	2.773 (4)
Er1—O1W	2.375 (3)		

Symmetry code: (i) $-x + 2, -y + 2, -z + 1$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2W—H2$WA\cdots$O21^i	0.85 (5)	1.88 (5)	2.703 (4)	164 (5)
O1W—H1$WB\cdots$O32	0.85 (5)	1.81 (5)	2.650 (6)	167 (5)
O1W—H1$WA\cdots$O11^{ii}	0.85 (5)	1.97 (5)	2.819 (5)	176 (5)
O2W—H2$WB\cdots$O51^{ii}	0.85 (5)	1.94 (5)	2.769 (5)	166 (5)

Symmetry codes: (i) $-x + 2, -y + 2, -z + 1$; (ii) $-x + 1, -y + 2, -z + 1$.

Compound (III)

Crystal data

[Y$_2$(C$_4$H$_5$O$_2$)$_6$(C$_{10}$H$_8$N$_2$O$_2$)-(H$_2$O)$_4$]·C$_{10}$H$_8$N$_2$O$_2$
$M_r = 1136.74$
Triclinic, $P\bar{1}$
$a = 9.1865$ (13) Å
$b = 12.0293$ (17) Å
$c = 12.7275$ (18) Å
$\alpha = 85.710$ (2)°

$\beta = 71.079$ (2)°
$\gamma = 69.175$ (2)°
$V = 1242.3$ (3) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 2.40$ mm^{-1}
$T = 298$ (2) K
$0.14 \times 0.14 \times 0.13$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.71$, $T_{max} = 0.74$

10592 measured reflections
5405 independent reflections
4364 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.117$
$S = 1.03$
5405 reflections
331 parameters
6 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.89$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 5
Selected bond lengths (Å) for (III).

Y1—O31	2.277 (2)	Y1—O11	2.399 (2)
Y1—O12^i	2.350 (2)	Y1—O21	2.429 (2)
Y1—O2W	2.360 (2)	Y1—O22	2.478 (2)
Y1—O41	2.368 (2)	Y1—O12	2.761 (3)
Y1—O1W	2.388 (2)		

Symmetry code: (i) $-x + 2, -y + 2, -z + 1$.

Table 6
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2W—H2$WA\cdots$O21^i	0.84 (3)	1.88 (3)	2.697 (3)	166 (3)
O1W—H1$WB\cdots$O32	0.85 (3)	1.81 (3)	2.639 (4)	167 (3)
O1W—H1$WA\cdots$O11^{ii}	0.85 (3)	1.96 (3)	2.806 (3)	173 (4)
O2W—H2$WB\cdots$O51^{ii}	0.84 (3)	1.94 (3)	2.762 (4)	166 (3)

Symmetry codes: (i) $-x + 2, -y + 2, -z + 1$; (ii) $-x + 1, -y + 2, -z + 1$.

Table 7
C31—O32$\cdots Cg2^{ii}$ contacts in all three title structures (Å, °).

Compound	O32$\cdots Cg2$	O32$\cdots Cg2$(perp)	Offset angle
(I)	4.033 (4)	3.631	25.7
(II)	3.864 (6)	3.521	24.35
(II)	3.871 (4)	3.529	24.28

Symmetry code: (ii) -x+1, -y+2, -z+1.

H atoms attached to carbon were placed at idealized positions (C—H = 0.96 Å for CH$_3$ and C—H = 0.93 Å for CH) and allowed to ride. Those corresponding to aqua ligands were found in difference maps and were refined with restrained O—H distances [0.85 (2) Å]. All H atoms were assigned U_{iso}(H) parameters of xU_{eq}(host), with $x = 1.2$, except for methyl H atoms for which $x = 1.5$.

For all compounds, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2001); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2001); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

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