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Triaquatris(*μ*-oxydiacetato)dipraseodymium(III) pentahydrate and hexaaquatris(*μ*-oxydiacetato)dineodymium(III) oxydiacetic acid solvate dihydrate

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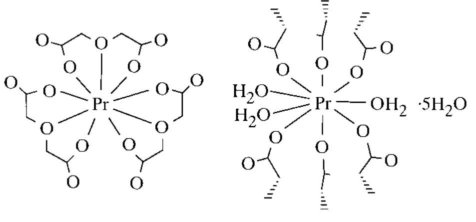
Two new complexes of the $Ln_2(oda)_3{\cdot}nH_2O$ (oda = $-O_2CCH_2OCH_2CO_2-$) series are reported, *i.e.* $\{[Pr_2(C_4H_4O_5)_3(H_2O)_3]{\cdot}5H_2O\}_n$ and $\{[Nd_2(C_4H_4O_5)_3(H_2O)_6]{\cdot}C_4H_6O_5{\cdot}2H_2O\}_n$. The former is isostructural with the reported La analogue, while the latter is a new structural variety within the series. Each compound exhibits two independent nine-coordinated Ln centres showing a variety of coordination geometries.

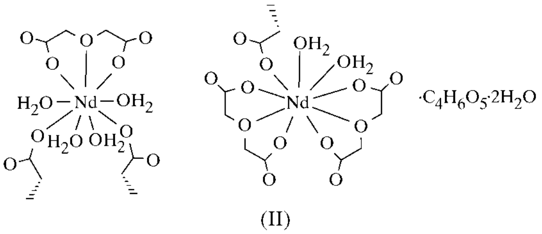
Comment

The self-assembly of lanthanide(III) metal centres with oxydiacetate ligands (oda = $-O_2CCH_2OCH_2CO_2-$) leads to a series of crystalline coordination solids formulated as $Ln_2(oda)_3{\cdot}nH_2O$ with an interesting variety of crystal-packing motifs. This is in accordance with the experience that the crystal structures of the lanthanide compounds frequently change along the series as a result of the lanthanide contraction. The crystals formed by the larger lanthanum $[La_2(C_4H_4O_5)_3(H_2O)_3{\cdot}5H_2O]_n$ are hexagonal ($P\bar{6}2c$; Baggio *et al.*, 1996) and present two nine-coordinated La centres; those for the intermediate gadolinium and europium compounds are orthorhombic (*Ama*2; Aramendia *et al.*, 2000), and present a mixture of nine- and eight-coordinated Ln centres, as is also the case for the smaller Er (Elding, 1977) and Y (Baggio *et al.*, 1998) analogues, which crystallize in the orthorhombic space group $C222_1$.

Focusing our attention primarily on the structural aspects of these extended polymeric 4*f* complexes, we report herein the preparation and structural characterization of the analogous compounds comprising praseodymium and neodymium, *i.e.* $\{[Pr_2(C_4H_4O_5)_3(H_2O)_3]{\cdot}5H_2O\}_n$, (I), and $\{[Nd_2(C_4H_4O_5)_3(H_2O)_6]{\cdot}2H_2O{\cdot}C_4H_6O_5\}_n$, (II).



(I)



(II)

Compound (I) is isostructural with the lanthanum polymer (Baggio *et al.*, 1996) and will not be described in too much detail here. Selected bond lengths and angles are listed in Table 1, and Fig. 1(*a*) gives a sketch of its coordination scheme. The two metal centres are highly symmetric, with Pr2 occupying a site *a* of local symmetry 32, and coordinated to three tridentate oda units, while Pr1, which occupies a site *d* of symmetry $\bar{6}$, receives six bonds from the outer carboxylate O atoms, as well as those from three aqua molecules. Both coordination polyhedra have the shape of tricapped trigonal prisms, the one around Pr2 being regular and the one centred at Pr1 displaying a rotation of *ca* 13° between opposite triangular faces. The fact that all the carboxylate as well as the ether O atoms take part in the connectivity to the cations leads to a tightly woven three-dimensional network, leaving only a few empty spaces, filled in turn by the (disordered) hydration water molecules, which attach to the main structure *via* hydrogen bonding (see Table 2 for short O···O contacts).

Compound (II) presents, instead, a novel disposition of the ligands not found before in any member of the series. Selected bond lengths and angles are listed in Table 3. As already stated, two independent Nd centres are present: Nd1 is bonded to two tridentate oda groups (oda1 and oda2) and to two water molecules (O1*W* and O2*W*). The ninth bond (O41) is provided by a [010] translationally related oda1 ligand, resulting in a linear polymeric chain along the short unique *b* axis.

As is often the case with lanthanide cations bound to three tridentate oda groups, or to two tridentate odas plus three extra monodentate units completing the ninefold environment (the present case), the Nd1 polyhedron displays a tricapped trigonal prismatic geometry. The three monodentate ligands (O1*W*, O2*W* and O41) adopt a planar configuration very much resembling that of the missing third oda unit. The resulting polyhedron is one with only slight modifications from the regular environment found in much more symmetric polyhedra [*e.g.* the one around Pr1 in (I)].

A completely different arrangement is found for Nd2, which is bonded to a single tridentate oxydiacetate group (oda3) and to six monodentate units, four of which are water molecules (O3*W* to O6*W*), and the remaining two, O atoms from bridging carboxylates. One of these is O43 from a neigbouring (also a [010] translationally related) oxydiacetate unit, again resulting in linear chains parallel to those already defined by the Nd1 polyhedra. The second, O42, is provided by these latter groups; the Nd—O42 bonds transversally link both types of linear arrays, acting as the rungs of a firmly connected ladder-like strip (Fig. 2).

The presence of a single tridentate and six monodentate ligands favours a less constrained environment around Nd2 in the form of a monocapped square antiprism in which O33 occupies the capping position, O13, O53, O4*W* and O5*W* are in the equatorial plane, and the remaining two water molecules plus the two remaining bridging carboxylate O atoms (O42 and O43) are in the basal plane. The largest distortion in the polyhedron is observed for the rather long Nd2—O3*W* distance [2.674 (9) Å]. The structure is completed by two non-coordinated water molecules (O7 and a triply disordered O8*W*) and an H_2oda neutral molecule. All of them, as well as the six coordinated water molecules, play an active role as hydrogen donors in a dense hydrogen-bonding network in which the O atoms from the coordinated oda groups act mainly as acceptors. Although the H atoms bonded to O atoms could not be reliably located, the hydrogen-bonding interaction scheme could be confidently guessed both from the shortest (<3.0 Å) O···O contacts (shown in Table 4) and from some significant structural details (*viz* C14—O24 and C44—O44 are sensibly longer than C14—O14 and C44—O54, respectively, at the same time that O24···O22 and O44···O51 are rather short). Charge-balance and IR data (see *Experimental*) required the presence of two OH groups in oda4; the preceding geometrical arguments, in turn, point almost unambiguously to the protonated character of O24 and O44.

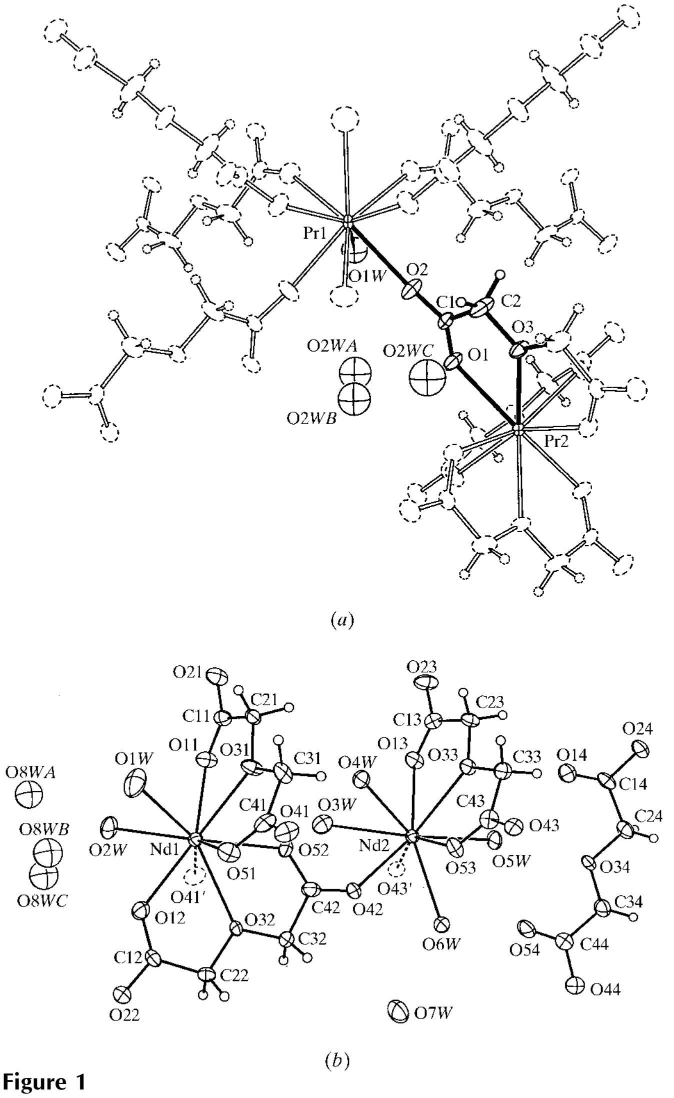


Figure 1
Molecular diagrams showing the atom numbering and coordination schemes of (*a*) compound (I) and (*b*) compound (II). Independent atoms are shown in full line and symmetry-related atoms in dotted lines. Displacement ellipsoids are drawn at the 40% probability level.

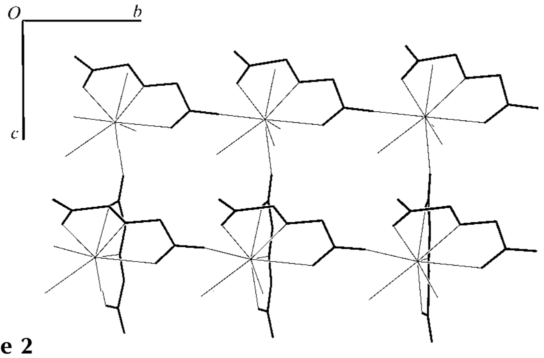


Figure 2
Schematic diagram along **a*** showing a ladder-like strip in (II) built up along the unique axis *b*.

Experimental

The reaction of Pr_2O_3 and Nd_2O_3 with excess oxydiacetic acid in water (1:7:100) and subsequent work-up afforded light-green crystals of (I) and light-blue crystals of (II) in good yields. The procedure has been described previously in detail (Baggio *et al.*, 1996). The IR spectra of the two compounds show significant changes in the COOH range. In fact, the IR spectrum of compound (II) shows the characteristic absorptions of the acyl carbonyl groups (1738–1683 cm^{-1}) in addition to the bands of the carboxylate anions (1597 and 1445 cm^{-1}) and water molecules (~1641 and ~3550–3400 cm^{-1}) also observed for compound (I). Thermogravimetric analyses (TGA) measurements show that both compounds lose almost exactly eight water molecules per formula unit well below 450 K.

All chemicals were of reagent grade purity and were used as received. Water was purified by a Millipore milli-Q system. Elemental analyses (C, H) were performed with a Carlo Erba EA 1108 analyser. IR spectra were recorded as KBr discs with a Nicolet 510P FT–IR spectrophotometer. Thermogravimetric analyses were recorded on a Shimadzu DTG50 thermal analyzer under an atmosphere of air at a heating rate of 5 K min^{-1}.

Compound (I)

Crystal data

$[Pr_2(C_4H_4O_5)_3(H_2O)_3]\cdot 5H_2O$
M_r = 822.16
Hexagonal, $P\bar{6}2c$
a = 9.4003 (12) Å
V = 1327.8 (4) Å^3
Z = 2
D_x = 2.06 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 7.5–12.5°
μ = 3.72 mm^{-1}
T = 293 (2) K
Prism, light green
0.35 × 0.15 × 0.14 mm

Data collection

Siemens $R3m$ diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*XEMP* in *SHELXTL*/*PC*; Sheldrick, 1994)
T_{min} = 0.35, T_{max} = 0.60
1693 measured reflections
490 independent reflections (plus 290 Friedel-related reflections)
738 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.01°
$h = -11 \rightarrow 0$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 20$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.059
S = 1.083
780 reflections
63 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 2.733P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max}$ = 0.94 e Å^{-3}
$\Delta\rho_{min}$ = −0.87 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.02 (4)

Table 1
Selected geometric parameters (Å) for (I).

Pr1—O2	2.444 (4)	Pr2—O3	2.552 (5)
Pr1—O1*W*	2.666 (7)	O1—C1	1.259 (7)
Pr2—O1	2.478 (4)	O2—C1	1.251 (7)

Table 2
Contact distances (Å) for (I).

O1···O2*WA*	2.99 (1)	O1*W*···O2*WA*^{i}	2.63 (2)
O1···O2*WB*	2.94 (2)	O1*W*···O2*WB*^{i}	2.96 (3)

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

Compound (II)

Crystal data

$[Nd(C_4H_4O_5)_3(H_2O)_6]\cdot C_4H_6O_5\cdot 2H_2O$
M_r = 962.91
Monoclinic, $P2_1/n$
a = 14.096 (2) Å
b = 6.844 (1) Å
c = 32.223 (3) Å
β = 99.59 (1)°
V = 3065.1 (6) Å^3
Z = 4
D_x = 2.09 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 7.5–15.0°
μ = 3.46 mm^{-1}
T = 293 (2) K
Plate, light blue
0.36 × 0.24 × 0.10 mm

Data collection

Siemens $R3m$ diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ-scan (*XEMP* in *SHELXTL*/*PC*; Sheldrick, 1994)
T_{min} = 0.38, T_{max} = 0.70
5674 measured reflections
5393 independent reflections
3568 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 25.00°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 8$
$l = -38 \rightarrow 37$
2 standard reflections every 98 reflections intensity decay: < 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.145
S = 1.03
5393 reflections
419 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 37.22P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.77 e Å^{-3}
$\Delta\rho_{min}$ = −0.89 e Å^{-3}

Table 3
Selected geometric parameters (Å) for (II).

Nd1—O12	2.412 (7)	Nd2—O3*W*	2.674 (9)
Nd1—O41^{i}	2.445 (8)	O11—C11	1.260 (13)
Nd1—O52	2.448 (7)	O21—C11	1.246 (13)
Nd1—O11	2.457 (7)	O41—C41	1.239 (14)
Nd1—O1*W*	2.462 (9)	O51—C41	1.280 (14)
Nd1—O32	2.531 (7)	O12—C12	1.253 (12)
Nd1—O51	2.557 (8)	O22—C12	1.256 (12)
Nd1—O2*W*	2.566 (8)	O42—C42	1.233 (13)
Nd1—O31	2.575 (7)	O52—C42	1.276 (13)
Nd2—O43^{i}	2.426 (7)	O13—C13	1.264 (13)
Nd2—O42	2.455 (7)	O23—C13	1.240 (13)
Nd2—O13	2.463 (7)	O43—C43	1.262 (13)
Nd2—O5*W*	2.464 (7)	O53—C43	1.257 (13)
Nd2—O53	2.485 (8)	O14—C14	1.208 (14)
Nd2—O4*W*	2.485 (8)	O24—C14	1.322 (13)
Nd2—O6*W*	2.555 (7)	O44—C44	1.298 (14)
Nd2—O33	2.568 (7)	O54—C44	1.200 (14)

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

Table 4
Contact distances (Å) for (II).

O1*W*···O23^{i}	2.61 (1)	O4*W*···O52	2.76 (1)
O1*W*···O8*WA*	2.70 (3)	O5*W*···O14	2.79 (1)
O2*W*···O41^{ii}	2.83 (1)	O5*W*···O34	2.90 (1)
O2*W*···O23^{iii}	2.75 (1)	O5*W*···O54	2.72 (1)
O2*W*···O8*WA*	2.89 (3)	O6*W*···O43^{ii}	2.99 (1)
O2*W*···O8*WC*^{iv}	2.81 (2)	O6*W*···O7*W*	2.74 (1)
O3*W*···O21^{iii}	2.73 (1)	O7*W*···O53^{v}	2.91 (1)
O3*W*···O43^{ii}	2.79 (1)	O8*WA*···O22^{iv}	2.74 (2)
O3*W*···O52	2.90 (1)	O24···O22^{vi}	2.55 (1)
O4*W*···O21^{i}	2.61 (1)	O44···O51^{v}	2.59 (1)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $x, y - 1, z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $-x, 1 - y, -z$; (v) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.

In both structures, some hydration water molecules appeared split over a number of sites of lower occupancy, thus making it difficult to assess their correct total number from the X-ray data alone. They were accordingly refined with adjustable populations constrained to add up to the value given by the thermogravimetric analysis, and a unique common isotropic displacement factor. As the H atoms could not be found in the difference Fourier synthesis, only those attached to carbon were included in idealized positions, and refined using a riding scheme, both in coordinates as in displacement factors.

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For both compounds, data collection: *P*3/*P*4-*PC* (Siemens, 1991); cell refinement: *P*3/*P*4-*PC*; data reduction: *XDISK* in *SHELXTL*/*PC* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*/*PC*; software used to prepare material for publication: *CIFTAB* (Sheldrick, 1993), *PARST* (Nardelli, 1983) and CSD (Allen *et al.*, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1511). Services for accessing these data are described at the back of the journal.

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