

Poly[[tetra- $\mu_3$ -acetato-hexa- $\mu_2$ -acetato-diaqua- $\mu_2$ -oxalato-tetra-praseodymium(III)] dihydrate]Karin Gutkowski,<sup>a,‡</sup> Eleonora Freire<sup>b,c,\*‡</sup> and Ricardo Baggio<sup>b,\*</sup><sup>a</sup>Gerencia de Química, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Argentina, <sup>b</sup>Gerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, and <sup>c</sup>Escuela de Ciencia y Tecnología, Universidad Nacional General San Martín, Buenos Aires, Argentina

Correspondence e-mail: freire@tandar.cnea.gov.ar, baggio@cnea.gov.ar

Received 1 February 2011

Accepted 14 February 2011

Online 18 February 2011

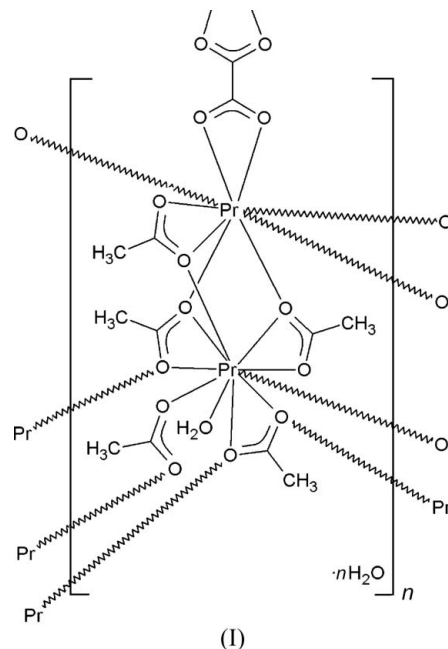
The title complex,  $\{[\text{Pr}_4(\text{C}_2\text{H}_3\text{O}_2)_{10}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}\}_n$ , was synthesized under hydrothermal conditions from praseodymium acetate and the ionic liquid 1-butyl-3-methylimidazolium chloride *via* an *in situ* oxalate-ligand synthesis. The compound is a two-dimensional polymer and in the structure presents tightly bound planes parallel to (100), which are in turn linked into a three-dimensional network by hydrogen bonds involving both coordinated and solvent water molecules. The oxalate anion lies across an inversion centre and acts as a bridge between pairs of Pr atoms within a tetranuclear segment of the polymer.

## Comment

Lanthanides are characterized by a high affinity for ligands with hard donor atoms such as O and/or N (Brunet *et al.*, 2007). The compounds thus formed may possess unique photophysical and magnetic properties that make them suitable for applications in advanced materials (Steckl & Zavada, 1999; de Sa *et al.*, 2000; Kido & Okamoto, 2002). The construction of extended structures containing praseodymium or other *f*-elements bridged by carboxylate groups is of interest because of the large variety of architectures that result from the high and variable coordination numbers of the lanthanides, as well as the versatility of carboxylate ligands.

Ionic liquids (ILs) are a group of ionic compounds having a broad temperature range at which they remain liquid, combined with very low vapour pressures, and they have been proposed as potential replacements for conventional organic solvents. ILs are generally composed of an organic cation (such as imidazolium, pyridinium or pyrrolidinium) and an

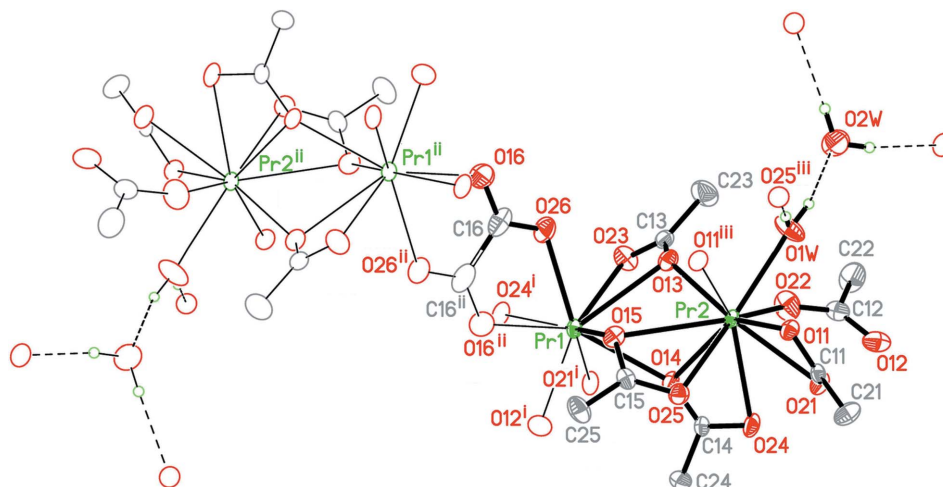
anion (such  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{Cl}^-$ , *etc.*); they have been shown to act both as solvents and as reactants which may be incorporated into the final reaction product (for instance, behaving as a charge neutralizer; Cocalia *et al.*, 2006). The use of ILs in the *in situ* synthesis of ligands in coordination compounds has increased in the last few years, along with efforts to elucidate the mechanisms of the reactions involved (Reichert *et al.*, 2006).



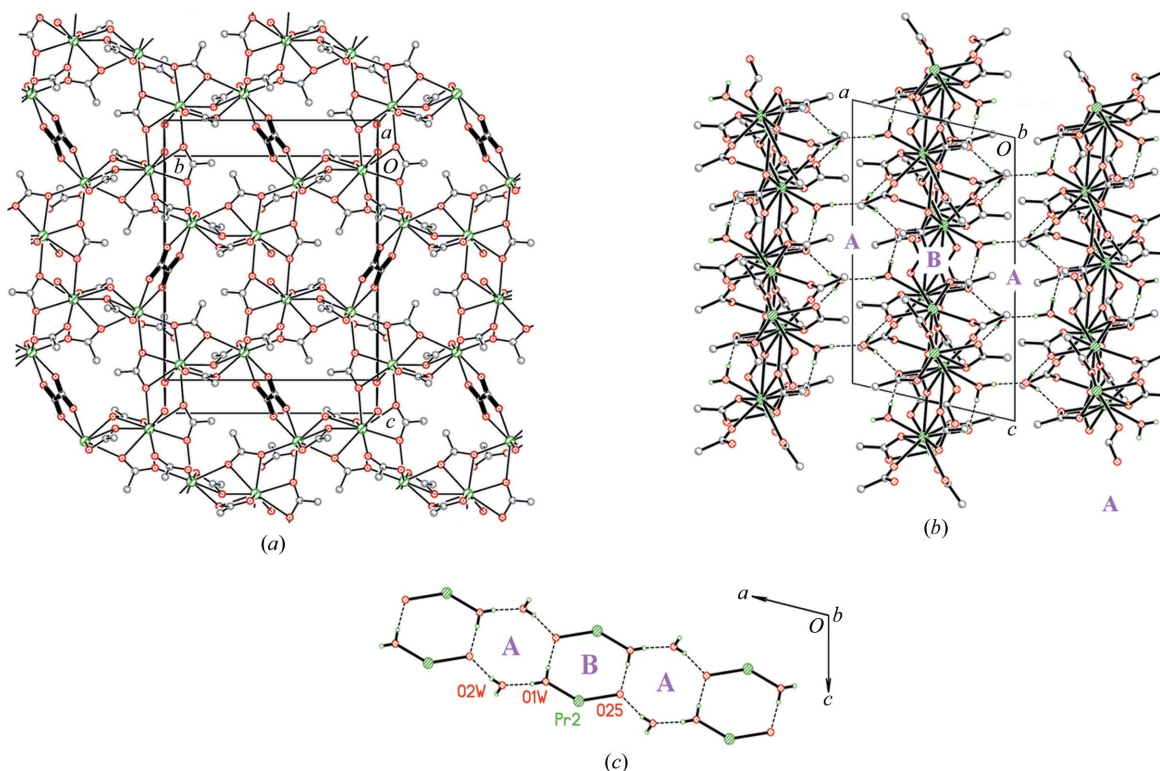
Reported herein is the two-dimensional polymer poly[[tetra- $\mu_3$ -acetato-hexa- $\mu_2$ -acetato-diaqua- $\mu_2$ -oxalato-tetra-praseodymium(III)] dihydrate], (I), obtained under hydrothermal conditions *via* praseodymium acetate and the IL 1-butyl-3-methylimidazolium (bmim) chloride. Fig. 1 shows a view of a tetranuclear segment of the polymeric structure of (I), where each ligand is identified by a unique trailing number, *viz.* acetates 1–5 and oxalate 6.

A tetranuclear segment of the polymeric structure lies across an inversion centre located at the centre of the bridging oxalate ligand, so that the asymmetric unit is composed of two  $\text{Pr}^{\text{III}}$  cations, one water ligand, five acetate anions and half of an oxalate anion; a solvent water molecule completes the asymmetric unit. The two symmetry-independent  $\text{Pr}^{\text{III}}$  cations (Pr1 and Pr2) are each coordinated by O atoms from six different acetate anions, in each case involving all five of the symmetry-independent anions. The oxalate anion coordinates only to Pr1 and the water ligand only to Pr2. As a result, the metal cations present different  $\text{PrO}_9$  (Pr1) and  $\text{PrO}_{10}$  (Pr2) environments (Table 1), with Pr–O distances in the range 2.417 (3)–2.698 (3) Å for Pr1 and 2.388 (3)–2.786 (3) Å for Pr2, and bond-valence sums of 3.33 and 3.22, respectively. The five acetate ligands, in turn, bind in three different bridging modes: as  $\mu_2\text{-}\kappa^2\text{O}:\text{O}'$  (simple bridge, acetate 2), as  $\mu_2\text{-}\kappa^3\text{O}:\text{O}':\text{O}'$  (simple bridge–simple chelate, acetates 3 and 5) and as  $\mu_3\text{-}\kappa^4\text{O}:\text{O}:\text{O}':\text{O}'$  (double bridge–simple chelate, acetates 1

<sup>‡</sup> Member of the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).


**Figure 1**

A tetranuclear fragment of (I), with displacement ellipsoids drawn at the 50% probability level, showing both Pr coordination polyhedra and the bridging mode of the oxalate ion, which sits across an inversion centre. Dashed lines show the way in which water molecules are involved in hydrogen bonding. [Symmetry codes: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + 1, -y + 1, -z + 2$ ; (iii)  $-x + 1, -y + 2, -z + 2$ .]


**Figure 2**

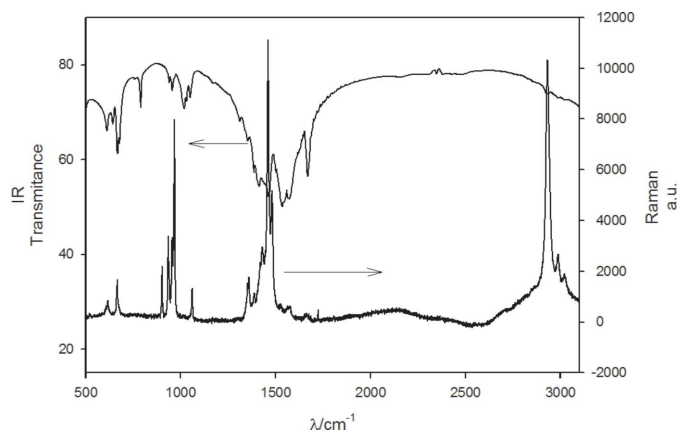
(a) The packing in (I), showing the two-dimensional structure parallel to (100). For clarity, no solvent molecules or H atoms are shown. (b) A projection of the layers shown in (a), at right angles to the former view, as well as their interaction *via* hydrogen bonding (dashed lines). Note the hydrogen-bonding loops formed, *viz.* an  $R_6^4(12)$  ring (denoted **A**) and an  $R_2^2(8)$  ring (denoted **B**). (c) A detailed view of the chain of hydrogen-bonded rings described in (b) shown in the same orientation.

and 4). The oxalate anion, as usual, binds in a  $\mu_2$ - $\kappa^4 O^1, O^{1'}:O^2, O^{2'}$  (simple bridge–double chelate) mode.

This intricate bonding scheme results in a tight two-dimensional mesh of interlinked Pr<sup>III</sup> coordination polyhedra, with the metals joined by a variety of ‘short’ (Pr–O–Pr) and ‘long’ (Pr–O–C–O–Pr) bridges to give Pr $\cdots$ Pr distances of 4.0618 (3) Å (Pr1 $\cdots$ Pr2, three short bridges), 4.2224 (3)

(Pr1 $\cdots$ Pr2<sup>i</sup>, two short bridges), 6.4045 (3) Å (Pr1 $\cdots$ Pr1<sup>ii</sup>, two long oxalate bridges) and 4.4995 (3) Å (Pr2 $\cdots$ Pr2<sup>iii</sup>, two short bridges) [symmetry codes: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + 1, -y + 1, -z + 2$ ; (iii)  $-x + 1, -y + 2, -z + 2$ ].

Fig. 2(a) shows a view of one such mesh, parallel to (100). It can be seen that the cations, water ligands and acetate anions generate an infinite layer (represented by light lines) with



**Figure 3**  
The Raman (lower line) and IR (upper line) spectra of (I).

large centrosymmetric ‘holes’ in it, where the oxalate anions (heavy lines) lie, linking symmetry-related Pr1 centres together. These strongly connected planar structures are further stabilized by a strong ‘intraplanar’ hydrogen bond (Table 2, first entry), while being linked to each other *via* the other three ‘interplanar’ hydrogen bonds (Table 2, entries 2–4). Figs. 2(a) and 2(b) depict these hydrogen bonds in full detail, while Fig. 2(c) sketches the way in which they operate in the interplanar linkage, through a rather simple chain made out of ‘conjugated’ hydrogen-bonded rings (**A** and **B**) threading through a line of inversion centres across the planes. The rings, characterized by graph-set descriptors (Bernstein *et al.*, 1995)  $R_6^4(12)$  (ring **A**) and  $R_2^2(8)$  (ring **B**), are formed by just four non-H atoms (O1W, O2W, Pr2 and O25; Fig. 2c).

Fig. 3 shows the IR and Raman spectra of (I), in the range 500–3000  $\text{cm}^{-1}$ , in which the oxalate and acetate bands can be observed. The peaks are assigned according to previously reported data (Frost, 2004; Ito & Bernstein, 1956). The range 1500–1400  $\text{cm}^{-1}$  in the Raman spectrum shows the bands associated with double bonds, *i.e.* C=O stretching of both acetate and oxalate. The antisymmetric C=O stretching extends to 1700  $\text{cm}^{-1}$  in the IR spectrum. The bands between 1100 and 500  $\text{cm}^{-1}$  correspond to C–C stretching. The acetate can be distinguished from the oxalate group in the range 3100–2900  $\text{cm}^{-1}$ , in which only the CH stretching vibrations of the acetate are seen.

As a final remark, it should be stated that the reaction responsible for the presence of the oxalate bridge in the final product is not yet fully understood. This situation is by no means unique; *in situ* oxalate-anion formation under hydrothermal conditions has already been reported, and has been related to the rearrangement or cleavage of organic compounds (Knope & Cahill, 2007; Zhang *et al.*, 2006). However, the mechanisms that lead to oxalate-bridge formation remain to be understood.

## Experimental

Compound (I) was synthesized from an aqueous solution of praseodymium acetate (41 mg) and sodium acetate (13 mg) in a 1:1.5

**Table 1**  
Selected bond lengths ( $\text{\AA}$ ).

Pr1—O12 <sup>i</sup>	2.417 (3)	Pr2—O13	2.428 (2)
Pr1—O24 <sup>i</sup>	2.463 (2)	Pr2—O1W	2.469 (3)
Pr1—O26	2.476 (3)	Pr2—O11 <sup>iii</sup>	2.513 (2)
Pr1—O16 <sup>ii</sup>	2.483 (3)	Pr2—O25	2.555 (3)
Pr1—O23	2.504 (3)	Pr2—O21	2.590 (2)
Pr1—O15	2.496 (2)	Pr2—O14	2.606 (2)
Pr1—O14	2.526 (2)	Pr2—O11	2.711 (2)
Pr1—O21 <sup>i</sup>	2.554 (2)	Pr2—O24	2.747 (3)
Pr1—O13	2.698 (3)	Pr2—O15	2.786 (3)
Pr2—O22	2.388 (3)		

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

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1WA...O25 <sup>iii</sup>	0.85 (3)	1.98 (3)	2.823 (4)	172 (5)
O1W—H1WB...O2W	0.84 (3)	1.82 (2)	2.664 (4)	174 (4)
O2W—H2WA...O23 <sup>iv</sup>	0.84 (3)	1.91 (3)	2.751 (4)	171 (5)
O2W—H2WB...O25 <sup>v</sup>	0.85 (3)	2.08 (3)	2.920 (4)	173 (5)

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

ratio, in the presence of the ionic liquid 1-butyl-3-methylimidazolium chloride (3:1 water–IL ratio). Crystals of (I) were grown in a 45 ml Teflon-lined autoclave under hydrothermal conditions over a period of a few days at 400 K and after slow cooling.

### Crystal data

$[\text{Pr}_4(\text{C}_2\text{H}_3\text{O}_2)_{10}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	$\beta = 103.085 (3)^\circ$
$M_r = 1314.16$	$V = 1908.45 (10) \text{\AA}^3$
Monoclinic, $P2_1/c$	$Z = 2$
$a = 9.3772 (3) \text{\AA}$	Mo $K\alpha$ radiation
$b = 13.1249 (3) \text{\AA}$	$\mu = 5.11 \text{ mm}^{-1}$
$c = 15.9198 (5) \text{\AA}$	$T = 291 \text{ K}$
	$0.22 \times 0.18 \times 0.12 \text{ mm}$

### Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer	14838 measured reflections
Absorption correction: multi-scan ( <i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	4526 independent reflections
$T_{\min} = 0.33, T_{\max} = 0.54$	3935 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.056$	$\Delta\rho_{\max} = 1.07 \text{ e \AA}^{-3}$
$S = 1.03$	$\Delta\rho_{\min} = -0.90 \text{ e \AA}^{-3}$
4526 reflections	
256 parameters	
6 restraints	

Water H atoms were refined with restrained distances [O—H = 0.85 (1)  $\text{\AA}$  and H...H = 1.36 (1)  $\text{\AA}$ ]. Methyl groups were idealized (C—H = 0.96  $\text{\AA}$ ) and allowed to ride. In all cases, H-atom displacement parameters were taken as  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl groups or  $1.2U_{\text{eq}}(\text{C}, \text{O})$  otherwise.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008);

molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

The authors acknowledge the Spanish Research Council (CSIC) for providing a free-of-charge licence to the Cambridge Structural Database (Allen, 2002). We are also grateful to Beatriz Halac for the measurement of the Raman spectra and to Mireille Perec for a careful reading of the manuscript.

---

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3378). Services for accessing these data are described at the back of the journal.

---

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Brunet, E., Juanes, O. & Rodriguez-Urbis, J. C. (2007). *Curr. Chem. Biol.* **1**, 11–39.
- Cocalia, V. A., Gutowski, K. E. & Rogers, R. D. (2006). *Coord. Chem. Rev.* **250**, 755–764.
- Frost, R. L. (2004). *Anal. Chim. Acta*, **517**, 207–214.
- Ito, K. & Bernstein, H. J. (1956). *Can. J. Chem.* **34**, 170–178.
- Kido, J. & Okamoto, Y. (2002). *Chem. Rev.* **102**, 2357–2368.
- Knope, K. E. & Cahill, C. L. (2007). *Inorg. Chem.* **46**, 6607–6612.
- Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Reichert, W. M., Holbrey, J. D., Vigour, K. B., Morgan, T. D., Broker, G. A. & Rogers, R. D. (2006). *Chem. Commun.* pp. 4767–4779.
- Sa, G. F. de, Malta, O. L., Donega, C. D., Simas, A. M., Longo, R. L., Santa-Cruz, P. A. & da Silva, E. F. (2000). *Coord. Chem. Rev.* **196**, 165–195.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Steckl, A. J. & Zavada, J. M. (1999). *Mater. Res. Bull.* **24**, 33–38.
- Zhang, J.-P., Lin, Y.-Y., Huang, X.-C. & Chen, X.-M. (2006). *Eur. J. Inorg. Chem.* pp. 3407–3412.