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2,2′-Bipyridyl-2-ium aqua(2,2′-bipyridyl-κ^2N,N')-tetakis(nitrato-κ^2O,O')praseodymium(III) 2,2′-bipyridyl hemisolvate

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Key indicators

Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.005 Å
R factor = 0.029
wR factor = 0.067
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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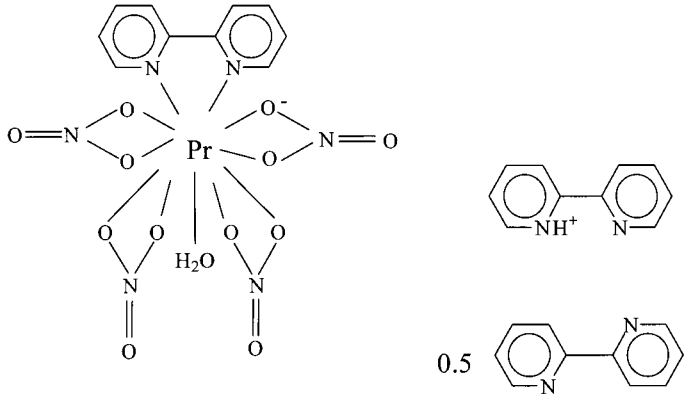
The Pr atom in the title complex, $(C_{10}H_9N_2)[Pr(NO_3)_4(C_{10}H_8N_2)(H_2O)]\cdot 0.5C_{10}H_8N_2$, is 11-coordinated. Hydrogen bonds between the coordinated water molecule, the uncoordinated 2,2′-bipyridylium [$(HBipy)^+$] and the centrosymmetric 2,2′-bipyridyl (Bipy) solvent molecules link the structural components into layers parallel to the *ab* plane.

Comment

The title compound, $(HBipy)[Pr(NO_3)_4(Bipy)(H_2O)]\cdot 0.5Bipy$ (Bipy is 2,2′-bipyridyl), (I), is a new complex characterized by a high coordination number of Pr. The Pr atom is eleven-coordinated (Fig. 1). The 2,2′-bipyridyl solvent molecules lie on crystallographic inversion centers.



(I)

Among the Bipy complexes of lanthanides, the coordination number of 11 has been found only for $[La(NO_3)_3(Bipy)(H_3COH)(H_2O)_2]\cdot C_{10}H_{20}O_5$, (II) (Zhen & Rogers, 1994). Four nitrate anions in the $[Pr(NO_3)_4(Bipy)(H_2O)]^-$ complex anion of (I) are coordinated in bidentate mode. One of the Pr—O(nitrate) bonds is significantly elongated [2.752 (2) Å] in comparison to the seven others [average 2.612 (2) Å]. A similar elongation of one of the La—O(nitrate) bonds was found also in the neutral $[La(NO_3)_3(Bipy)(H_3COH)(H_2O)_2]$ complex of (II) (Zhen & Rogers, 1994). Several types of hydrogen bonds, Ow—H···O(nitrate), Ow—H···N(Bipy) and N(Bipy)—H···O(nitrate) link all the structural components of (I). Each $(HBipy)^+$ cation acts as proton donor to form a hydrogen bond with a coordinated nitrate anion. The coordinated water molecule forms two hydrogen bonds. The first is with a terminal atom of one nitrate anion of a neighboring complex; two such bonds form a centrosymmetric dimeric complex (Fig. 2). The second is with a solvent Bipy molecule. Each solvent Bipy molecule has two hydrogen

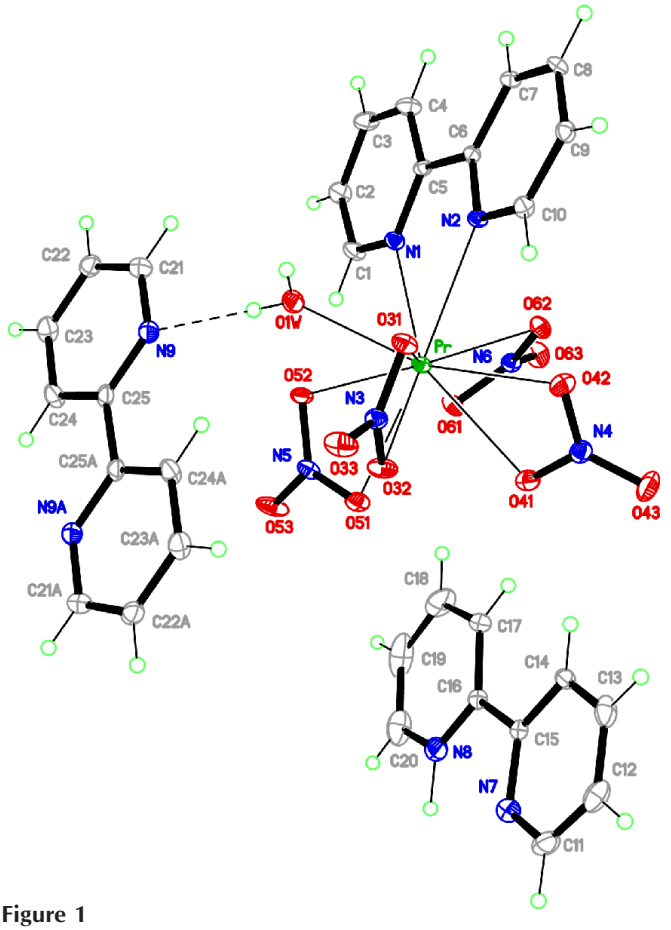


Figure 1
*ORTEP*III/*ORTEP*-3 (Burnett & Johnson, 1996; Farrugia, 1997) view of (I), showing 30% probability displacement ellipsoids. The dashed line indicates a hydrogen bond.

bonds of this type, linking the dimers into infinite chains. The chains form layers parallel to the *ab* plane (Fig. 2).

Experimental

The crystals were obtained by slow evaporation at 293 K of a xylenol solution (1 ml) containing $Pr(NO_3)_3{\cdot}6H_2O$ (0.05 mol) and Bipy (the Pr^{3+}–Bipy molar ratio is 1:1).

Crystal data

$(C_{10}H_9N_2)[Pr(NO_3)_4(C_{10}H_8N_2)(H_2O)]{\cdot}0.5C_{10}H_8N_2$
M_r = 798.43
Monoclinic, $C2/c$
a = 17.7935 (4) Å
b = 10.2712 (3) Å
c = 32.8924 (8) Å
β = 100.0016 (11)°
V = 5920.1 (3) Å^3
Z = 8
D_x = 1.792 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 166 reflections
θ = 2–27.5°
μ = 1.73 mm^{-1}
T = 130 (2) K
Prism, green
0.36 × 0.22 × 0.18 mm

Data collection

Nonius KappaCCD diffractometer
φ–ω scans
Absorption correction: multi-scan (*MULABS*; Blessing, 1995)
T_{min} = 0.638, T_{max} = 0.732
15166 measured reflections
5632 independent reflections
5000 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 27.5°
$h = -21 \rightarrow 21$
$k = -13 \rightarrow 12$
$l = -33 \rightarrow 42$

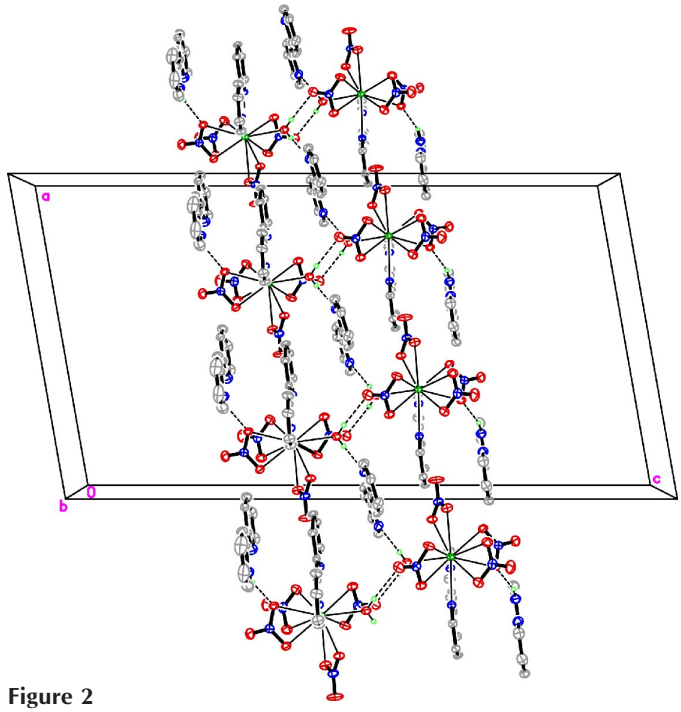


Figure 2
CAMERON (Watkin *et al.*, 1993) view of the packing of (I), showing the hydrogen-bonding interactions as dashed lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.067
S = 1.13
5632 reflections
442 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0144P)^2 + 13.7668P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.64 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N8—H8···O62^{i}	1.07 (4)	2.03 (4)	3.028 (4)	155 (3)
O1W—H12···N9	0.75 (4)	2.00 (4)	2.751 (3)	177 (4)
O1W—H11···O33^{ii}	0.73 (4)	2.09 (4)	2.809 (3)	171 (4)

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

All H atoms on carbon were positioned geometrically (C—H = 0.93 Å) and refined using the riding model [U_{iso}(H) = 1.2U_{eq}(C)]. H atoms of the water molecule were located in difference Fourier maps and refined with U_{iso}(H) = 1.5U_{eq}(O). The H atom on nitrogen was refined with a fixed displacement parameter [U_{iso}(H) = 1.2U_{eq}(N)].

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *HKL* (Otwinowski & Minor, 1997); data reduction: *HKL*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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