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# Surface-grafted lanthanoid complexes of the tungstosilicate polyanion $[SiW_{12}O_{40}]^{4-}$: a synthetic, structural and computational investigation

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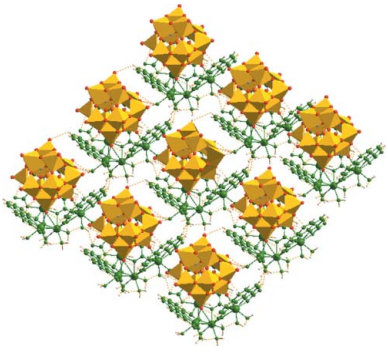
**Supporting information**: this article has supporting information at journals.iucr.org/c

As an extension of our continued interest in the preparation of inorganic–organic hybrids, we report the successful hydrothermal synthesis of sodium tris[triaqua($\mu$-1,10-phenanthroline-2,9-dicarboxylato)dysprosium(III)] silicododecatungstate dodecahydrate, $\{[DyNa(C_{14}H_6N_2O_4)_3(H_2O)_9(SiW_{12}O_{40})]\cdot 12H_2O\}_n$ or $Na[Dy(PDA)(H_2O)_3]_3[SiW_{12}O_{40}]\cdot 12H_2O$ (**1**), and sodium aqua tris[tetraaqua($\mu$-4-hydroxypyridine-2,6-dicarboxylato)praseodymium(III)] silicododecatungstate dodecahydrate, $\{[NaPr(C_7H_3NO_5)_3(H_2O)_{13}(SiW_{12}O_{40})]\cdot 12H_2O\}_n$ or $Na(H_2O)[Pr(pydc\text{-}OH)(H_2O)_4]_3[SiW_{12}O_{40}]\cdot 12H_2O$ (**2**) (in which $H_2PDA$ is 1,10-phenanthroline-2,9-dicarboxylic acid and $H_2pydc\text{-}OH$ is 4-hydroxypyridine-2,6-dicarboxylic acid or chelidamic acid). Both compounds have been characterized using elemental analysis, IR spectroscopy and X-ray diffraction methods. Structural characterization by single-crystal X-ray diffraction reveals that these compounds consist of $[SiW_{12}O_{40}]^{4-}$ Keggin-type polyoxometalates (POMs), where a single $\{W_3O_{13}\}$ triad is decorated with a trinuclear Ln complex. Moreover, the decorated polyanions are involved in a series of intermolecular interactions, such as hydrogen bonds and anion–$\pi$ interactions, resulting in three-dimensional supramolecular architectures. Density functional theory (DFT) studies were conducted to support these intermolecular interactions in both **1** and **2**, and have been rationalized using molecular electrostatic potential (MEP) surface calculations.

## 1. Introduction

Based on an analysis of the Cambridge Structural Database (CSD; Groom *et al.*, 2016), ligand preorganization means that a ligand undergoes a specific coordination mode in complexation reactions under different conditions. By following the above-mentioned definition, a particular coordination mode can be anticipated (Najafi *et al.*, 2016). This improves the ability of the ligand to complex a given metal due to the chelate effect and other entropic considerations (Glushko *et al.*, 2017). According to the Hancock definition, for an efficient preorganized ligand, the configurational and conformational flexibilities need to be reduced (Carolan *et al.*, 2013). Complexation of a variety of metal ions by preorganized ligands results in improved thermodynamic stability and high ion selectivity leading to biomedical (Sessler *et al.*, 2005; Longin *et al.*, 2017), biological (Bencini *et al.*, 2002; Zhang *et al.*, 2017) and environmental applications like metal-ion separation and the development of sensors for metal ions (Burdette & Lippard, 2001). Significant preorganization provides thermodynamic stability to the complexes and



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greater selectivity for metal ions. Selectivity for one metal ion over another is measured as the difference in log $K_1$, as is commonly used in environmental research and metal-ion separation (Hancock *et al.*, 2007).

Phenanthroline ligands with donor groups at the 2- and 9-positions, *i.e.* alcohols, amides, carboxylates and oximes (PDOX) (Hancock, 2013), are well-known examples of preorganized ligands. Some metal-ion complexing properties of PDOX have been reported (Boone *et al.*, 2011; Miao *et al.*, 2011). Complexes of PDOX with small metal ions like zinc(II) present tridentate coordination, with one oximate group remaining uncoordinated (Fig. S3 of the supporting information). In contrast, with larger ions like lead(II), PDOX acts as a tetradentate ligand. In the PDOX complexes, one proton is retained on the oxime group at lower pH. For the smaller metal ions, where one oxime group of PDOX is not coordinated, this noncoordinated oxime has a p$K_a$ value quite close to that of the free ligand (*i.e.* 10.55) (see Fig. 1) (Boone, 2006). The initial interest in PDOX was due to the fact that it has four N-atom donors to potentially bind metal ions, thus likely leading to enhanced selectivity for $Ln^{III}$ ions. Unfortunately, it was found that PDOX decomposes slowly to PDA over a period of a few days at low pH, which ruled out its use as the functional group of a solvent extractant (Boone, 2006). 1,10-Phenanthroline-2,9-dicarboxylic acid (PDA) exhibits selectivity for larger metal ions using these principles of ligand design. Formation constants, *i.e.* log $K_1$ values, for large metal ions were shown to be substantially higher for the preorganized structure of PDA, compared to the nonpreorganized analog of PDA (Melton, 2005). Furthermore, PDA displays strong size-based selectivity, owing to the formation of three rigid five-membered chelate rings upon complex formation. More precisely, PDA provides a fixed distance between the two potentially coordinating O-atom donors of the carboxylate groups (4.8 Å), which requires large metal ions to fit into this cavity (Bencini & Lippolis, 2010; Ogden *et al.*, 2013; Williams *et al.*, 2009). Classification of the coordination modes found for PDA ligands in the CSD have been gathered (in Fig. S4 in the supporting information). Identification of the possible coordination modes of PDA in all currently reported crystal structures (45 compounds) allows classification into 13 different modes (denoted I–XIII, see Fig. S4 in the supporting information). The structures of PDA complexes with lanthanoid ions exemplify how a metal ion with an appropriate size can bind to all four donor atoms of the pocket, with $M$—N and $M$—O bond lengths in the expected ranges. In addition, if comparatively small ions are present (for instance, mode IV), two $M$—O bonds are formed at the expense of an elongation of the $M$—N bonds (Alipour *et al.*, 2016).

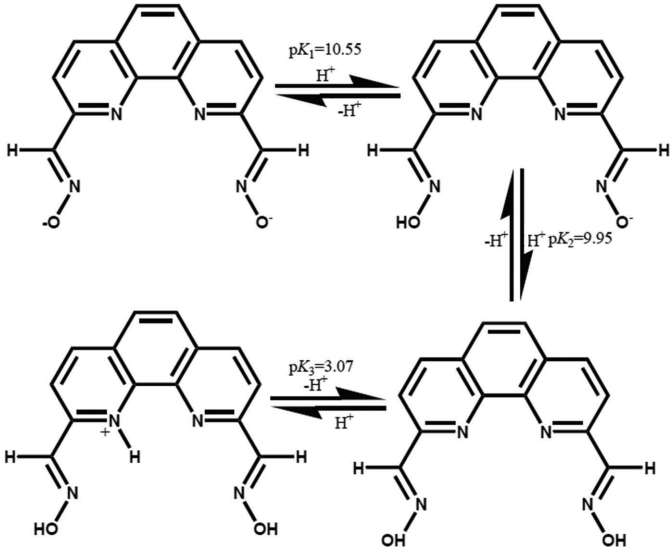


**Figure 1**
A diagram showing the three protonation events of PDOX (Boone, 2006).

The design and synthesis of inorganic–organic hybrid materials containing polyoxometalates (POMs) have attracted considerable attention in recent years (Mirzaei, Eshtiagh-Hosseini, Alipour *et al.*, 2014; Taleghani *et al.*, 2016; Richie *et al.*, 2018) because of their intriguing architectures and properties (Spillane *et al.*, 2017), as well as their potential applications in catalysis (Liu, 2016), magnetism (Clemente-Juan *et al.*, 2012; Wang *et al.*, 2018), sequestration of radioactive elements (Dong *et al.*, 2017), electro/photochromic systems (Sha *et al.*, 2017), macromolecular crystallography and medicine (Wang *et al.*, 2014; Xie *et al.*, 2018; Xu *et al.*, 2018). Furthermore, Keggin-type POMs have been mostly employed due to their size suitability and structural stability. The roles of Keggin-type POMs in hybrid compounds can be divided into two types: type 1 are structures with covalent bonds between Keggin and metal–organic complexes (MOCs) in which the polyanion behaves as a mono- or polydentate inorganic ligand through its nucleophilic terminal and bridging O atoms, and type 2 are structures with noncovalent interactions between Keggin and MOCs where the polyanion is a charge-balancing anion (Mirzaei, Eshtiagh-Hosseini, Alipour *et al.*, 2014).

POMs themselves can form one- to three-dimensional polymeric structures (Mandic *et al.*, 2013; Ritchie *et al.*, 2008; Streb *et al.*, 2007), while their hybrids can be either covalent POM-based MOFs or supramolecular MOFs (SMOFs). The organic ligand (flexible or rigid), the POM charge and the oxidation state of the metal affect the hybrid structure (Alipour *et al.*, 2016; Mirzaei, Eshtiagh-Hosseini, Alipour *et al.*, 2015; Najafi *et al.*, 2016). Moreover, the reaction conditions, such as temperature, time, pH, solvothermal, reflux, *etc.*, are also very important for the final architecture of either MOFs or SMOFs.

Our group has previously used organic ligands like 4-hydroxypyridine-2,6-dicarboxylic acid ($H_2$pydc-OH) and 1,10-phenanthroline-2,9-dicarboxylic acid (PDA) to study the structural variations of POM-based MOFs (Fig. S2 in the supporting information) (Najafi & Mirzaei, 2017; Alipour *et al.*, 2016; Lotfian *et al.*, 2014; Mirzaei, Eshtiagh-Hosseini, Lotfian *et al.*, 2014). In this article, we report the synthesis of two inorganic–organic hybrid materials based on Keggin-type tungstosilicates using these ligands; these are $\{Na[Dy(PDA)(H_2O)_3]_3\}[SiW_{12}O_{40}]\cdot 12H_2O$ (**1**) and $\{Na(H_2O)[Pr(pydc–OH)(H_2O)_4]_3\}[SiW_{12}O_{40}]\cdot 12H_2O$ (**2**). In both com-


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**Table 1**
Experimental details.

| | (**1**) | (**2**) |
|---|---|---|
| Crystal data | | |
| Chemical formula | $[DyNa(C_{14}H_6N_2O_4)_3(H_2O)_9(SiW_{12}O_{40})]\cdot 12H_2O$ | $[NaPr(C_7H_3NO_5)_3(H_2O)_{13}(SiW_{12}O_{40})]\cdot 12H_2O$ |
| $M_r$ | 4527.40 | 4307.67 |
| Crystal system, space group | Trigonal, *R*3 | Trigonal, *R*3 |
| Temperature (K) | 130 | 100 |
| *a*, *c* (Å) | 20.3334 (3), 18.7836 (3) | 18.119 (3), 21.078 (3) |
| *V* (Å$^3$) | 6725.60 (19) | 5993 (2) |
| *Z* | 3 | 3 |
| Radiation type | Cu *Kα* | Mo *Kα* |
| $\mu$ (mm$^{-1}$) | 41.93 | 19.14 |
| Crystal size (mm) | 0.07 × 0.05 × 0.03 | 0.24 × 0.13 × 0.12 |
| Data collection | | |
| Diffractometer | Agilent SuperNova Dual Source diffractometer with an Atlas detector | Bruker SMART APEX CCD |
| Absorption correction | Gaussian (*CrysAlis PRO*; Rigaku OD, 2015) | Multi-scan (*TWINABS*; Sheldrick, 2009) |
| $T_{min}$, $T_{max}$ | 0.097, 0.369 | 0.09, 0.22 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 16672, 5475, 5450 | 74256, 7142, 6106 |
| $R_{int}$ | 0.030 | 0.085 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.632 | 0.686 |
| Refinement | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.036, 0.098, 1.02 | 0.030, 0.065, 1.00 |
| No. of reflections | 5475 | 7142 |
| No. of parameters | 426 | 385 |
| No. of restraints | 1 | 241 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.53, −1.89 | 1.97, −2.07 |
| Absolute structure | Classical Flack method preferred over Parsons because s.u. lower | Flack *x* determined using 2688 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013) |
| Absolute structure parameter | 0.013 (7) | 0.006 (7) |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2016), *CELL_NOW* (Sheldrick, 2008), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *SHELXL2018* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Bruker, 2016).

pounds, the lanthanoid metal centre bears a high coordination number (CN = 7–9) and the $[SiW_{12}O_{40}]^{4-}$ anion participates in anion–$\pi$ noncovalent interactions that have been studied using density functional theory (DFT) calculations and rationalized by means of the calculation of the molecular electrostatic potential (MEP) surfaces of the complexed ligands.

## 2. Experimental

### 2.1. Materials and methods

All commercially available chemicals were of reagent grade and were used without further purification, except for 1,10-phenanthroline-2,9-dicarbaldehyde dioxime ($H_2$phendox or PDOX), which was synthesized according to a reported procedure (Fig. S1 in the supporting information) (Angeloff *et al.*, 2000; Chandler *et al.*, 1981). IR spectra were recorded from KBr pellets in the 4000–400 cm$^{-1}$ region using a Buck 500 IR spectrometer. Elemental analysis (CHN) was performed using a Thermo Finning Flash-1112EA microanalyzer.

### 2.2. Synthesis and crystallization

**2.2.1. Synthesis of (1).** A mixture of $H_4[SiW_{12}O_{40}]$ (144 mg, 0.05 mmol), $Dy(NO_3)_3\cdot 6H_2O$ (43.5 mg, 0.125 mmol), PDOX (33.5 mg, 0.125 mmol) and deionized water/ethanol (5:1 *v*/*v*, 12 ml) was stirred in air for 30 min. $NH_4VO_3$ (11 mg, 0.1 mmol) was then added and the solution was stirred for an extra 30 min. Finally, the pH was adjusted to 3.5 with aqueous NaOH (1 *M*) solution. The mixture was transferred into a Teflon-lined autoclave and kept at 403 K for 3 d. After slow cooling for 2 d, the solution was filtered off and crystals were obtained by slow evaporation of the filtrate over a period of a few weeks. Pale-yellow blade-like crystals of **1** were obtained in 58% yield (based on W). Analysis calculated for $C_{42}H_{18}Dy_3N_6NaO_{61}SiW_{12}$: C 11.65, H 0.42, N 1.94%; found: C 10.92, H 0.47, N 2.11%. IR (KBr pellet, cm$^{-1}$): 3423, 1613, 1568, 1468, 1388, 1307, 967, 914, 789, 712.

**2.2.2. Synthesis of (2).** A mixture of $Pr(NO_3)_3\cdot 6H_2O$ (65 mg, 0.2 mmol), $H_2$pydc-OH (25 mg, 0.15 mmol) and $H_4[SiW_{12}O_{40}]$ (107 mg, 0.05 mmol) in distilled water (10 ml) was stirred for half an hour at room temperature in air. The pH was adjusted to a value of 3 using NaOH (1 *M*) and the resulting mixture stirred for another half an hour. The mixture was sealed in a 23 ml Teflon-lined reactor. The reactor was heated at 403 K for 96 h and then cooled to room temperature at a rate of 5 K h$^{-1}$. Green cubic crystals of **2** were obtained in 61% yield (based on W). Analysis calculated for $C_{21}H_{35}N_3NaO_{68}Pr_3SiW_{12}$: C 6.15, H 0.85, N 1.03%; found: C 6.08, H 0.91, N 1.01%. IR (KBr pellet, cm$^{-1}$): 3429, 1602, 1432, 1389, 1342, 1229, 1121, 1025, 975, 922, 882, 798.


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### 2.3. IR spectroscopy

The IR spectra of compounds **1** and **2** are very similar. The presence of $[SiW_{12}O_{40}]^{4-}$ Keggin-type anions is confirmed by the characteristic vibration patterns in the region with wavenumbers lower than 1000 $cm^{-1}$. Four bands are attributed to $\nu(Si-O_a)$, $\nu(W{=}O_t)$, $\nu(W-O_b)$ and $\nu(W-O_c)$ stretching vibrations which appear at averages of 922, 975, 882 and 798 $cm^{-1}$, respectively (where $O_t$ is a terminal oxygen, $O_b$ is a bridging oxygen, $O_a$ is an internal oxygen and $O_c$ is a bridging oxygen within the edge-sharing octahedra) (Rocchiccioli-Deltcheff *et al.*, 1983; Thouvenot *et al.*, 1984). Compared with the typical parent anion in $H_4[\alpha\text{-}SiW_{12}O_{40}]$, the vibrational frequencies related to the terminal oxide groups ($W{=}O_t$) are red shifted by 15 $cm^{-1}$. This shows that the terminal O atoms ($O_t$) are most affected by coordination to the lanthanoid centres. Moreover, the vibrational band associated with the $\nu(W-O_c)$ stretching vibration is split into two bands because of the lowered symmetry of the Keggin anion in both compounds.

**2.3.1. For 1.** The characteristic pattern in the region from 1000 to 1600 $cm^{-1}$ is attributed to the coordinated PDA ligands. The absence of $\nu(C{=}O)$ stretching vibrations at around 1700–1720 $cm^{-1}$ demonstrates the complete deprotonation of the carboxylic acid groups in the PDA ligands. Strong asymmetric and symmetric stretching frequencies for the carboxylate groups appear at 1613 and 1388 $cm^{-1}$, respectively. The bands resulting from the vibrations of the aromatic skeleton also appear in the 1468 $cm^{-1}$ region. The band centred at 3423 $cm^{-1}$ is attributed to the $\nu(OH)$ vibration of the lattice and coordinated water molecules (Fig. S5*a* in the supporting information).

**2.3.2. For 2.** The IR spectrum of **2** is consistent with its structural characteristics. The band at about 1229 $cm^{-1}$ is assigned to the noncoordinated hydroxy group of pydc-OH. However, the symmetric and asymmetric stretching vibrations of the carboxylic acid fragments lie at about 1400 and 1600 $cm^{-1}$. Finally, the broad band around 3400 $cm^{-1}$ is assigned to the water molecules and other hydrogen-bonding interactions (Fig. S5*b* in the supporting information) (Mirzaei, Eshtiagh-Hosseini, Bolouri *et al.*, 2015).

### 2.4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For **1**, all non-H atoms were refined anisotropically, with the exception of the fractionally occupied solvent water molecules, which were refined isotropically. For **2**, H atoms were included as riding contributions in idealized positions or in positions to generate favourable hydrogen bonding as much as possible (this proved impossible for three lattice water molecules). The crystal used for **2** was twinned. Details of the detection of the twinning and the subsequent data reduction and refinement can be found in the _exptl_section_special_details and _refine_special_details sections of the CIF in the supporting information.

### 2.5. Theoretical methods

The energies of the complexes studied herein were computed at the BP86-D3/def2-TZVP level of theory using the

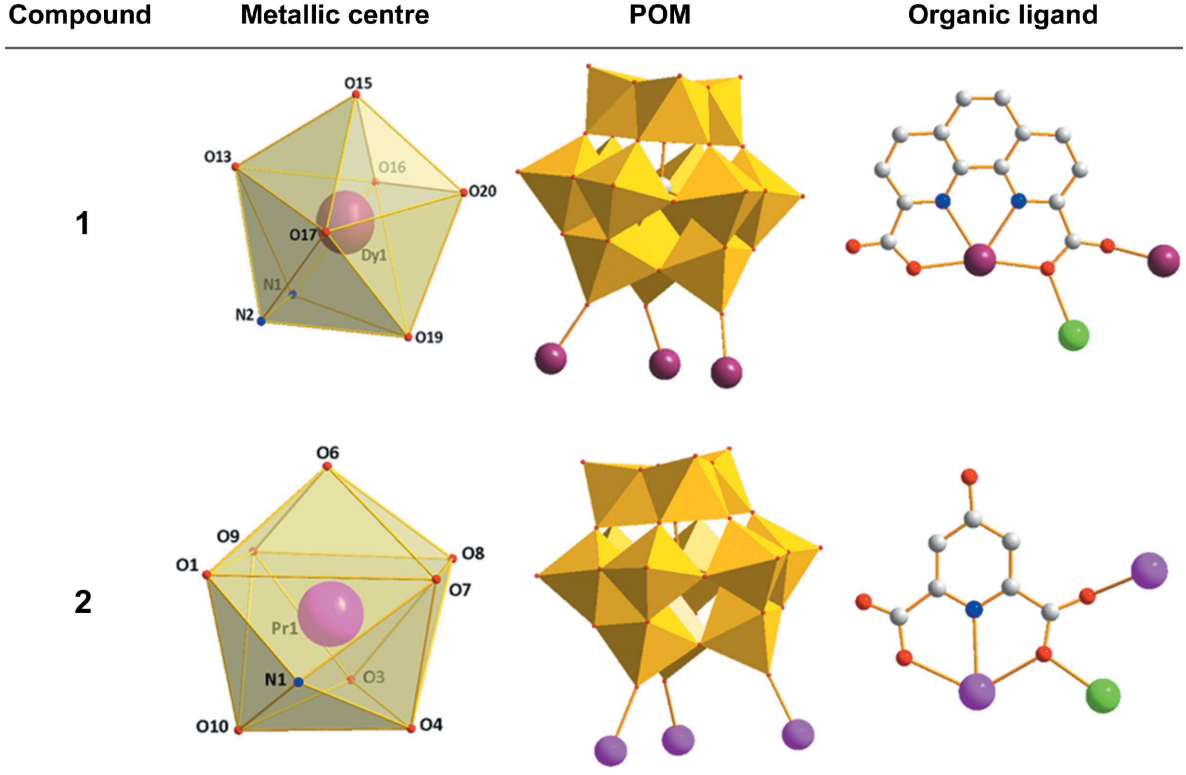


**Figure 2**
The coordination modes of the lanthanoid, POM and organic ligand in hybrids **1** and **2**.


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**Table 2**
Selected bond lengths (Å) for **1** and **2**.

| Compound **1** | | Compound **2** | |
|---|---|---|---|
| Dy1—O15$^{i}$ | 2.306 (10) | Pr1—O1 | 2.407 (11) |
| Dy1—O13 | 2.375 (11) | Pr1—O3$^{ii}$ | 2.468 (10) |
| Dy1—O17 | 2.329 (11) | Pr1—O2$^{ii}$ | 2.477 (11) |
| Dy1—O20 | 2.379 (13) | Pr1—O6 | 2.496 (13) |
| Dy1—O16 | 2.374 (11) | Pr1—O9 | 2.509 (12) |
| Dy1—N1 | 2.469 (13) | Pr1—O10 | 2.554 (9) |
| Dy1—N2 | 2.482 (14) | Pr1—N1$^{ii}$ | 2.567 (12) |
| Dy1—O19 | 2.364 (12) | Pr1—O8 | 2.567 (11) |
| | | Pr1—O7 | 2.593 (12) |

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

crystallographic coordinates. For the W, Pr and Dy atoms, the def2-SVP basis set was used within the *TURBOMOLE7.0* package (Ahlrichs *et al.*, 1989). For the calculations, we used the BP86 functional with the latest available correction for dispersion (D3) (Grimme *et al.*, 2010). The MEP analysis (Shao *et al.*, 2006) was performed using the *GAUSSIAN09* program (Frisch *et al.*, 2009) with the LAN2DZ basis set for the transition metal atom and 6-31+G* for the other atoms.

## 3. Results and discussion

### 3.1. Synthesis

The successful syntheses of compounds **1** and **2** were achieved by the hydrothermal reaction of lanthanoid salts, organic ligands and $H_4SiW_{12}O_{40}\cdot xH_2O$ as inorganic ligands. Moreover, the two main factors in synthesizing hybrid structures, *i.e.* pH and temperature, in this specific reaction were adjusted to about 3–3.5 and 403 K, respectively. The resultant crystals are insoluble in deionized water or common organic solvents. The mixture was stirred in air for 30 min. $NH_4VO_3$ was then added and the solution was stirred for an extra 30 min for compound **1** (Gao *et al.*, 2010; Sha, Peng, Tian *et al.*, 2007; Han *et al.*, 2010). Finally, the pH was adjusted to approximately 3 with aqueous NaOH solution. The mixture was transferred to a Teflon-lined autoclave and kept at 403 K for 3 d. After slow cooling for about 2 d, the solution was filtered off and crystals were obtained by slow evaporation of the filtrate over a period of a few months. It was found that PDOX decomposed slowly to PDA after a few days at low pH.

### 3.2. Crystal description

**3.2.1. For 1.** Compound **1** possesses a crystallographic $C_3$ axis and crystallizes in the chiral trigonal space group $R3$ with a Flack parameter of 0.013 (7) (Table 1). Thus, only a third of the molecule is in the asymmetric unit. The symmetry-generated lanthanoid-decorated polyanion observed in compound **1** is composed of a cationic sodium-templated PDA-ligated dysprosium trimer, $\{Na[Dy(PDA)(H_2O)_3]_3\}^{4+}$, attached to the terminal O-atom ligands of a single $\{W_3O_{13}\}$ triad belonging to a $[SiW_{12}O_{40}]^{4-}$ polyoxoanion (Fig. S8 in the supporting information). The $[SiW_{12}O_{40}]^{4-}$ polyoxoanion exhibits the $\alpha$-Keggin structure, in which the central $\{SiO_4\}$ tetrahedron is surrounded by four vertices sharing $\{W_3O_{13}\}$ trimers. All W atoms have a $\{WO_6\}$ octahedral environment and, according to the kind of O atom bonded to the W atoms, the W—O bond lengths are divided into three groups. The W—$O_c$ bond lengths ($O_c$ is an edge-shared O atom) are the longest [2.296 (10)–2.356 (9) Å], the W—$O_b$ bond lengths ($O_b$ is a corner-shared O atom) are intermediate [1.974 (11)–1.853 (10) Å] and the W—$O_t$ bond lengths ($O_t$ is a terminal O atom) are the shortest [1.689 (11)–1.716 (10) Å]. The Si—O

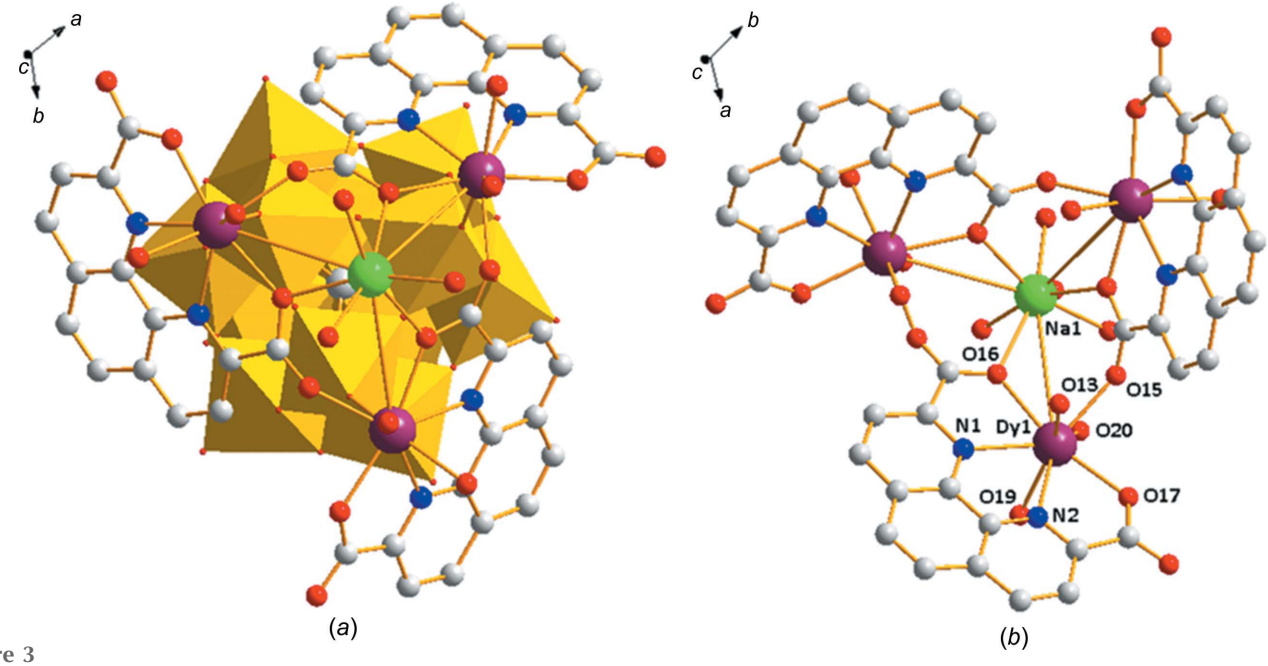


**Figure 3**
(*a*) A view of the molecular structure of **1**. (*b*) The structure of the trinuclear dysprosium cluster. Interstitial water molecules and H atoms have been omitted for clarity. Colour code: Dy purple, O red, W yellow, Na green, N blue and C grey.


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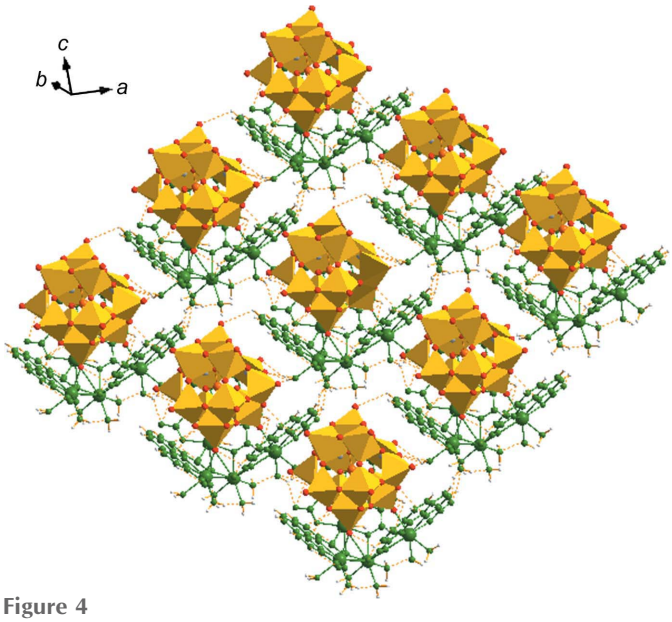


**Figure 4**
A view of the 3D supramolecular structure in **1**.

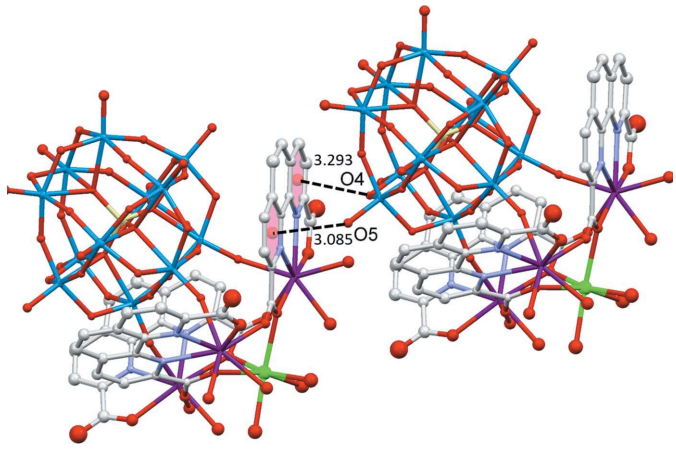


**Figure 5**
A partial view of the crystal packing of compound **1**, showing the intermolecular anion–$\pi$ interactions (in Å) established between the organic ligand and atom O5 of the Keggin ion.

bond lengths are in the range 1.615 (19)–1.633 (10) Å (Table S2 in the supporting information). All W—O and the central Si—O distances correspond to those in the literature (Howell *et al.*, 2001). As shown in Fig. 2, the $[SiW_{12}O_{40}]^{4-}$ anion can be viewed as a tridentate inorganic ligand that bonds to three ions through terminal O atoms to generate a trinuclear dysprosium cluster. An interesting structural feature is that all the coordinating O atoms belong to a corner-sharing $\{W_3O_{13}\}$ triad, thereby resulting in a discrete molecule. To the best of our knowledge, this uncommon coordination pattern of a Keggin-type polyoxoanion is still relatively rare (Sha, Peng, Liu *et al.*, 2007).

A view of the dysprosium cluster is presented in Fig. 3. In **1**, the presence of a $C_3$ axis requires the Dy centres to be crystallographically equivalent. Each Dy ion is eight-coordinated and exhibits a dodecahedral geometry (Fig. 2), namely, three carboxylate O atoms from two PDA ligands [Dy—O(carboxylate) = 2.306 (10)–2.375 (11) Å], two N atoms of phen rings [Dy—N(phen) = 2.469 (13) and 2.482 (14) Å], one terminal O atom from the $W_{12}$ subunit [Dy—O(POM) = 2.38 (11) Å] and two water molecules [Dy—O(water) = 2.364 (12)–2.379 (13) Å]. As shown in Table 2, the variation in the Dy—O bond lengths consists of the following sequence: Dy—O(POM) > Dy—O(water) > Dy—O(ligand), which indicates that the electron-donating ability of O atoms is in the order O(ligand) > O(water) > O(POM), and that the Dy—O(ligand) bonds are more stable than the Dy—O(POM) or Dy—O(water) bonds. In the coordination configuration of $Dy^{3+}$, the O15, O16, O17 and O20 atoms, and the O13, O19, N1 and N2 atoms define two square faces of the dodecahedron, with an angle of 4.14° between the two planes. The distances of the Dy1 centre from the two planes are 1.111 and 1.323 Å, respectively. These data indicate that the geometry of the $Dy^{3+}$ dodecahedra is distorted. Interestingly, the sodium ions are found trapped at the centre of the trinuclear Dy cluster, are located on the $C_3$-symmetry axis and lie below the $Dy_3$ plane by 1.916 Å. Although heterometallic structures based on 3*d*–4*f* assemblies are often encountered, such a network based on 4*f* metal and main-group elements is really infrequent (Shen *et al.*, 2004). Furthermore, as can be seen in Fig. 3(*b*), this central sodium ion is rarely three-coordinated by three $\mu_3$-O atoms of carboxylate groups of three ligands. It should be noted that each PDA in **1** acts as both a chelating and a bridging ligand and binds three cations (two equivalent $Dy^{3+}$ and one $Na^+$) in a pentadentate fashion. The unique asymmetric coordination mode of the ligand is shown in Fig. 2, in which one carboxylate group adopts a bidentate coordination mode coordinating to two $Dy^{3+}$ ions, whereas the other carboxylate group behaves as a $\mu_3$-linker with the O16 atom bridging $Dy^{3+}$ and $Na^+$, and the O15 atom connecting to another $Dy^{3+}$ ion (Fig. 3*b*). In the packing arrangement, the anion–$\pi$ interactions and hydrogen bonds connect the discrete molecules into a 3D supramolecular framework (Fig. 4).

As shown in Fig. 5, the bridging O5 and O4 atoms of the Keggin moieties are oriented toward the $\pi$ face of one of the phen rings of a neighbouring unit. The distances between the O5 and O4 atoms and the centroid of the phen rings are 3.085 and 3.295 Å, respectively, which are in the range of typical anion–$\pi$ contacts and thus a clear indication of binding (Frontera, 2013). This interaction can be also viewed as a lone pair (lp)–$\pi$ interaction in which one free lone pair of bridging O5 and O4 atoms points toward the $\pi$-face of the phen system that is coordinated to the metal thus enhancing its $\pi$ acidity. Fig. 4 shows how the terminal O atoms of Keggin and the carboxylate groups of organic ligands from one molecular unit interact with the O atoms of the coordinated water from neighbouring units through hydrogen bonds to form a 3D flower-like supramolecular network. The lattice water molecules reside as guests in the interstices of the 3D supramolecular framework through extensive hydrogen-bonding interactions. All of these contacts make the crystal structure more stable. The Ln—O and Ln—N bond lengths in the crystals of **1** and **2** are given in Table 2.


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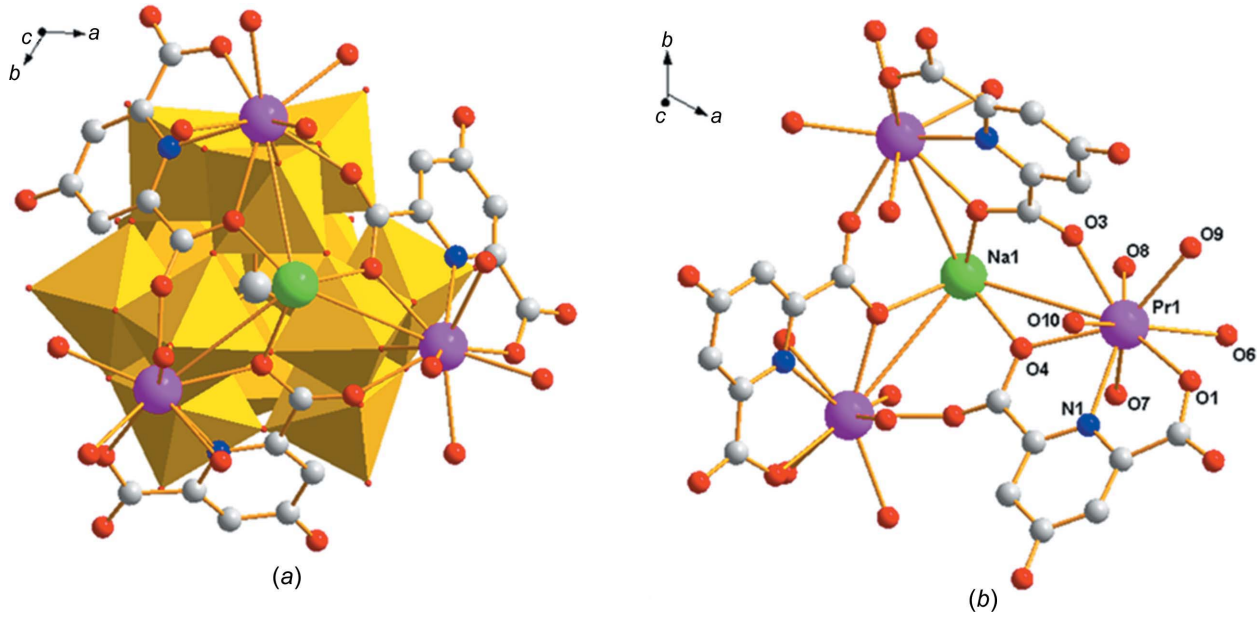


**Figure 6**
(*a*) A view of the molecular structure of **2**. (*b*) The structure of the trinuclear praseodymium cluster. Interstitial water molecules and H atoms have been omitted for clarity. Colour code: Pr magenta, O red, W yellow, Na green, N blue and C grey.

**3.2.2. For 2.** Compound **2** is a three-dimensional superstructure in which every discrete fragment consists of a chiral *R*3 (trigonal system) aggregation of POM and lanthanoid–organic coordinated species. Five free water molecules also exist within the lattice (Fig. 6). The metal–organic moiety is an ordered triangular structure of Pr complexes. The coordination environment of Pr1 is ninefold and consists of one N atom from the pyridine ring of the organic ligand (N1), three O atoms (O1, O3 and O4) from the carboxylate groups of the pydc-OH ligands, one terminal O10 atom of $\{SiW_{12}O_{40}\}$ and finally four terminal aqua ligands (O7*W*, O8*W*, O9*W* and O10*W*), exhibiting a monocapped square-antiprismatic geometry (Fig. 2). The polyhedron around the Pr1 centre is defined by the atom groups O3/O4/O10/N1 and O1/O7/O8/O9, where the dihedral angle between these two mean planes is 6.63° and atom O6 is the cap. The bond lengths Pr1—N, Pr1—O(pydc-OH), Pr1—O($SiW_{12}$) and Pr1—O*W* are 2.567 (12), 2.407 (11)–2.477 (11), 2.554 (9) and 2.496 (13)–2.593 (12) Å, respectively. The organic ligand is pentadentate and behaves as a bridging and chelating ligand simultaneously. Moreover, the inorganic $\{SiW_{12}O_{40}\}$ ligand exhibits typical $\alpha$-Keggin structural features. The Si—O bond lengths are 1.629 (9)–1.633 (16) Å and the O—Si—O angles are similar [108.9 (4) and 110.0 (4)°], thereby indicating that the $SiO_4$ unit is nearly a regular tetrahedron. Each $\{W_3O_{13}\}$ group is composed of three $\{WO_6\}$ octahedra linked in a triangular arrangement by sharing edges. The W—O bond lengths fall into four types because there are four different types of O atoms, defined as terminal ($O_t$), terminal linked to praseodymium ($O_{t'}$), corner-shared ($O_b$) and edge-shared ($O_c$); the W—$O_t$, W—$O_{t'}$, W—$O_b$ and W—$O_c$ distances are 1.693 (10)–1.714 (10), 1.724 (9), 1.864 (10)–1.927 (10) and 2.32 (8)–2.367 (9) Å, respectively. The W—O and Si—O distances in this compound are comparable to reported values (Rocchiccioli-Deltcheff *et al.*, 1983; Thouvenot *et al.*, 1984). Besides the POM structure, it should be mentioned that it is a symmetric ligand and covalently bonds three Pr fragments *via* O10—Pr bonds with a length of 2.554 (9) Å. The $C_3$ symmetry axis specifically makes the Pr complexes crystallographically equivalent. Nonetheless, the H atoms were not determined accurately, as described in the *Refinement* section (§2.4), so a discussion of the details of intermolecular interactions is not feasible.

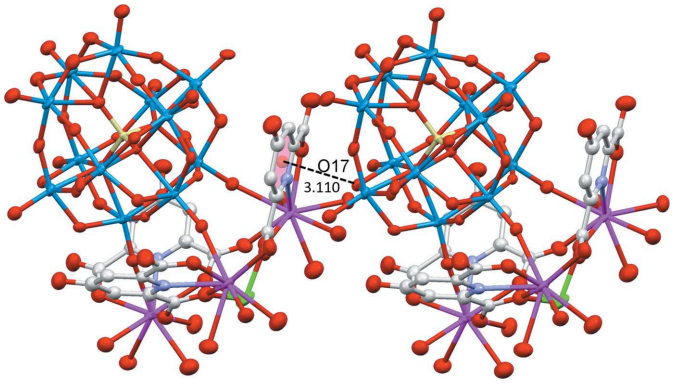


**Figure 7**
A partial view of the crystal packing of compound **2**, showing the intermolecular lone pair–$\pi$ interactions (in Å) established between the organic ligand and atom O17 of the Keggin ion.

### 3.3. DFT theoretical study

We have focused our theoretical study on an analysis of the remarkable anion–$\pi$ interactions observed in the crystal packing of the hybrid inorganic–organic POMs highlighted in Figs. 5 and 7. First of all, we computed the molecular elec-


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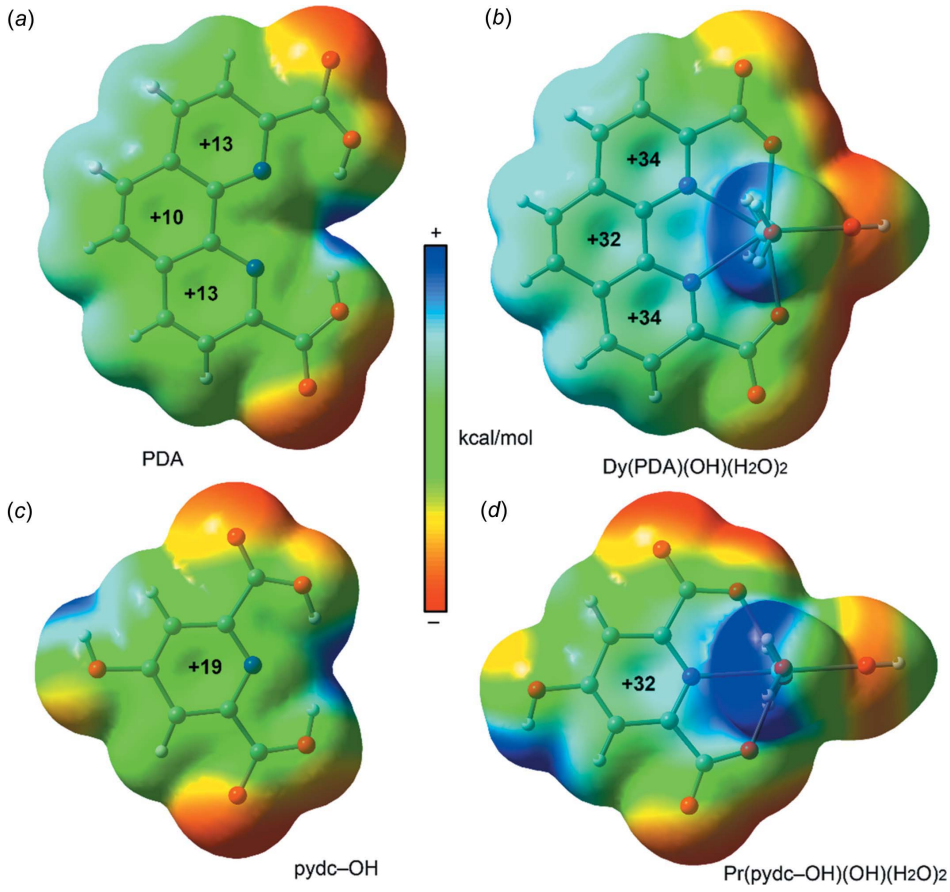


**Figure 8**
MEP plotted onto the van der Waals surfaces of (*a*) PDA, (*b*) Dy(PDA)(OH)($H_2O$)$_2$, (*c*) pydc-OH and (*d*) Pr(pydc-OH)(OH)($H_2O$)$_2$. The MEP values over the centres of the rings are given in kcal mol$^{-1}$.

trostatic potential (MEP) surfaces plotted onto the van der Waals surfaces of the ligands and also the ligands coordinated to the lanthanoids Pr and Dy in order to examine the effect of the metal coordination on the $\pi$-acidity of the ligands. For this preliminary study, we have used simple Pr and Dy neutral complexes with PDA and pydc-OH organic ligands, water molecules and the $OH^-$ co-ligand as counter-ion (see Fig. 8). Remarkably, both free ligands present small and positive MEP values over the ring centre, indicating that the rings are electron deficient due to the presence of the electron-withdrawing carboxylate groups and the N atoms. Interestingly, the $\pi$-acidity of the rings increases considerably upon coordination of the metal centres. Both complexes exhibit similar MEP values (34 kcal mol$^{-1}$; 1 kcal mol$^{-1}$ = 4.184 kJ mol$^{-1}$); however, PDA presents a more extended $\pi$-system suitable for interaction with electron-rich atoms.

A study of the energetic features of the anion–$\pi$ interactions observed in both compounds requires high-level DFT calculations. Therefore, we have used several theoretical models of the X-ray structures, which are shown in Fig. 9, in order to keep the size of the system computationally approachable. We are particularly interested in the anion–$\pi$ interactions between the POM and the organic ligand, and also the contribution of the Dy/Pr-coordinated water molecules to the binding energy of the supramolecular assembly. In Fig. 9, part (*a*) shows the model used to evaluate the interactions in compound **1**, where one of the POM moieties has been replaced by three $OH^-$ ligands (see small arrows). The binding energy of this assembly is very favourable, *i.e.* $\Delta E_1 = -43.6$ kcal mol$^{-1}$, due to the combination of two anion–$\pi$ and one hydrogen-bonding interaction. We have computed an additional theoretical model (see Fig. 9*b*) in which the water molecule that establishes the hydrogen-bonding interactions has been eliminated. The interaction energy is thus reduced to $\Delta E_2 = -29.5$ kcal mol$^{-1}$, which can be attributed to the anion–$\pi$ interaction. It is interesting to note that two O atoms of the POM that are involved in the interaction are close to the six-membered rings of the ligand that present larger MEP values (see Fig. 8), thus justifying the large anion–$\pi$ binding energy. In Fig. 9(*c*), we show the theoretical model used to evaluate the interactions in compound **2**, where one of the POM moieties has been replaced by three $OH^-$ ligands. Similar to **1**, the binding energy of this assembly is also very favourable ($\Delta E_3 = -37.2$ kcal mol$^{-1}$), in this case due to the combination of one anion–$\pi$ and two hydrogen-bonding interactions. We have computed an additional theoretical model (see Fig. 9*d*), in which the water molecule that establish the hydrogen-bonding interactions has been eliminated. The


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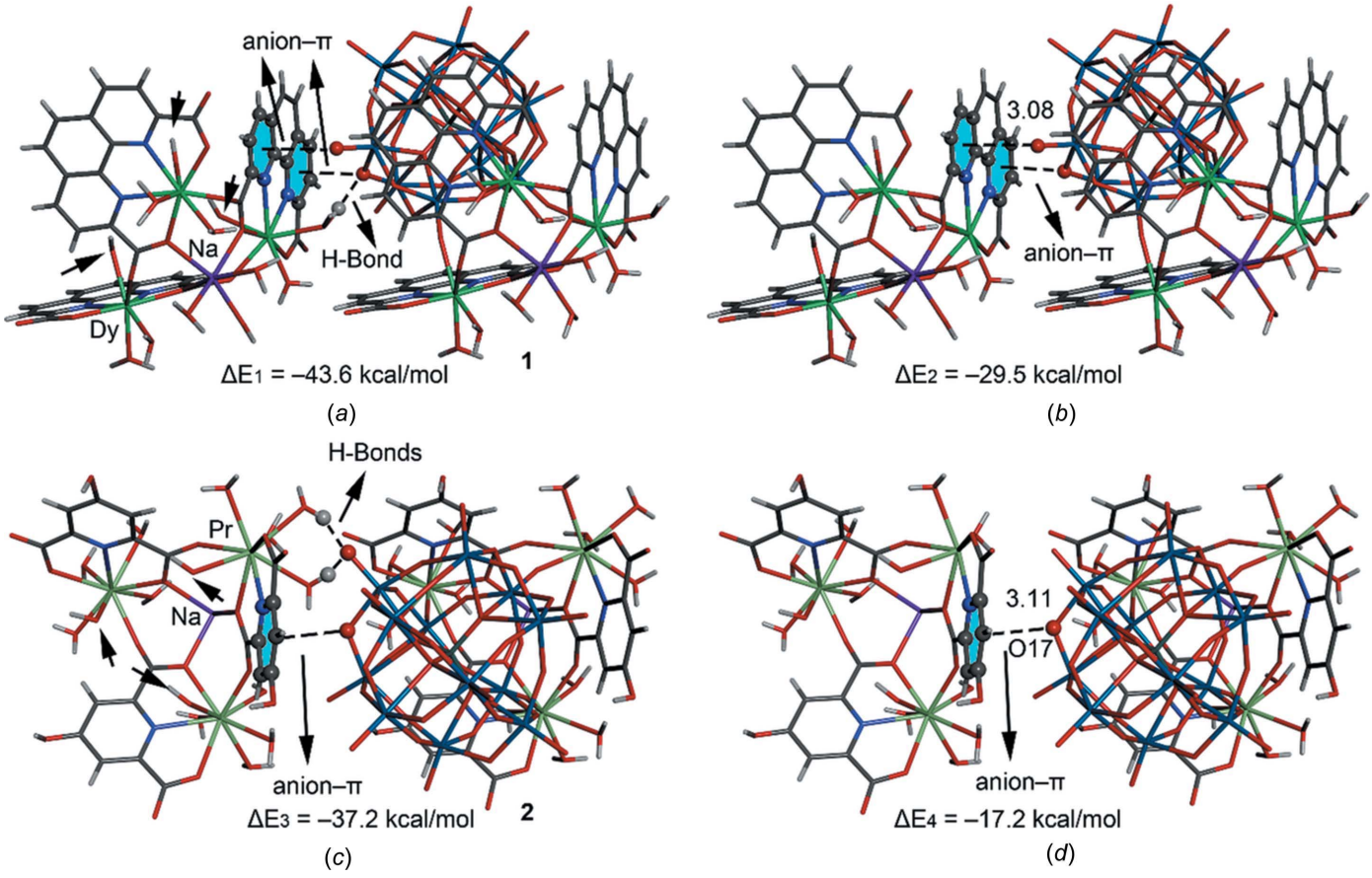


**Figure 9**
Theoretical models used to evaluate the anion–$\pi$ and hydrogen-bonding interactions in (*a*)/(*b*) compound **1** and (*c*)/(*d*) compound **2**. Distances are given in Å.

interaction energy is thus significantly reduced to $\Delta E_4 = -17.2$ kcal mol$^{-1}$, which can be attributed to an anion–$\pi$ interaction. In this compound, the interaction is less favourable because only one anion–$\pi$ contact is established. The difference ($\Delta E_4 - \Delta E_3 = -20.0$ kcal mol$^{-1}$) is the contribution of the two hydrogen bonds between the coordinated water molecules and the POM moiety.

## 4. Concluding remarks

We have synthesized and characterized by X-ray diffraction analysis two hybrid inorganic–organic assemblies generated from Keggin-type polyoxometalates (POM) and trinuclear lanthanoid clusters with the formulae $\{Na[Dy(PDA)(H_2O)_3]_3[SiW_{12}O_{40}]\}\cdot 12H_2O$ (**1**) and $\{Na(H_2O)[Pr(pydc\text{-}OH)(H_2O)_4]_3[SiW_{12}O_{40}]\}\cdot 12H_2O$ (**2**). We have highlighted and explored the role of strong anion–$\pi$ and hydrogen-bonding interactions between the POM, which is a polyanion, and the aromatic ring. The combination of both interactions plays a crucial role in the crystal-packing formation. A DFT study reveals that the effect of the coordination of the ligand to the metal centre is crucial for increasing the $\pi$-acidity of the aromatic ring, and consequently increasing its ability to establish anion–$\pi$ interactions. This explanation has been confirmed by computing the MEP surfaces of the free ligands and their complexes with Pr and Dy. Finally, further experiments with other polyoxometalates and lanthanoids are in progress in our laboratory to obtain different supramolecular assemblies to gain further insight into this type of hybrid inorganic–organic compound. Continued efforts to explore the construction of functional hybrids based on POMs incorporating other pyridinedicarboxylic acid and azide ligands are underway (Hassanpoor *et al.*, 2018).

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# supporting information

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## Surface-grafted lanthanoid complexes of the tungstosilicate polyanion $[SiW_{12}O_{40}]^{4-}$: a synthetic, structural and computational investigation

**Shadi Derakhshanrad, Masoud Mirzaei, Atefeh Najafi, Chris Ritchie, Antonio Bauzá, Antonio Frontera and Joel T. Mague**

### Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015) for d23_4; *APEX3* (Bruker, 2016) for jtm570b_4_a. Cell refinement: *CrysAlis PRO* (Rigaku OD, 2015) for d23_4; *SAINT* (Bruker, 2016) for jtm570b_4_a. Data reduction: *CrysAlis PRO* (Rigaku OD, 2015) for d23_4; *SAINT* (Bruker, 2016) and *CELL_NOW* (Sheldrick, 2008) for jtm570b_4_a. Program(s) used to solve structure: SHELXT (Sheldrick, 2015a) for d23_4; *SHELXT* (Sheldrick, 2015*a*) for jtm570b_4_a. Program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b) for d23_4; *SHELXL2018* (Sheldrick, 2015*b*) for jtm570b_4_a. Molecular graphics: OLEX2 (Dolomanov *et al.*, 2009) for d23_4; *DIAMOND* (Brandenburg & Putz, 2012) for jtm570b_4_a. Software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009) for d23_4; *SHELXTL* (Bruker, 2016) for jtm570b_4_a.

### Sodium tris[triaqua(*μ*-1,10-phenanthroline-2,9-dicarboxylato)dysprosium(III)] silicododecatungstate dodecahydrate (d23_4)

*Crystal data*

$[DyNa(C_{14}H_6N_2O_4)_3(H_2O)_9(SiW_{12}O_{40})]\cdot 12H_2O$
$M_r$ = 4527.40
Trigonal, *R*3
*a* = 20.3334 (3) Å
*c* = 18.7836 (3) Å
*V* = 6725.60 (19) Å$^3$
*Z* = 3
*F*(000) = 6033
$D_x$ = 3.353 Mg m$^{-3}$
Cu *Kα* radiation, *λ* = 1.54184 Å
Cell parameters from 11603 reflections
*θ* = 4.3–76.8°
*μ* = 41.93 mm$^{-1}$
*T* = 130 K
Block, yellow
0.07 × 0.05 × 0.03 mm

*Data collection*

SuperNova, Dual, Cu at zero, Atlas diffractometer
Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.2273 pixels mm$^{-1}$
*ω* scans
Absorption correction: gaussian (CrysAlis PRO; Rigaku OD, 2015)
$T_{min}$ = 0.097, $T_{max}$ = 0.369
16672 measured reflections
5475 independent reflections
5450 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030
$\theta_{max}$ = 77.1°, $\theta_{min}$ = 3.4°
*h* = −25→25
*k* = −25→22
*l* = −17→23



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*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.098$
$S = 1.02$
5475 reflections
426 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 182.8632P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.53$ e Å$^{-3}$
$\Delta\rho_{min} = -1.89$ e Å$^{-3}$
Extinction correction: SHELXL2014 (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.000018 (3)
Absolute structure: Classical Flack method preferred over Parsons because s.u. lower
Absolute structure parameter: 0.013 (7)

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| W4 | 0.44911 (3) | 0.69357 (3) | 0.56892 (4) | 0.01497 (17) | |
| W1 | 0.41288 (4) | 0.77239 (4) | 0.87226 (4) | 0.01785 (18) | |
| W2 | 0.52603 (4) | 0.80714 (4) | 0.70932 (4) | 0.01734 (18) | |
| W3 | 0.48229 (4) | 0.62447 (4) | 0.71593 (4) | 0.02049 (19) | |
| Dy1 | 0.51195 (5) | 0.65952 (5) | 0.37516 (5) | 0.0164 (2) | |
| Si1 | 0.3333 | 0.6667 | 0.7162 (4) | 0.0118 (11) | |
| Na1 | 0.3333 | 0.6667 | 0.2727 (9) | 0.043 (3) | |
| O3 | 0.4885 (6) | 0.7885 (6) | 0.8053 (6) | 0.017 (2) | |
| O8 | 0.5293 (6) | 0.7869 (5) | 0.6112 (6) | 0.0158 (19) | |
| O12 | 0.4913 (6) | 0.6406 (6) | 0.6149 (6) | 0.016 (2) | |
| O11 | 0.4427 (5) | 0.6170 (6) | 0.8083 (6) | 0.017 (2) | |
| O6 | 0.6133 (6) | 0.8872 (6) | 0.7191 (7) | 0.021 (2) | |
| O7 | 0.5555 (5) | 0.7296 (6) | 0.7265 (6) | 0.017 (2) | |
| O2 | 0.4173 (6) | 0.6883 (6) | 0.9140 (6) | 0.017 (2) | |
| O1 | 0.4622 (7) | 0.8404 (7) | 0.9358 (6) | 0.024 (2) | |
| O15 | 0.2638 (6) | 0.4988 (7) | 0.3514 (7) | 0.024 (2) | |
| O10 | 0.5381 (6) | 0.5854 (6) | 0.7255 (6) | 0.020 (2) | |
| C10 | 0.5397 (10) | 0.5640 (10) | 0.5073 (9) | 0.024 (3) | |
| O13 | 0.4852 (6) | 0.7001 (6) | 0.4845 (6) | 0.018 (2) | |
| O17 | 0.6409 (6) | 0.7464 (6) | 0.3883 (8) | 0.030 (3) | |
| O20 | 0.5127 (8) | 0.6757 (8) | 0.2497 (7) | 0.033 (3) | |
| C9 | 0.5742 (12) | 0.5423 (11) | 0.5605 (11) | 0.031 (4) | |
| O21 | 0.3066 (8) | 0.5641 (8) | 0.1948 (9) | 0.038 (3) | |
| O16 | 0.3803 (6) | 0.5977 (7) | 0.3480 (7) | 0.022 (2) | |
| N1 | 0.4311 (7) | 0.5416 (7) | 0.4422 (7) | 0.017 (2) | |
| O9 | 0.4179 (5) | 0.6902 (5) | 0.6868 (5) | 0.0102 (17) | |
| C1 | 0.3314 (8) | 0.5341 (8) | 0.3712 (8) | 0.017 (3) | |



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| | | | | | |
|---|---|---|---|---|---|
| C4 | 0.3389 (10) | 0.4085 (9) | 0.5160 (10) | 0.026 (3) | |
| H4 | 0.3069 | 0.3627 | 0.5409 | 0.031* | |
| C6 | 0.4613 (9) | 0.5179 (8) | 0.4940 (9) | 0.018 (3) | |
| C2 | 0.3576 (8) | 0.5003 (9) | 0.4272 (9) | 0.019 (3) | |
| C8 | 0.5273 (12) | 0.4744 (12) | 0.5997 (11) | 0.033 (4) | |
| H8 | 0.5501 | 0.4596 | 0.6357 | 0.040* | |
| O18 | 0.7546 (9) | 0.7895 (10) | 0.4416 (16) | 0.081 (8) | |
| C12 | 0.6903 (10) | 0.6552 (12) | 0.5338 (11) | 0.034 (4) | |
| H12 | 0.7430 | 0.6887 | 0.5413 | 0.041* | |
| C13 | 0.6505 (9) | 0.6725 (9) | 0.4802 (11) | 0.027 (4) | |
| C3 | 0.3093 (10) | 0.4326 (10) | 0.4634 (11) | 0.029 (4) | |
| H3 | 0.2570 | 0.4039 | 0.4516 | 0.035* | |
| N2 | 0.5771 (7) | 0.6266 (7) | 0.4684 (8) | 0.020 (3) | |
| C5 | 0.4156 (11) | 0.4509 (10) | 0.5333 (12) | 0.030 (4) | |
| C11 | 0.6533 (12) | 0.5922 (13) | 0.5729 (11) | 0.036 (5) | |
| H11 | 0.6792 | 0.5807 | 0.6085 | 0.043* | |
| C7 | 0.4529 (13) | 0.4307 (11) | 0.5880 (11) | 0.035 (4) | |
| H7 | 0.4241 | 0.3862 | 0.6157 | 0.041* | |
| C14 | 0.6855 (10) | 0.7409 (10) | 0.4339 (14) | 0.038 (5) | |
| O4 | 0.3333 | 0.6667 | 0.8022 (9) | 0.011 (3) | |
| O14 | 0.3542 (5) | 0.6058 (6) | 0.5595 (6) | 0.017 (2) | |
| O5 | 0.4639 (6) | 0.8485 (6) | 0.6953 (6) | 0.016 (2) | |
| O19 | 0.5444 (8) | 0.5750 (7) | 0.3202 (8) | 0.033 (3) | |
| O25 | 0.9043 (12) | 0.8861 (17) | 0.3944 (13) | 0.097 (10) | |
| O23 | 0.440 (2) | 0.5157 (19) | 0.207 (2) | 0.135 (15) | |
| O26 | 0.7339 (19) | 0.992 (3) | 0.622 (2) | 0.066 (11) | 0.5 |
| O28 | 0.525 (2) | 1.000 (2) | 0.950 (2) | 0.058 (9)* | 0.5 |
| O27 | 0.578 (2) | 1.010 (2) | 0.775 (2) | 0.061 (9)* | 0.5 |
| O22 | 0.3333 | 0.6667 | 0.126 (3) | 0.050 (13)* | 0.5 |
| O24 | 0.362 (3) | 0.473 (3) | 0.083 (2) | 0.087 (16) | 0.5 |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| W4 | 0.0123 (3) | 0.0143 (3) | 0.0178 (4) | 0.0062 (2) | 0.0011 (2) | −0.0014 (2) |
| W1 | 0.0173 (3) | 0.0159 (3) | 0.0187 (4) | 0.0071 (2) | −0.0012 (2) | −0.0036 (2) |
| W2 | 0.0118 (3) | 0.0150 (3) | 0.0229 (4) | 0.0049 (2) | −0.0009 (2) | −0.0024 (2) |
| W3 | 0.0175 (3) | 0.0197 (3) | 0.0263 (4) | 0.0108 (3) | −0.0022 (3) | −0.0013 (3) |
| Dy1 | 0.0146 (4) | 0.0155 (4) | 0.0208 (5) | 0.0089 (3) | 0.0030 (3) | 0.0004 (3) |
| Si1 | 0.0097 (15) | 0.0097 (15) | 0.016 (3) | 0.0048 (8) | 0.000 | 0.000 |
| Na1 | 0.040 (5) | 0.040 (5) | 0.050 (9) | 0.020 (2) | 0.000 | 0.000 |
| O3 | 0.017 (5) | 0.019 (5) | 0.014 (5) | 0.008 (4) | −0.002 (4) | 0.001 (4) |
| O8 | 0.016 (5) | 0.010 (4) | 0.019 (5) | 0.005 (4) | −0.001 (4) | 0.002 (4) |
| O12 | 0.016 (5) | 0.018 (5) | 0.019 (6) | 0.012 (4) | −0.005 (4) | −0.005 (4) |
| O11 | 0.011 (4) | 0.018 (5) | 0.016 (5) | 0.004 (4) | 0.001 (4) | 0.003 (4) |
| O6 | 0.009 (4) | 0.019 (5) | 0.032 (6) | 0.005 (4) | 0.002 (4) | −0.001 (4) |
| O7 | 0.011 (4) | 0.013 (5) | 0.020 (5) | 0.001 (4) | −0.002 (4) | −0.001 (4) |
| O2 | 0.015 (4) | 0.017 (5) | 0.019 (6) | 0.008 (4) | 0.002 (4) | 0.003 (4) |



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| | | | | | | |
|---|---|---|---|---|---|---|
| O1 | 0.029 (6) | 0.025 (6) | 0.017 (6) | 0.013 (5) | 0.000 (4) | −0.003 (4) |
| O15 | 0.014 (5) | 0.031 (6) | 0.027 (6) | 0.011 (4) | −0.001 (4) | −0.008 (5) |
| O10 | 0.017 (5) | 0.025 (5) | 0.019 (5) | 0.012 (4) | −0.001 (4) | −0.003 (4) |
| C10 | 0.028 (8) | 0.033 (8) | 0.018 (8) | 0.021 (7) | −0.006 (6) | −0.013 (6) |
| O13 | 0.015 (5) | 0.019 (5) | 0.019 (6) | 0.008 (4) | −0.003 (4) | −0.003 (4) |
| O17 | 0.015 (5) | 0.020 (6) | 0.051 (8) | 0.005 (4) | 0.005 (5) | 0.002 (5) |
| O20 | 0.042 (7) | 0.048 (8) | 0.021 (7) | 0.031 (7) | 0.005 (5) | 0.004 (5) |
| C9 | 0.044 (11) | 0.032 (9) | 0.026 (9) | 0.026 (8) | 0.002 (8) | 0.001 (7) |
| O21 | 0.034 (7) | 0.035 (7) | 0.046 (9) | 0.017 (6) | 0.010 (6) | 0.004 (6) |
| O16 | 0.013 (5) | 0.027 (6) | 0.026 (6) | 0.010 (4) | −0.005 (4) | −0.002 (5) |
| N1 | 0.020 (6) | 0.016 (5) | 0.019 (6) | 0.013 (5) | 0.001 (5) | −0.007 (5) |
| O9 | 0.012 (4) | 0.007 (4) | 0.011 (5) | 0.004 (3) | −0.003 (3) | −0.002 (3) |
| C1 | 0.020 (7) | 0.021 (7) | 0.013 (7) | 0.014 (6) | −0.002 (5) | −0.003 (5) |
| C4 | 0.027 (8) | 0.015 (7) | 0.030 (9) | 0.007 (6) | 0.008 (7) | 0.007 (6) |
| C6 | 0.021 (7) | 0.019 (7) | 0.019 (8) | 0.014 (6) | 0.003 (6) | −0.005 (5) |
| C2 | 0.018 (7) | 0.022 (7) | 0.017 (8) | 0.010 (6) | 0.008 (5) | −0.003 (6) |
| C8 | 0.048 (11) | 0.046 (11) | 0.027 (9) | 0.040 (10) | 0.006 (8) | 0.014 (8) |
| O18 | 0.018 (7) | 0.035 (9) | 0.17 (3) | −0.001 (6) | −0.006 (10) | 0.017 (12) |
| C12 | 0.023 (8) | 0.044 (11) | 0.033 (11) | 0.015 (8) | −0.017 (7) | −0.013 (8) |
| C13 | 0.015 (7) | 0.018 (7) | 0.045 (11) | 0.006 (6) | −0.007 (7) | −0.010 (7) |
| C3 | 0.028 (8) | 0.020 (7) | 0.039 (11) | 0.011 (7) | 0.001 (7) | 0.000 (7) |
| N2 | 0.019 (6) | 0.024 (6) | 0.025 (7) | 0.016 (5) | 0.001 (5) | −0.006 (5) |
| C5 | 0.033 (9) | 0.019 (7) | 0.044 (11) | 0.017 (7) | 0.004 (8) | 0.000 (7) |
| C11 | 0.038 (10) | 0.053 (12) | 0.032 (10) | 0.033 (9) | −0.016 (8) | −0.017 (9) |
| C7 | 0.054 (12) | 0.026 (8) | 0.028 (10) | 0.024 (9) | 0.000 (8) | 0.005 (7) |
| C14 | 0.019 (8) | 0.018 (8) | 0.076 (16) | 0.009 (7) | −0.011 (8) | −0.008 (8) |
| O4 | 0.011 (4) | 0.011 (4) | 0.011 (8) | 0.005 (2) | 0.000 | 0.000 |
| O14 | 0.013 (4) | 0.016 (5) | 0.021 (6) | 0.007 (4) | −0.005 (4) | −0.003 (4) |
| O5 | 0.017 (5) | 0.015 (5) | 0.016 (5) | 0.009 (4) | 0.003 (4) | −0.003 (4) |
| O19 | 0.053 (8) | 0.025 (6) | 0.036 (8) | 0.030 (6) | 0.018 (6) | 0.010 (5) |
| O25 | 0.045 (11) | 0.14 (2) | 0.048 (14) | 0.000 (12) | −0.003 (9) | 0.015 (13) |
| O23 | 0.18 (4) | 0.11 (2) | 0.16 (4) | 0.11 (3) | −0.08 (3) | −0.07 (2) |
| O26 | 0.030 (16) | 0.09 (3) | 0.06 (2) | 0.016 (17) | −0.015 (15) | −0.02 (2) |
| O24 | 0.11 (4) | 0.11 (4) | 0.04 (2) | 0.06 (3) | 0.00 (2) | 0.04 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| W4—O8 | 1.949 (10) | Na1—O21$^{ii}$ | 2.378 (18) |
| W4—O12 | 1.888 (10) | Na1—O21$^{i}$ | 2.378 (18) |
| W4—O13 | 1.725 (11) | Na1—O21 | 2.378 (18) |
| W4—O9 | 2.296 (10) | Na1—O16$^{i}$ | 2.494 (15) |
| W4—O14$^{i}$ | 1.940 (10) | Na1—O16 | 2.494 (15) |
| W4—O14 | 1.870 (10) | Na1—O16$^{ii}$ | 2.494 (15) |
| W1—O3 | 1.884 (11) | Na1—O22 | 2.76 (7) |
| W1—O11$^{i}$ | 1.909 (10) | O11—W1$^{ii}$ | 1.909 (10) |
| W1—O2$^{i}$ | 1.952 (10) | O2—W1$^{ii}$ | 1.952 (10) |
| W1—O2 | 1.924 (10) | O15—Dy1$^{ii}$ | 2.306 (10) |
| W1—O1 | 1.719 (11) | O15—C1 | 1.247 (19) |



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| | | | |
|---|---|---|---|
| W1—O4 | 2.343 (10) | C10—C9 | 1.41 (3) |
| W2—O3 | 1.921 (11) | C10—C6 | 1.41 (2) |
| W2—O8 | 1.896 (11) | C10—N2 | 1.33 (2) |
| W2—O6 | 1.716 (10) | O17—C14 | 1.29 (2) |
| W2—O7 | 1.974 (11) | C9—C8 | 1.43 (3) |
| W2—O9 | 2.332 (9) | C9—C11 | 1.43 (3) |
| W2—O5 | 1.853 (10) | O16—C1 | 1.25 (2) |
| W3—O12 | 1.919 (11) | N1—C6 | 1.36 (2) |
| W3—O11 | 1.886 (11) | N1—C2 | 1.33 (2) |
| W3—O7 | 1.908 (10) | C1—C2 | 1.49 (2) |
| W3—O10 | 1.689 (11) | C4—C3 | 1.37 (3) |
| W3—O9 | 2.356 (9) | C4—C5 | 1.39 (3) |
| W3—O5$^{ii}$ | 1.938 (10) | C6—C5 | 1.41 (2) |
| Dy1—O15$^{i}$ | 2.306 (10) | C2—C3 | 1.40 (2) |
| Dy1—O13 | 2.375 (11) | C8—C7 | 1.34 (3) |
| Dy1—O17 | 2.329 (11) | O18—C14 | 1.26 (2) |
| Dy1—O20 | 2.379 (13) | C12—C13 | 1.44 (3) |
| Dy1—O16 | 2.374 (11) | C12—C11 | 1.34 (3) |
| Dy1—N1 | 2.469 (13) | C13—N2 | 1.32 (2) |
| Dy1—N2 | 2.482 (14) | C13—C14 | 1.48 (3) |
| Dy1—O19 | 2.364 (12) | C5—C7 | 1.45 (3) |
| Si1—O9 | 1.633 (10) | O4—W1$^{i}$ | 2.343 (10) |
| Si1—O9$^{ii}$ | 1.633 (10) | O4—W1$^{ii}$ | 2.343 (10) |
| Si1—O9$^{i}$ | 1.633 (10) | O14—W4$^{ii}$ | 1.940 (10) |
| Si1—O4 | 1.615 (19) | O5—W3$^{i}$ | 1.938 (10) |

| | | | |
|---|---|---|---|
| O8—W4—O9 | 73.7 (4) | O9$^{i}$—Si1—O9 | 109.2 (4) |
| O12—W4—O8 | 88.4 (4) | O9$^{ii}$—Si1—O9 | 109.2 (4) |
| O12—W4—O9 | 74.9 (4) | O4—Si1—O9$^{ii}$ | 109.8 (4) |
| O12—W4—O14$^{i}$ | 157.7 (5) | O4—Si1—O9 | 109.8 (4) |
| O13—W4—O8 | 100.6 (5) | O4—Si1—O9$^{i}$ | 109.8 (4) |
| O13—W4—O12 | 99.6 (5) | O21$^{ii}$—Na1—O21$^{i}$ | 86.1 (7) |
| O13—W4—O9 | 172.0 (4) | O21$^{ii}$—Na1—O21 | 86.1 (7) |
| O13—W4—O14$^{i}$ | 102.6 (5) | O21$^{i}$—Na1—O21 | 86.1 (7) |
| O13—W4—O14 | 100.6 (5) | O21—Na1—O16$^{ii}$ | 104.8 (4) |
| O14—W4—O8 | 158.4 (5) | O21—Na1—O16$^{i}$ | 162.2 (4) |
| O14$^{i}$—W4—O8 | 85.4 (4) | O21—Na1—O16 | 80.8 (5) |
| O14—W4—O12 | 92.6 (5) | O21$^{i}$—Na1—O16$^{ii}$ | 162.2 (4) |
| O14$^{i}$—W4—O9 | 82.8 (4) | O21$^{i}$—Na1—O16 | 104.8 (4) |
| O14—W4—O9 | 85.7 (4) | O21$^{i}$—Na1—O16$^{i}$ | 80.8 (5) |
| O14—W4—O14$^{i}$ | 85.6 (6) | O21$^{ii}$—Na1—O16 | 162.2 (4) |
| O3—W1—O11$^{i}$ | 86.9 (5) | O21$^{ii}$—Na1—O16$^{i}$ | 104.8 (4) |
| O3—W1—O2$^{i}$ | 158.6 (4) | O21$^{ii}$—Na1—O16$^{ii}$ | 80.8 (5) |
| O3—W1—O2 | 91.7 (4) | O21—Na1—O22 | 52.0 (5) |
| O3—W1—O4 | 85.1 (4) | O21$^{i}$—Na1—O22 | 52.0 (5) |
| O11$^{i}$—W1—O2$^{i}$ | 86.9 (4) | O21$^{ii}$—Na1—O22 | 52.0 (5) |
| O11$^{i}$—W1—O2 | 158.5 (5) | O16$^{i}$—Na1—O16 | 91.0 (6) |
| O11$^{i}$—W1—O4 | 84.1 (4) | O16$^{ii}$—Na1—O16 | 91.0 (6) |



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| | | | |
|---|---|---|---|
| O2—W1—O2$^{i}$ | 86.7 (6) | O16$^{ii}$—Na1—O16$^{i}$ | 91.0 (6) |
| O2—W1—O4 | 74.4 (4) | O16$^{ii}$—Na1—O22 | 124.5 (4) |
| O2$^{i}$—W1—O4 | 73.9 (4) | O16$^{i}$—Na1—O22 | 124.5 (4) |
| O1—W1—O3 | 103.1 (5) | O16—Na1—O22 | 124.5 (4) |
| O1—W1—O11$^{i}$ | 101.7 (5) | W1—O3—W2 | 150.5 (6) |
| O1—W1—O2 | 99.5 (5) | W2—O8—W4 | 120.3 (5) |
| O1—W1—O2$^{i}$ | 98.2 (5) | W4—O12—W3 | 121.2 (5) |
| O1—W1—O4 | 170.1 (5) | W3—O11—W1$^{ii}$ | 151.5 (6) |
| O3—W2—O7 | 86.4 (5) | W3—O7—W2 | 120.0 (5) |
| O3—W2—O9 | 83.7 (4) | W1—O2—W1$^{ii}$ | 120.1 (6) |
| O8—W2—O3 | 157.4 (4) | C1—O15—Dy1$^{ii}$ | 141.1 (10) |
| O8—W2—O7 | 85.9 (4) | C6—C10—C9 | 119.4 (17) |
| O8—W2—O9 | 73.8 (4) | N2—C10—C9 | 123.5 (16) |
| O6—W2—O3 | 101.9 (5) | N2—C10—C6 | 117.1 (15) |
| O6—W2—O8 | 100.3 (5) | W4—O13—Dy1 | 158.6 (6) |
| O6—W2—O7 | 99.0 (5) | C14—O17—Dy1 | 125.2 (11) |
| O6—W2—O9 | 170.9 (4) | C10—C9—C8 | 118.1 (18) |
| O6—W2—O5 | 101.6 (5) | C10—C9—C11 | 116.9 (18) |
| O7—W2—O9 | 73.9 (4) | C11—C9—C8 | 125.0 (19) |
| O5—W2—O3 | 86.0 (5) | Dy1—O16—Na1 | 118.1 (5) |
| O5—W2—O8 | 93.8 (4) | C1—O16—Dy1 | 125.2 (10) |
| O5—W2—O7 | 159.1 (4) | C1—O16—Na1 | 116.6 (9) |
| O5—W2—O9 | 85.9 (4) | C6—N1—Dy1 | 120.7 (10) |
| O12—W3—O9 | 72.9 (4) | C2—N1—Dy1 | 119.8 (11) |
| O12—W3—O5$^{ii}$ | 85.8 (5) | C2—N1—C6 | 119.5 (13) |
| O11—W3—O12 | 157.5 (4) | W4—O9—W2 | 92.2 (3) |
| O11—W3—O7 | 93.3 (5) | W4—O9—W3 | 91.0 (3) |
| O11—W3—O9 | 85.6 (4) | W2—O9—W3 | 91.6 (3) |
| O11—W3—O5$^{ii}$ | 84.9 (4) | Si1—O9—W4 | 124.8 (6) |
| O7—W3—O12 | 87.5 (5) | Si1—O9—W2 | 123.7 (5) |
| O7—W3—O9 | 74.5 (4) | Si1—O9—W3 | 123.9 (5) |
| O7—W3—O5$^{ii}$ | 157.4 (4) | O15—C1—O16 | 124.7 (14) |
| O10—W3—O12 | 99.0 (5) | O15—C1—C2 | 119.4 (14) |
| O10—W3—O11 | 103.0 (5) | O16—C1—C2 | 116.0 (13) |
| O10—W3—O7 | 100.6 (5) | C3—C4—C5 | 120.2 (16) |
| O10—W3—O9 | 170.5 (5) | C10—C6—C5 | 121.8 (16) |
| O10—W3—O5$^{ii}$ | 101.7 (5) | N1—C6—C10 | 116.8 (15) |
| O5$^{ii}$—W3—O9 | 82.9 (4) | N1—C6—C5 | 121.3 (15) |
| O15$^{i}$—Dy1—O13 | 72.5 (4) | N1—C2—C1 | 114.1 (14) |
| O15$^{i}$—Dy1—O17 | 84.8 (4) | N1—C2—C3 | 122.0 (16) |
| O15$^{i}$—Dy1—O20 | 71.1 (5) | C3—C2—C1 | 123.9 (15) |
| O15$^{i}$—Dy1—O16 | 81.1 (4) | C7—C8—C9 | 123.0 (17) |
| O15$^{i}$—Dy1—N1 | 132.5 (4) | C11—C12—C13 | 120.2 (16) |
| O15$^{i}$—Dy1—N2 | 134.4 (4) | C12—C13—C14 | 124.9 (15) |
| O15$^{i}$—Dy1—O19 | 141.5 (4) | N2—C13—C12 | 121.1 (17) |
| O13—Dy1—O20 | 142.7 (4) | N2—C13—C14 | 114.0 (16) |
| O13—Dy1—N1 | 74.9 (4) | C4—C3—C2 | 119.0 (16) |
| O13—Dy1—N2 | 74.3 (4) | C10—N2—Dy1 | 121.3 (10) |



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| O17—Dy1—O13 | 90.6 (4) | C13—N2—Dy1 | 119.5 (12) |
| O17—Dy1—O20 | 94.2 (5) | C13—N2—C10 | 119.2 (15) |
| O17—Dy1—O16 | 165.4 (4) | C4—C5—C6 | 117.9 (17) |
| O17—Dy1—N1 | 129.3 (5) | C4—C5—C7 | 124.8 (17) |
| O17—Dy1—N2 | 65.1 (5) | C6—C5—C7 | 117.3 (17) |
| O17—Dy1—O19 | 88.9 (5) | C12—C11—C9 | 119.1 (18) |
| O20—Dy1—N1 | 126.5 (5) | C8—C7—C5 | 120.3 (18) |
| O20—Dy1—N2 | 140.3 (4) | O17—C14—C13 | 116.1 (15) |
| O16—Dy1—O13 | 88.6 (4) | O18—C14—O17 | 124 (2) |
| O16—Dy1—O20 | 77.8 (4) | O18—C14—C13 | 120 (2) |
| O16—Dy1—N1 | 64.4 (4) | W1$^{i}$—O4—W1$^{ii}$ | 91.6 (5) |
| O16—Dy1—N2 | 128.4 (4) | W1—O4—W1$^{ii}$ | 91.6 (5) |
| N1—Dy1—N2 | 64.1 (4) | W1$^{i}$—O4—W1 | 91.6 (5) |
| O19—Dy1—O13 | 145.6 (4) | Si1—O4—W1$^{i}$ | 124.2 (3) |
| O19—Dy1—O20 | 71.5 (5) | Si1—O4—W1 | 124.2 (3) |
| O19—Dy1—O16 | 99.9 (5) | Si1—O4—W1$^{ii}$ | 124.2 (3) |
| O19—Dy1—N1 | 79.0 (4) | W4—O14—W4$^{ii}$ | 151.9 (6) |
| O19—Dy1—N2 | 74.4 (5) | W2—O5—W3$^{i}$ | 153.0 (6) |
| O9$^{i}$—Si1—O9$^{ii}$ | 109.2 (4) | | |

| | | | |
|---|---|---|---|
| Dy1$^{ii}$—O15—C1—O16 | −87 (2) | O9$^{ii}$—Si1—O9—W2 | 177.8 (4) |
| Dy1$^{ii}$—O15—C1—C2 | 92.5 (19) | O9$^{i}$—Si1—O9—W2 | 58.5 (10) |
| Dy1—O17—C14—O18 | −178 (2) | O9$^{i}$—Si1—O9—W3 | 177.8 (4) |
| Dy1—O17—C14—C13 | 1 (2) | O9$^{ii}$—Si1—O9—W3 | −62.9 (10) |
| Dy1—O16—C1—O15 | −172.7 (11) | O9—Si1—O4—W1$^{i}$ | 178.1 (3) |
| Dy1—O16—C1—C2 | 8.1 (18) | O9$^{i}$—Si1—O4—W1 | −61.9 (3) |
| Dy1—N1—C6—C10 | 0.5 (17) | O9$^{ii}$—Si1—O4—W1 | 178.1 (3) |
| Dy1—N1—C6—C5 | 179.4 (12) | O9—Si1—O4—W1 | 58.1 (3) |
| Dy1—N1—C2—C1 | −2.9 (16) | O9$^{i}$—Si1—O4—W1$^{ii}$ | 178.1 (3) |
| Dy1—N1—C2—C3 | 179.6 (12) | O9$^{ii}$—Si1—O4—W1$^{ii}$ | 58.1 (3) |
| Na1—O16—C1—O15 | 11 (2) | O9—Si1—O4—W1$^{ii}$ | −61.9 (3) |
| Na1—O16—C1—C2 | −168.5 (10) | O9$^{ii}$—Si1—O4—W1$^{i}$ | −61.9 (3) |
| O3—W2—O8—W4 | 3.7 (15) | O9$^{i}$—Si1—O4—W1$^{i}$ | 58.1 (3) |
| O3—W2—O5—W3$^{i}$ | −27.3 (13) | C1—C2—C3—C4 | −177.1 (15) |
| O8—W4—O12—W3 | 72.3 (6) | C4—C5—C7—C8 | 178.6 (19) |
| O8—W4—O13—Dy1 | 145.2 (15) | C6—C10—C9—C8 | −1 (2) |
| O8—W4—O14—W4$^{ii}$ | 39 (2) | C6—C10—C9—C11 | −178.3 (16) |
| O8—W2—O5—W3$^{i}$ | 130.1 (13) | C6—C10—N2—Dy1 | −1.1 (19) |
| O12—W4—O13—Dy1 | 55.1 (16) | C6—C10—N2—C13 | 178.4 (14) |
| O12—W4—O14—W4$^{ii}$ | 131.1 (14) | C6—N1—C2—C1 | 178.0 (12) |
| O12—W3—O11—W1$^{ii}$ | 40 (2) | C6—N1—C2—C3 | 0 (2) |
| O11$^{i}$—W1—O3—W2 | −24.7 (12) | C6—C5—C7—C8 | 0 (3) |
| O6—W2—O8—W4 | 172.6 (6) | C2—N1—C6—C10 | 179.7 (13) |
| O6—W2—O5—W3$^{i}$ | −128.6 (13) | C2—N1—C6—C5 | −1 (2) |
| O7—W2—O8—W4 | 74.2 (6) | C8—C9—C11—C12 | −178 (2) |
| O7—W2—O5—W3$^{i}$ | 42 (2) | C12—C13—N2—Dy1 | −179.8 (13) |
| O7—W3—O11—W1$^{ii}$ | 130.9 (13) | C12—C13—N2—C10 | 1 (2) |
| O2—W1—O3—W2 | 133.9 (13) | C12—C13—C14—O17 | 179.3 (18) |



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| O2$^{i}$—W1—O3—W2 | 49 (2) | C12—C13—C14—O18 | −2 (3) |
| O1—W1—O3—W2 | −125.9 (13) | C13—C12—C11—C9 | 0 (3) |
| O15—C1—C2—N1 | 177.7 (13) | C3—C4—C5—C6 | −1 (3) |
| O15—C1—C2—C3 | −5 (2) | C3—C4—C5—C7 | −180.0 (18) |
| O10—W3—O11—W1$^{ii}$ | −127.4 (13) | N2—C10—C9—C8 | 178.6 (16) |
| C10—C9—C8—C7 | 0 (3) | N2—C10—C9—C11 | 1 (3) |
| C10—C9—C11—C12 | −1 (3) | N2—C10—C6—N1 | 0 (2) |
| C10—C6—C5—C4 | −179.3 (15) | N2—C10—C6—C5 | −178.5 (15) |
| C10—C6—C5—C7 | 0 (2) | N2—C13—C14—O17 | −1 (3) |
| O13—W4—O12—W3 | 172.8 (6) | N2—C13—C14—O18 | 178 (2) |
| O13—W4—O14—W4$^{ii}$ | −128.6 (14) | C5—C4—C3—C2 | 0 (3) |
| C9—C10—C6—N1 | 179.9 (14) | C11—C9—C8—C7 | 177.5 (19) |
| C9—C10—C6—C5 | 1 (2) | C11—C12—C13—N2 | 0 (3) |
| C9—C10—N2—Dy1 | 179.4 (12) | C11—C12—C13—C14 | 179.6 (19) |
| C9—C10—N2—C13 | −1 (2) | C14—C13—N2—Dy1 | 0 (2) |
| C9—C8—C7—C5 | 0 (3) | C14—C13—N2—C10 | −179.3 (15) |
| O16—C1—C2—N1 | −3.0 (19) | O4—W1—O3—W2 | 59.7 (12) |
| O16—C1—C2—C3 | 174.5 (15) | O4—Si1—O9—W4 | 176.8 (4) |
| N1—C6—C5—C4 | 2 (2) | O4—Si1—O9—W2 | −61.9 (6) |
| N1—C6—C5—C7 | −179.3 (15) | O4—Si1—O9—W3 | 57.4 (6) |
| N1—C2—C3—C4 | 0 (3) | O14—W4—O12—W3 | −86.1 (7) |
| O9—W4—O12—W3 | −1.3 (5) | O14$^{i}$—W4—O12—W3 | −1.2 (15) |
| O9—W4—O14—W4$^{ii}$ | 56.5 (13) | O14$^{i}$—W4—O13—Dy1 | −127.2 (15) |
| O9—W2—O8—W4 | −0.3 (5) | O14—W4—O13—Dy1 | −39.4 (16) |
| O9—W2—O5—W3$^{i}$ | 56.7 (13) | O14$^{i}$—W4—O14—W4$^{ii}$ | −26.6 (16) |
| O9—W3—O11—W1$^{ii}$ | 56.8 (13) | O5—W2—O8—W4 | −84.9 (6) |
| O9$^{i}$—Si1—O9—W4 | −62.8 (6) | O5$^{ii}$—W3—O11—W1$^{ii}$ | −26.5 (13) |
| O9$^{ii}$—Si1—O9—W4 | 56.4 (7) | | |

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

## Sodium aqua tris[tetraaqua(μ-4-hydroxypyridine-2,6-dicarboxylato)praseodymium(III)] silicododecatungstate dodecahydrate (jtm570b_4_a)

*Crystal data*

$[NaPr(C_7H_3NO_5)_3(H_2O)_{13}(SiW_{12}O_{40})]\cdot 12H_2O$
$M_r$ = 4307.67
Trigonal, $R3$
$a$ = 18.119 (3) Å
$c$ = 21.078 (3) Å
$V$ = 5993 (2) Å$^3$
$Z$ = 3
$F(000)$ = 5790
$D_x$ = 3.601 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9882 reflections
$\theta$ = 2.3–29.1°
$\mu$ = 19.14 mm$^{-1}$
$T$ = 100 K
Column, light yellow
0.24 × 0.13 × 0.12 mm

*Data collection*

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2009)
$T_{min}$ = 0.09, $T_{max}$ = 0.22
74256 measured reflections
7142 independent reflections
6106 reflections with $I > 2\sigma(I)$



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$R_{int}$ = 0.085
$\theta_{max}$ = 29.2°, $\theta_{min}$ = 1.6°
$h$ = −24→24
$k$ = −24→24
$l$ = −28→28

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.065
$S$ = 1.00
7142 reflections
385 parameters
241 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.97 e Å$^{-3}$
$\Delta\rho_{min}$ = −2.07 e Å$^{-3}$
Absolute structure: Flack $x$ determined using 2688 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.006 (7)

*Special details*

**Experimental**. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in $\omega$, colllected at $\varphi$ = 0.00, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in $\varphi$, collected at $\omega$ = -30.00 and 210.00°. The scan time was 10 sec/frame. Analysis of 1347 reflections having I/$\sigma$(I) > 12 and chosen from the full data set with *CELL_NOW* (Sheldrick, 2008) showed the crystal to belong to the trigonal system and to have a very minor twin component. The raw data were processed using the multi-component version of *SAINT* under control of the two-component orientation file generated by *CELL_NOW*.

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger. Hatoms attached to carbon were placed in calculated positions (C—H = 0.95 Å) while those attached to oxygen were placed in positions that would generate the most favorable hydrogen bonding interactions with O—H = 0.87 Å. All were included as riding contributions with displacement parameters 1.2 - 1.5 times those of the attached atoms. An attempt to refine the model with the full twinned data led to some atoms becoming NPD and since the twin component was minor, it was not included in the final refinement.
the crystal used was mounted on a nylon loop with a drop of heavy oil and mounted in a cold nitrogen stream on a Bruker Smart *APEX* CCD diffractometer. A full sphere of data was collected from which it was determined that the crystal consisted of two components (*CELL*-NOW). The raw data were converted to $F^2$ values using the multi-component version of *SAINT* under the control of the 2-component orientation file generated by *CELL*-NOW. Correction for absorption and merging of equivalent reflections for the 2-component reflection file was carried out with TWINABS which also extracted a single-component reflection file from the full data set for structure solution. The structure was solved by direct methods and refined by full-matrix, least squares.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Na1 | 0.333333 | 0.666667 | 0.2314 (5) | 0.038 (3) | |
| W1 | 0.25977 (4) | 0.53062 (4) | 0.48154 (2) | 0.00999 (12) | |
| W2 | 0.13249 (4) | 0.48260 (4) | 0.60810 (2) | 0.01449 (13) | |
| W3 | 0.15307 (4) | 0.69539 (4) | 0.61336 (2) | 0.01467 (14) | |
| W4 | 0.21000 (4) | 0.61161 (4) | 0.75405 (3) | 0.01871 (15) | |



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| Pr1 | 0.16948 (6) | 0.42412 (6) | 0.29909 (4) | 0.0231 (2) |
| Si1 | 0.333333 | 0.666667 | 0.6130 (3) | 0.0060 (10) |
| O1 | 0.3227 (7) | 0.4982 (7) | 0.2939 (5) | 0.025 (2) |
| O2 | 0.4232 (7) | 0.6357 (7) | 0.2907 (5) | 0.031 (3) |
| O3 | 0.6776 (7) | 0.7460 (7) | 0.3773 (5) | 0.024 (2) |
| O4 | 0.7212 (8) | 0.6804 (8) | 0.4459 (5) | 0.039 (3) |
| O5 | 0.4381 (9) | 0.4029 (8) | 0.4840 (6) | 0.042 (3) |
| H5 | 0.389837 | 0.364795 | 0.471572 | 0.063* |
| O6 | 0.2088 (10) | 0.4350 (9) | 0.1846 (6) | 0.056 (4) |
| H6A | 0.263966 | 0.464596 | 0.181036 | 0.085* |
| H6B | 0.186077 | 0.460446 | 0.164136 | 0.085* |
| O7 | 0.0718 (9) | 0.4521 (9) | 0.2250 (6) | 0.053 (4) |
| H7A | 0.019239 | 0.421080 | 0.237491 | 0.079* |
| H7B | 0.076639 | 0.438468 | 0.186281 | 0.079* |
| O8 | 0.0681 (7) | 0.2813 (7) | 0.2456 (5) | 0.032 (3) |
| H8A | 0.097665 | 0.261656 | 0.226972 | 0.047* |
| H8B | 0.037425 | 0.289026 | 0.217472 | 0.047* |
| O9 | 0.2233 (7) | 0.3224 (7) | 0.3174 (5) | 0.037 (3) |
| H9A | 0.183122 | 0.275868 | 0.334543 | 0.056* |
| H9B | 0.267011 | 0.345728 | 0.342743 | 0.056* |
| O10 | 0.2354 (6) | 0.4843 (6) | 0.4074 (4) | 0.015 (2) |
| O11 | 0.0276 (7) | 0.4063 (7) | 0.6181 (5) | 0.022 (2) |
| O12 | 0.1309 (7) | 0.5762 (7) | 0.8086 (5) | 0.025 (2) |
| O13 | 0.0551 (7) | 0.6863 (7) | 0.6217 (5) | 0.024 (2) |
| O14 | 0.3762 (5) | 0.6132 (5) | 0.4720 (4) | 0.0095 (18) |
| O15 | 0.2857 (6) | 0.4523 (6) | 0.5222 (4) | 0.015 (2) |
| O16 | 0.1485 (6) | 0.4700 (6) | 0.5200 (4) | 0.016 (2) |
| O17 | 0.1244 (6) | 0.5798 (6) | 0.5935 (4) | 0.016 (2) |
| O18 | 0.1632 (6) | 0.5225 (6) | 0.6932 (4) | 0.019 (2) |
| O19 | 0.1760 (6) | 0.6706 (6) | 0.6954 (4) | 0.018 (2) |
| O20 | 0.2894 (6) | 0.7213 (6) | 0.7886 (5) | 0.022 (2) |
| O21 | 0.2267 (6) | 0.8131 (6) | 0.6237 (4) | 0.015 (2) |
| O22 | 0.2918 (5) | 0.7230 (5) | 0.5879 (4) | 0.0076 (17) |
| O23 | 0.333333 | 0.666667 | 0.6905 (7) | 0.011 (3) |
| N1 | 0.5262 (8) | 0.6094 (7) | 0.3649 (6) | 0.020 (3) |
| C1 | 0.3930 (11) | 0.5599 (11) | 0.3123 (8) | 0.029 (4) |
| C2 | 0.4468 (10) | 0.5463 (10) | 0.3609 (7) | 0.021 (3) |
| C3 | 0.4127 (11) | 0.4739 (10) | 0.3990 (7) | 0.028 (4) |
| H3 | 0.355016 | 0.429804 | 0.395111 | 0.033* |
| C4 | 0.4670 (11) | 0.4694 (11) | 0.4427 (8) | 0.027 (4) |
| C5 | 0.5495 (10) | 0.5347 (10) | 0.4472 (7) | 0.021 (3) |
| H5A | 0.586555 | 0.531993 | 0.477771 | 0.026* |
| C6 | 0.5795 (10) | 0.6054 (10) | 0.4071 (7) | 0.017 (3) |
| C7 | 0.6672 (9) | 0.6826 (9) | 0.4105 (7) | 0.018 (3) |
| O24 | 0.8781 (10) | 0.7242 (11) | 0.3652 (7) | 0.076 (5) |
| H24A | 0.832420 | 0.675348 | 0.358365 | 0.114* |
| H24B | 0.908181 | 0.718589 | 0.394985 | 0.114* |
| O25 | 0.9855 (12) | 0.7199 (12) | 0.4581 (8) | 0.078 (5) |



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| O26 | 0.419 (3) | 0.796 (3) | 0.162 (3) | 0.089 (17) | 0.333 |
| H26A | 0.407985 | 0.833191 | 0.180072 | 0.133* | 0.3333 |
| H26B | 0.398461 | 0.801453 | 0.126332 | 0.133* | 0.3333 |
| O27 | 0.8519 (17) | 0.8712 (16) | 0.3783 (11) | 0.047 (7) | 0.5 |
| H27A | 0.894064 | 0.862536 | 0.386301 | 0.071* | 0.5 |
| H27B | 0.845674 | 0.872527 | 0.337500 | 0.071* | 0.5 |
| O28 | 0.1006 (19) | 0.5532 (18) | 0.1200 (14) | 0.062 (8) | 0.5 |
| H28A | 0.106582 | 0.552073 | 0.160863 | 0.093* | 0.5 |
| H28B | 0.057832 | 0.560834 | 0.111714 | 0.093* | 0.5 |
| O29 | 0.539 (2) | 0.4313 (19) | 0.5778 (13) | 0.030 (5) | 0.3822 |
| H29A | 0.575381 | 0.471452 | 0.602593 | 0.045* | 0.3822 |
| H29B | 0.489431 | 0.427642 | 0.581411 | 0.045* | 0.3822 |
| O29A | 0.843 (2) | 1.032 (2) | 0.2569 (17) | 0.030 (5) | 0.3047 |
| H29C | 0.820662 | 1.043854 | 0.224200 | 0.045* | 0.3047 |
| H29D | 0.842092 | 1.061804 | 0.289391 | 0.045* | 0.3047 |
| O29B | 0.860 (2) | 0.949 (2) | 0.2776 (17) | 0.030 (5) | 0.3134 |
| H29E | 0.865937 | 0.999268 | 0.275746 | 0.045* | 0.3134 |
| H29F | 0.858118 | 0.929738 | 0.239316 | 0.045* | 0.3134 |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Na1 | 0.051 (5) | 0.051 (5) | 0.013 (6) | 0.025 (2) | 0.000 | 0.000 |
| W1 | 0.0121 (3) | 0.0115 (3) | 0.0055 (2) | 0.0051 (2) | −0.0007 (2) | −0.0016 (2) |
| W2 | 0.0142 (3) | 0.0158 (3) | 0.0107 (3) | 0.0054 (3) | 0.0044 (2) | 0.0018 (2) |
| W3 | 0.0154 (3) | 0.0195 (3) | 0.0107 (3) | 0.0099 (3) | 0.0037 (2) | 0.0002 (2) |
| W4 | 0.0241 (3) | 0.0247 (3) | 0.0068 (3) | 0.0118 (3) | 0.0057 (2) | 0.0023 (2) |
| Pr1 | 0.0280 (5) | 0.0301 (5) | 0.0095 (4) | 0.0132 (4) | −0.0055 (3) | −0.0069 (3) |
| Si1 | 0.0078 (15) | 0.0078 (15) | 0.002 (2) | 0.0039 (7) | 0.000 | 0.000 |
| O1 | 0.024 (5) | 0.026 (5) | 0.024 (5) | 0.011 (4) | 0.004 (4) | −0.005 (4) |
| O2 | 0.033 (5) | 0.029 (5) | 0.026 (5) | 0.012 (4) | 0.001 (4) | 0.001 (4) |
| O3 | 0.025 (5) | 0.025 (5) | 0.025 (5) | 0.015 (4) | −0.001 (4) | −0.003 (4) |
| O4 | 0.037 (6) | 0.039 (7) | 0.029 (6) | 0.010 (5) | −0.014 (5) | 0.004 (5) |
| O5 | 0.056 (8) | 0.037 (7) | 0.032 (6) | 0.023 (6) | 0.016 (6) | 0.009 (5) |
| O6 | 0.061 (8) | 0.073 (9) | 0.030 (7) | 0.030 (7) | 0.003 (6) | −0.003 (6) |
| O7 | 0.052 (8) | 0.060 (8) | 0.019 (6) | 0.007 (6) | −0.020 (5) | 0.007 (5) |
| O8 | 0.024 (5) | 0.035 (6) | 0.035 (6) | 0.015 (5) | −0.007 (5) | −0.020 (5) |
| O9 | 0.024 (6) | 0.031 (6) | 0.049 (7) | 0.008 (5) | 0.002 (5) | −0.008 (5) |
| O10 | 0.012 (4) | 0.016 (4) | 0.010 (4) | 0.003 (3) | 0.001 (3) | −0.004 (3) |
| O11 | 0.022 (5) | 0.024 (5) | 0.019 (5) | 0.011 (5) | 0.003 (4) | 0.001 (4) |
| O12 | 0.032 (6) | 0.031 (6) | 0.014 (5) | 0.017 (5) | 0.005 (4) | 0.007 (4) |
| O13 | 0.023 (5) | 0.029 (6) | 0.019 (5) | 0.012 (5) | 0.003 (4) | 0.002 (4) |
| O14 | 0.014 (4) | 0.011 (4) | 0.002 (4) | 0.006 (3) | −0.001 (3) | −0.001 (3) |
| O15 | 0.016 (4) | 0.014 (4) | 0.012 (4) | 0.006 (3) | 0.002 (3) | −0.001 (3) |
| O16 | 0.021 (4) | 0.016 (4) | 0.011 (4) | 0.010 (4) | −0.001 (3) | −0.001 (3) |
| O17 | 0.012 (4) | 0.022 (4) | 0.012 (4) | 0.008 (4) | 0.001 (3) | −0.002 (3) |
| O18 | 0.020 (4) | 0.023 (5) | 0.012 (4) | 0.009 (4) | 0.003 (4) | 0.001 (4) |
| O19 | 0.022 (4) | 0.019 (4) | 0.013 (4) | 0.009 (4) | 0.005 (4) | −0.003 (3) |



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|---|---|---|---|---|---|---|
| O20 | 0.025 (5) | 0.026 (5) | 0.015 (4) | 0.014 (4) | −0.001 (4) | −0.003 (4) |
| O21 | 0.021 (4) | 0.018 (4) | 0.010 (4) | 0.013 (4) | 0.000 (3) | −0.001 (3) |
| O22 | 0.008 (2) | 0.008 (2) | 0.007 (2) | 0.0039 (15) | −0.0016 (13) | 0.0004 (13) |
| O23 | 0.013 (4) | 0.013 (4) | 0.005 (5) | 0.0067 (18) | 0.000 | 0.000 |
| N1 | 0.028 (5) | 0.016 (5) | 0.018 (5) | 0.013 (4) | −0.003 (4) | −0.006 (4) |
| C1 | 0.030 (6) | 0.030 (6) | 0.028 (6) | 0.016 (5) | 0.005 (5) | −0.008 (5) |
| C2 | 0.025 (6) | 0.022 (6) | 0.018 (6) | 0.013 (5) | −0.001 (5) | −0.004 (5) |
| C3 | 0.027 (6) | 0.029 (6) | 0.026 (6) | 0.013 (5) | 0.011 (5) | −0.001 (5) |
| C4 | 0.030 (6) | 0.028 (6) | 0.023 (6) | 0.015 (5) | 0.014 (5) | −0.007 (5) |
| C5 | 0.022 (6) | 0.026 (6) | 0.017 (6) | 0.012 (5) | −0.003 (5) | −0.004 (5) |
| C6 | 0.021 (6) | 0.021 (6) | 0.010 (5) | 0.012 (5) | 0.001 (4) | −0.006 (4) |
| C7 | 0.021 (6) | 0.021 (6) | 0.015 (5) | 0.012 (5) | 0.002 (4) | −0.004 (4) |
| O24 | 0.054 (9) | 0.103 (11) | 0.058 (9) | 0.030 (8) | −0.006 (7) | −0.004 (8) |
| O25 | 0.098 (10) | 0.076 (10) | 0.069 (9) | 0.050 (8) | −0.012 (8) | −0.011 (8) |
| O26 | 0.09 (2) | 0.10 (2) | 0.08 (2) | 0.047 (15) | −0.009 (13) | 0.017 (13) |
| O27 | 0.062 (12) | 0.048 (12) | 0.028 (11) | 0.025 (10) | 0.001 (9) | 0.002 (9) |
| O28 | 0.073 (14) | 0.051 (12) | 0.058 (13) | 0.028 (10) | −0.019 (11) | 0.013 (10) |
| O29 | 0.036 (8) | 0.026 (7) | 0.028 (7) | 0.016 (6) | −0.003 (6) | 0.000 (6) |
| O29A | 0.036 (8) | 0.026 (7) | 0.028 (7) | 0.016 (6) | −0.003 (6) | 0.000 (6) |
| O29B | 0.036 (8) | 0.026 (7) | 0.028 (7) | 0.016 (6) | −0.003 (6) | 0.000 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Na1—O2$^{i}$ | 2.333 (13) | Si1—O22 | 1.629 (9) |
| Na1—O2$^{ii}$ | 2.333 (13) | Si1—O22$^{i}$ | 1.629 (9) |
| Na1—O2 | 2.333 (13) | Si1—O22$^{ii}$ | 1.629 (9) |
| Na1—O26 | 2.53 (5) | Si1—O23 | 1.633 (16) |
| Na1—O26$^{ii}$ | 2.53 (5) | O1—C1 | 1.264 (19) |
| Na1—O26$^{i}$ | 2.53 (5) | O2—C1 | 1.282 (19) |
| Na1—Pr1$^{i}$ | 4.137 (4) | O3—C7 | 1.276 (17) |
| Na1—Pr1 | 4.137 (4) | O4—C7 | 1.247 (18) |
| Na1—Pr1$^{ii}$ | 4.137 (4) | O5—C4 | 1.36 (2) |
| W1—O10 | 1.724 (9) | O5—H5 | 0.8399 |
| W1—O14 | 1.890 (9) | O6—H6A | 0.8699 |
| W1—O15 | 1.906 (9) | O6—H6B | 0.8701 |
| W1—O16 | 1.927 (10) | O7—H7A | 0.8699 |
| W1—O14$^{ii}$ | 1.938 (8) | O7—H7B | 0.8701 |
| W1—O22$^{i}$ | 2.320 (8) | O8—H8A | 0.8701 |
| W2—O11 | 1.714 (10) | O8—H8B | 0.8701 |
| W2—O17 | 1.864 (10) | O9—H9A | 0.8700 |
| W2—O18 | 1.911 (9) | O9—H9B | 0.8701 |
| W2—O16 | 1.911 (9) | N1—C2 | 1.318 (18) |
| W2—O21$^{i}$ | 1.969 (9) | N1—C6 | 1.340 (19) |
| W2—O22$^{i}$ | 2.321 (8) | C1—C2 | 1.52 (2) |
| W3—O13 | 1.708 (11) | C2—C3 | 1.39 (2) |
| W3—O21 | 1.879 (9) | C3—C4 | 1.38 (2) |
| W3—O19 | 1.884 (10) | C3—H3 | 0.9500 |
| W3—O17 | 1.936 (10) | C4—C5 | 1.37 (2) |



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|---|---|---|---|
| W3—O15$^{ii}$ | 1.945 (9) | C5—C6 | 1.40 (2) |
| W3—O22 | 2.367 (9) | C5—H5A | 0.9500 |
| W4—O12 | 1.693 (10) | C6—C7 | 1.51 (2) |
| W4—O18 | 1.897 (10) | O24—H24A | 0.8700 |
| W4—O20$^{i}$ | 1.919 (10) | O24—H24B | 0.8700 |
| W4—O20 | 1.922 (10) | O26—H26A | 0.8692 |
| W4—O19 | 1.926 (10) | O26—H26B | 0.8697 |
| W4—O23 | 2.357 (8) | O27—H27A | 0.8700 |
| Pr1—O1 | 2.407 (11) | O27—H27B | 0.8700 |
| Pr1—O3$^{ii}$ | 2.468 (10) | O28—H28A | 0.8699 |
| Pr1—O2$^{ii}$ | 2.477 (11) | O28—H28B | 0.8702 |
| Pr1—O6 | 2.496 (13) | O29—H29A | 0.8701 |
| Pr1—O9 | 2.509 (12) | O29—H29B | 0.8698 |
| Pr1—O10 | 2.554 (9) | O29A—H29C | 0.8702 |
| Pr1—N1$^{ii}$ | 2.567 (12) | O29A—H29D | 0.8699 |
| Pr1—O8 | 2.567 (11) | O29B—H29E | 0.8698 |
| Pr1—O7 | 2.593 (12) | O29B—H29F | 0.8701 |

| | | | |
|---|---|---|---|
| O2$^{i}$—Na1—O2$^{ii}$ | 94.0 (5) | O9—Pr1—O10 | 84.6 (3) |
| O2$^{i}$—Na1—O2 | 94.0 (5) | O1—Pr1—N1$^{ii}$ | 124.3 (4) |
| O2$^{ii}$—Na1—O2 | 94.0 (5) | O3$^{ii}$—Pr1—N1$^{ii}$ | 63.0 (4) |
| O2$^{i}$—Na1—O26 | 71.8 (14) | O2$^{ii}$—Pr1—N1$^{ii}$ | 63.5 (4) |
| O2$^{ii}$—Na1—O26 | 151.8 (13) | O6—Pr1—N1$^{ii}$ | 134.0 (4) |
| O2—Na1—O26 | 110.8 (12) | O9—Pr1—N1$^{ii}$ | 134.7 (4) |
| O2$^{i}$—Na1—O26$^{ii}$ | 151.8 (13) | O10—Pr1—N1$^{ii}$ | 66.7 (3) |
| O2$^{ii}$—Na1—O26$^{ii}$ | 110.8 (12) | O1—Pr1—O8 | 125.9 (3) |
| O2—Na1—O26$^{ii}$ | 71.8 (14) | O3$^{ii}$—Pr1—O8 | 69.6 (4) |
| O26—Na1—O26$^{ii}$ | 90.2 (18) | O2$^{ii}$—Pr1—O8 | 139.6 (4) |
| O2$^{i}$—Na1—O26$^{i}$ | 110.8 (12) | O6—Pr1—O8 | 71.8 (4) |
| O2$^{ii}$—Na1—O26$^{i}$ | 71.8 (14) | O9—Pr1—O8 | 70.8 (4) |
| O2—Na1—O26$^{i}$ | 151.8 (13) | O10—Pr1—O8 | 140.3 (3) |
| O26—Na1—O26$^{i}$ | 90.2 (18) | N1$^{ii}$—Pr1—O8 | 109.7 (4) |
| O26$^{ii}$—Na1—O26$^{i}$ | 90.2 (18) | O1—Pr1—O7 | 125.0 (4) |
| O2$^{i}$—Na1—Pr1$^{i}$ | 77.1 (3) | O3$^{ii}$—Pr1—O7 | 102.9 (4) |
| O2$^{ii}$—Na1—Pr1$^{i}$ | 121.4 (4) | O2$^{ii}$—Pr1—O7 | 66.6 (4) |
| O2—Na1—Pr1$^{i}$ | 31.7 (3) | O6—Pr1—O7 | 66.3 (5) |
| O26—Na1—Pr1$^{i}$ | 80.0 (12) | O9—Pr1—O7 | 142.2 (4) |
| O26$^{ii}$—Na1—Pr1$^{i}$ | 78.6 (14) | O10—Pr1—O7 | 132.4 (4) |
| O26$^{i}$—Na1—Pr1$^{i}$ | 165.0 (13) | N1$^{ii}$—Pr1—O7 | 70.2 (4) |
| O2$^{i}$—Na1—Pr1 | 121.4 (4) | O8—Pr1—O7 | 73.6 (4) |
| O2$^{ii}$—Na1—Pr1 | 31.7 (3) | O1—Pr1—Na1 | 51.4 (3) |
| O2—Na1—Pr1 | 77.1 (3) | O3$^{ii}$—Pr1—Na1 | 153.4 (3) |
| O26—Na1—Pr1 | 165.0 (13) | O2$^{ii}$—Pr1—Na1 | 29.7 (3) |
| O26$^{ii}$—Na1—Pr1 | 80.0 (12) | O6—Pr1—Na1 | 63.7 (4) |
| O26$^{i}$—Na1—Pr1 | 78.6 (14) | O9—Pr1—Na1 | 119.8 (3) |
| Pr1$^{i}$—Na1—Pr1 | 108.75 (14) | O10—Pr1—Na1 | 85.4 (3) |
| O2$^{i}$—Na1—Pr1$^{ii}$ | 31.7 (3) | N1$^{ii}$—Pr1—Na1 | 93.1 (3) |
| O2$^{ii}$—Na1—Pr1$^{ii}$ | 77.1 (3) | O8—Pr1—Na1 | 133.7 (3) |



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|---|---|---|---|
| O2—Na1—Pr1$^{ii}$ | 121.4 (4) | O7—Pr1—Na1 | 77.4 (3) |
| O26—Na1—Pr1$^{ii}$ | 78.6 (14) | O22—Si1—O22$^{i}$ | 110.0 (4) |
| O26$^{ii}$—Na1—Pr1$^{ii}$ | 165.0 (13) | O22—Si1—O22$^{ii}$ | 110.0 (4) |
| O26$^{i}$—Na1—Pr1$^{ii}$ | 80.0 (12) | O22$^{i}$—Si1—O22$^{ii}$ | 110.0 (4) |
| Pr1$^{i}$—Na1—Pr1$^{ii}$ | 108.75 (14) | O22—Si1—O23 | 108.9 (4) |
| Pr1—Na1—Pr1$^{ii}$ | 108.75 (14) | O22$^{i}$—Si1—O23 | 108.9 (4) |
| O10—W1—O14 | 101.6 (4) | O22$^{ii}$—Si1—O23 | 108.9 (4) |
| O10—W1—O15 | 98.3 (4) | C1—O1—Pr1 | 148.2 (10) |
| O14—W1—O15 | 92.6 (4) | C1—O2—Na1 | 118.2 (10) |
| O10—W1—O16 | 99.4 (4) | C1—O2—Pr1$^{i}$ | 122.8 (10) |
| O14—W1—O16 | 158.7 (4) | Na1—O2—Pr1$^{i}$ | 118.7 (5) |
| O15—W1—O16 | 87.9 (4) | C7—O3—Pr1$^{i}$ | 126.1 (9) |
| O10—W1—O14$^{ii}$ | 102.5 (4) | C4—O5—H5 | 108.1 |
| O14—W1—O14$^{ii}$ | 86.4 (5) | Pr1—O6—H6A | 109.1 |
| O15—W1—O14$^{ii}$ | 159.0 (4) | Pr1—O6—H6B | 109.3 |
| O16—W1—O14$^{ii}$ | 85.6 (4) | H6A—O6—H6B | 109.5 |
| O10—W1—O22$^{i}$ | 169.9 (4) | Pr1—O7—H7A | 109.0 |
| O14—W1—O22$^{i}$ | 86.3 (3) | Pr1—O7—H7B | 109.5 |
| O15—W1—O22$^{i}$ | 75.0 (3) | H7A—O7—H7B | 109.5 |
| O16—W1—O22$^{i}$ | 73.2 (3) | Pr1—O8—H8A | 109.5 |
| O14$^{ii}$—W1—O22$^{i}$ | 84.0 (3) | Pr1—O8—H8B | 109.2 |
| O11—W2—O17 | 101.7 (4) | H8A—O8—H8B | 109.5 |
| O11—W2—O18 | 100.7 (5) | Pr1—O9—H9A | 109.4 |
| O17—W2—O18 | 86.8 (4) | Pr1—O9—H9B | 109.3 |
| O11—W2—O16 | 101.3 (5) | H9A—O9—H9B | 109.5 |
| O17—W2—O16 | 92.3 (4) | W1—O10—Pr1 | 165.8 (5) |
| O18—W2—O16 | 157.7 (4) | W1—O14—W1$^{i}$ | 150.4 (5) |
| O11—W2—O21$^{i}$ | 99.9 (4) | W1—O15—W3$^{i}$ | 120.7 (5) |
| O17—W2—O21$^{i}$ | 158.2 (4) | W2—O16—W1 | 121.2 (5) |
| O18—W2—O21$^{i}$ | 86.6 (4) | W2—O17—W3 | 151.8 (5) |
| O16—W2—O21$^{i}$ | 86.1 (4) | W4—O18—W2 | 151.4 (6) |
| O11—W2—O22$^{i}$ | 171.1 (4) | W3—O19—W4 | 153.0 (5) |
| O17—W2—O22$^{i}$ | 85.9 (4) | W4$^{ii}$—O20—W4 | 121.9 (5) |
| O18—W2—O22$^{i}$ | 84.3 (4) | W3—O21—W2$^{ii}$ | 122.2 (5) |
| O16—W2—O22$^{i}$ | 73.4 (4) | Si1—O22—W1$^{ii}$ | 123.8 (5) |
| O21$^{i}$—W2—O22$^{i}$ | 72.8 (3) | Si1—O22—W2$^{ii}$ | 123.7 (4) |
| O13—W3—O21 | 102.2 (5) | W1$^{ii}$—O22—W2$^{ii}$ | 92.2 (3) |
| O13—W3—O19 | 103.0 (4) | Si1—O22—W3 | 124.6 (5) |
| O21—W3—O19 | 92.8 (4) | W1$^{ii}$—O22—W3 | 91.1 (3) |
| O13—W3—O17 | 102.4 (4) | W2$^{ii}$—O22—W3 | 91.9 (3) |
| O21—W3—O17 | 155.2 (4) | Si1—O23—W4 | 124.7 (3) |
| O19—W3—O17 | 85.0 (4) | Si1—O23—W4$^{ii}$ | 124.7 (3) |
| O13—W3—O15$^{ii}$ | 98.8 (4) | W4—O23—W4$^{ii}$ | 90.9 (4) |
| O21—W3—O15$^{ii}$ | 87.6 (4) | Si1—O23—W4$^{i}$ | 124.7 (3) |
| O19—W3—O15$^{ii}$ | 157.6 (4) | W4—O23—W4$^{i}$ | 90.9 (4) |
| O17—W3—O15$^{ii}$ | 85.3 (4) | W4$^{ii}$—O23—W4$^{i}$ | 90.9 (4) |
| O13—W3—O22 | 170.7 (4) | C2—N1—C6 | 119.9 (13) |
| O21—W3—O22 | 73.2 (3) | C2—N1—Pr1$^{i}$ | 120.3 (10) |



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|---|---|---|---|
| O19—W3—O22 | 85.5 (4) | C6—N1—Pr1$^{i}$ | 119.6 (10) |
| O17—W3—O22 | 82.0 (3) | O1—C1—O2 | 122.7 (15) |
| O15$^{ii}$—W3—O22 | 73.2 (3) | O1—C1—C2 | 120.6 (15) |
| O12—W4—O18 | 101.7 (5) | O2—C1—C2 | 116.7 (15) |
| O12—W4—O20$^{i}$ | 100.7 (5) | N1—C2—C3 | 123.9 (14) |
| O18—W4—O20$^{i}$ | 90.7 (4) | N1—C2—C1 | 114.5 (14) |
| O12—W4—O20 | 100.9 (5) | C3—C2—C1 | 121.6 (14) |
| O18—W4—O20 | 157.2 (4) | C4—C3—C2 | 116.6 (15) |
| O20$^{i}$—W4—O20 | 88.7 (6) | C4—C3—H3 | 121.7 |
| O12—W4—O19 | 101.6 (4) | C2—C3—H3 | 121.7 |
| O18—W4—O19 | 84.7 (4) | O5—C4—C5 | 119.5 (15) |
| O20$^{i}$—W4—O19 | 157.7 (4) | O5—C4—C3 | 120.5 (16) |
| O20—W4—O19 | 87.2 (4) | C5—C4—C3 | 119.8 (15) |
| O12—W4—O23 | 171.9 (5) | C4—C5—C6 | 120.5 (14) |
| O18—W4—O23 | 84.4 (4) | C4—C5—H5A | 119.8 |
| O20$^{i}$—W4—O23 | 73.6 (4) | C6—C5—H5A | 119.8 |
| O20—W4—O23 | 73.6 (4) | N1—C6—C5 | 119.3 (14) |
| O19—W4—O23 | 84.2 (4) | N1—C6—C7 | 115.9 (13) |
| O1—Pr1—O3$^{ii}$ | 131.7 (4) | C5—C6—C7 | 124.7 (13) |
| O1—Pr1—O2$^{ii}$ | 75.1 (4) | O4—C7—O3 | 126.4 (14) |
| O3$^{ii}$—Pr1—O2$^{ii}$ | 125.7 (4) | O4—C7—C6 | 118.6 (13) |
| O1—Pr1—O6 | 73.0 (4) | O3—C7—C6 | 115.0 (13) |
| O3$^{ii}$—Pr1—O6 | 141.3 (4) | H24A—O24—H24B | 109.5 |
| O2$^{ii}$—Pr1—O6 | 85.6 (4) | Na1—O26—H26A | 101.6 |
| O1—Pr1—O9 | 69.7 (4) | Na1—O26—H26B | 120.6 |
| O3$^{ii}$—Pr1—O9 | 76.4 (4) | H26A—O26—H26B | 91.2 |
| O2$^{ii}$—Pr1—O9 | 144.2 (4) | H27A—O27—H27B | 109.5 |
| O6—Pr1—O9 | 90.4 (4) | H28A—O28—H28B | 109.5 |
| O1—Pr1—O10 | 68.9 (3) | H29A—O29—H29B | 109.5 |
| O3$^{ii}$—Pr1—O10 | 74.7 (3) | H29C—O29A—H29D | 109.5 |
| O2$^{ii}$—Pr1—O10 | 76.6 (3) | H29E—O29B—H29F | 109.5 |
| O6—Pr1—O10 | 140.9 (4) | | |

| | | | |
|---|---|---|---|
| O14—W1—O10—Pr1 | −127 (2) | O22$^{i}$—Si1—O23—W4 | −58.5 (3) |
| O15—W1—O10—Pr1 | 138 (2) | O22$^{ii}$—Si1—O23—W4 | −178.5 (3) |
| O16—W1—O10—Pr1 | 49 (2) | O22—Si1—O23—W4$^{ii}$ | −58.5 (3) |
| O14$^{ii}$—W1—O10—Pr1 | −39 (2) | O22$^{i}$—Si1—O23—W4$^{ii}$ | −178.5 (3) |
| O22$^{i}$—W1—O10—Pr1 | 91 (3) | O22$^{ii}$—Si1—O23—W4$^{ii}$ | 61.5 (3) |
| O10—W1—O14—W1$^{i}$ | 131.2 (10) | O22—Si1—O23—W4$^{i}$ | −178.5 (3) |
| O15—W1—O14—W1$^{i}$ | −129.8 (10) | O22$^{i}$—Si1—O23—W4$^{i}$ | 61.5 (3) |
| O16—W1—O14—W1$^{i}$ | −39.1 (17) | O22$^{ii}$—Si1—O23—W4$^{i}$ | −58.5 (3) |
| O14$^{ii}$—W1—O14—W1$^{i}$ | 29.2 (11) | Pr1—O1—C1—O2 | −78 (3) |
| O22$^{i}$—W1—O14—W1$^{i}$ | −55.0 (10) | Pr1—O1—C1—C2 | 103 (2) |
| O11—W2—O17—W3 | 123.6 (11) | Na1—O2—C1—O1 | 13 (2) |
| O18—W2—O17—W3 | 23.4 (11) | Pr1$^{i}$—O2—C1—O1 | −160.3 (11) |
| O16—W2—O17—W3 | −134.3 (11) | Na1—O2—C1—C2 | −168.4 (10) |
| O21$^{i}$—W2—O17—W3 | −49.0 (18) | Pr1$^{i}$—O2—C1—C2 | 18.4 (18) |
| O22$^{i}$—W2—O17—W3 | −61.1 (11) | C6—N1—C2—C3 | 1 (2) |



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|---|---|---|---|
| O12—W4—O18—W2 | 127.5 (12) | Pr1$^{i}$—N1—C2—C3 | −174.0 (11) |
| O20$^{i}$—W4—O18—W2 | −131.4 (12) | C6—N1—C2—C1 | 178.7 (12) |
| O20—W4—O18—W2 | −42.9 (19) | Pr1$^{i}$—N1—C2—C1 | 3.9 (16) |
| O19—W4—O18—W2 | 26.7 (12) | O1—C1—C2—N1 | 164.6 (13) |
| O23—W4—O18—W2 | −57.9 (11) | O2—C1—C2—N1 | −14.1 (19) |
| O13—W3—O19—W4 | 130.1 (13) | O1—C1—C2—C3 | −17 (2) |
| O21—W3—O19—W4 | −126.7 (13) | O2—C1—C2—C3 | 163.8 (14) |
| O17—W3—O19—W4 | 28.6 (12) | N1—C2—C3—C4 | −1 (2) |
| O15$^{ii}$—W3—O19—W4 | −36 (2) | C1—C2—C3—C4 | −178.3 (13) |
| O22—W3—O19—W4 | −53.8 (12) | C2—C3—C4—O5 | 176.9 (13) |
| O13—W3—O21—W2$^{ii}$ | −171.8 (5) | C2—C3—C4—C5 | 1 (2) |
| O19—W3—O21—W2$^{ii}$ | 84.3 (6) | O5—C4—C5—C6 | −177.3 (14) |
| O17—W3—O21—W2$^{ii}$ | 0.2 (13) | C3—C4—C5—C6 | −1 (2) |
| O15$^{ii}$—W3—O21—W2$^{ii}$ | −73.3 (5) | C2—N1—C6—C5 | −1 (2) |
| O22—W3—O21—W2$^{ii}$ | −0.1 (4) | Pr1$^{i}$—N1—C6—C5 | 173.7 (10) |
| O22$^{i}$—Si1—O22—W1$^{ii}$ | −58.1 (6) | C2—N1—C6—C7 | −176.7 (12) |
| O22$^{ii}$—Si1—O22—W1$^{ii}$ | 63.2 (6) | Pr1$^{i}$—N1—C6—C7 | −1.9 (15) |
| O23—Si1—O22—W1$^{ii}$ | −177.4 (3) | C4—C5—C6—N1 | 1 (2) |
| O22$^{i}$—Si1—O22—W2$^{ii}$ | −178.2 (3) | C4—C5—C6—C7 | 176.4 (13) |
| O22$^{ii}$—Si1—O22—W2$^{ii}$ | −56.9 (9) | Pr1$^{i}$—O3—C7—O4 | 173.4 (11) |
| O23—Si1—O22—W2$^{ii}$ | 62.4 (5) | Pr1$^{i}$—O3—C7—C6 | −9.0 (16) |
| O22$^{i}$—Si1—O22—W3 | 61.3 (9) | N1—C6—C7—O4 | −175.5 (13) |
| O22$^{ii}$—Si1—O22—W3 | −177.5 (4) | C5—C6—C7—O4 | 9 (2) |
| O23—Si1—O22—W3 | −58.1 (5) | N1—C6—C7—O3 | 6.6 (17) |
| O22—Si1—O23—W4 | 61.5 (3) | C5—C6—C7—O3 | −168.6 (13) |

Symmetry codes: (i) −*y*+1, *x*−*y*+1, *z*; (ii) −*x*+*y*, −*x*+1, *z*.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O6—H6*A*···O26$^{ii}$ | 0.87 | 2.12 | 2.91 (6) | 151 |
| O7—H7*A*···O11$^{iii}$ | 0.87 | 2.36 | 3.084 (17) | 141 |
| O7—H7*A*···O21$^{iv}$ | 0.87 | 2.29 | 2.988 (18) | 138 |
| O7—H7*B*···O4$^{v}$ | 0.87 | 2.16 | 2.956 (19) | 152 |
| O8—H8*A*···O12$^{vi}$ | 0.87 | 2.17 | 2.929 (15) | 146 |
| O8—H8*B*···O4$^{v}$ | 0.87 | 2.40 | 3.103 (17) | 138 |
| O9—H9*A*···O29*B*$^{ii}$ | 0.87 | 2.50 | 3.09 (4) | 123 |
| C5—H5*A*···O29 | 0.95 | 2.64 | 3.28 (3) | 126 |
| O24—H24*A*···O11$^{vii}$ | 0.87 | 2.48 | 3.109 (19) | 130 |
| O26—H26*A*···O7$^{ii}$ | 0.87 | 2.23 | 3.10 (6) | 180 |
| O26—H26*B*···O27$^{viii}$ | 0.87 | 1.97 | 2.84 (6) | 179 |
| O27—H27*A*···O24 | 0.87 | 2.42 | 2.94 (3) | 120 |
| O27—H27*B*···O29*B* | 0.87 | 1.79 | 2.51 (4) | 138 |
| O28—H28*A*···O7 | 0.87 | 2.09 | 2.75 (3) | 132 |
| O29—H29*A*···O11$^{i}$ | 0.87 | 2.59 | 3.18 (3) | 127 |
| O29*A*—H29*C*···O5$^{ix}$ | 0.87 | 1.96 | 2.83 (4) | 180 |



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|---|---|---|---|---|
| O29*A*—H29*D*···O24$^{x}$ | 0.87 | 1.91 | 2.78 (4) | 175 |
| O29*B*—H29*F*···O12$^{xi}$ | 0.87 | 2.27 | 3.03 (4) | 146 |

Symmetry codes: (i) −*y*+1, *x*−*y*+1, *z*; (ii) −*x*+*y*, −*x*+1, *z*; (iii) −*y*+1/3, *x*−*y*+2/3, *z*−1/3; (iv) −*x*+*y*−2/3, −*x*+2/3, *z*−1/3; (v) *x*−2/3, *y*−1/3, *z*−1/3; (vi) −*x*+*y*−1/3, −*x*+1/3, *z*−2/3; (vii) −*x*+*y*+1/3, −*x*+2/3, *z*−1/3; (viii) −*x*+*y*+1/3, −*x*+5/3, *z*−1/3; (ix) *x*+1/3, *y*+2/3, *z*−1/3; (x) −*x*+*y*+1, −*x*+2, *z*; (xi) *x*+2/3, *y*+1/3, *z*−2/3.



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