Electronic Supplementary Information

Two 1-D multi-nickel substituted arsenotungstate aggregates

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1. The discussion on the location of protons in 1 and 2.

It is well known that protons can be not precisely localized by X-ray single-crystal diffraction, but four μ_3-OH bridges (O33, O68, O33A, O68A, A: $1 - x$, $-y$, $-z$) on the $Ni_{18}As_4W_{34}$ unit and eighteen coordination water molecules (O1W–O9W, O1WA–O9WA, A: $1 - x$, $-y$, $-z$) attached to the Ni cations in **1** are completely localized by BVS calculations.[1] Furthermore, two free en molecules should be diprotonated to form two $[enH_2]^{2+}$ cations. Actually, the phenomena that N-containing organic molecules are often protonated under either acidic or basic conditions are very common in POM chemistry and coordination chemistry.[2] For example, in 1995, Hölscher *et al.* reported a microporous solid $[H_3N(CH_2)_6NH_3]_4[W_{18}P_2O_{62}]\cdot3H_2O$ with prontonated 1,6-diaminohexane molecules under acidic conditions.[2a] In 2008, Dolbecq *et al.* provided the examples $(C_2N_2H_{10})_{11}[\{(B-\alpha-PW_9\,O_{34})Fe_3(OH)_3\}_4(PO_4)_4Fe]\cdot38H_2O$ and $K_4(C_2N_2H_{10})_{12}[(\alpha-PW_{10}\,Fe_2O_{39})_4]\cdot30H_2O$, in which en molecules are also protonated under weak basic conditions.[2b,3] Therefore, the formula of **1** can be written as $[enH_2]_2[Ni(H_2O)_4]_2[Ni(en)_2]_2[Ni(en)]_2\{[(\alpha-AsW_6O_{26})$ $Ni_6(OH)_2(H_2O)_3(en)(B-\alpha-AsW_9O_{34})]_2$ $[W_4O_{16}][Ni_3(H_2O)_2(en)]_2\}\cdot16H_2O$.

Four μ_3-OH bridges (O35, O36, O35A, O36A, A: $-x$, $1 - y$, $1 - z$) on the $Ni_{20}As_4W_{34}$ unit and all the coordination water molecules attached to the Ni cations in **2** are completely localized by bond valence sum (BVS) calculations (Table S1).[1] Considering the charge-neutrality principle, it is necessary to supplement four protons to the molecular unit of **2**. To determine the possible sites binding four protons, BVS calculations have been also performed on all remaining oxygen atoms (Table S1).[9] The results indicate that BVS values of all remaining oxygen atoms are in the range of 1.19–2.08, which suggests that it is very difficult to accurately localize the possible sites binding four protons, as a result, four protons may be delocalized on the whole $Ni_{20}As_4W_{34}$ framework. In fact, such phenomenon that protons are delocalized on the whole polyoxoanion backbone is very common in POM chemistry.[4]

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3   C. Pichon, A. Dolbecq, P. Mialane, J. Marrot, E. Rivièreb and F. Sécheresse, *Dalton Trans.,* 2008, 71.

4   (a) R. Contant and A.Tézé, *Inorg. Chem.,* 1985, **24**, 4610; (b) D.-L. Long, H. Abbas, P. Kögerler and L. Cronin, *J. Am. Chem. Soc.,* 2004, **126**, 13880; (c) H. N. Miras, J. Yan, D.-L. Long and L. Cronin, *Angew. Chem., Int. Ed.,* 2008, **47**, 8420.

2. The analyses on the relation between the magnetic behavior and the structure of 1.

In the molecular structural unit of **1**, apart from two pendent $[Ni2(en)]^{2+}$, $[Ni2A(en)]^{2+}$, four bridging $[Ni1(en)_2]^{2+}$, $[Ni1A(en)_2]^{2+}$, $[Ni3(H_2O)_4]^{2+}$ and $[Ni3A(H_2O)_4]^{2+}$ cations, the remaining Ni^{II} centers (Ni4, Ni5, Ni6, Ni7, Ni8, Ni9, Ni10, Ni11, Ni12, Ni4A, Ni5A, Ni6A, Ni7A, Ni8A, Ni9A, Ni10A, Ni11A, Ni12A) are all anchored by two $[B\text{-}\alpha\text{-}AsW_9O_{34}]^{9-}$, two $[\alpha\text{-}AsW_6O_{26}]^{11-}$ and one $[W_4O_{16}]^{8-}$ fragments (Figures 2a,2b). On one hand, the Ni7, Ni8, Ni9, Ni10, Ni11, Ni12 group and Ni7A, Ni8A, Ni9A, Ni10A, Ni11A, Ni12A group construct two symmetrically equivalent hexa-Ni^{II} $[Ni_6(OH)_2(H_2O)_3(en)]^{10+}$ clusters, which are respectively sandwiched by a nonmagnetic $[B\text{-}\alpha\text{-}AsW_9O_{34}]^{9-}$ fragment and a nonmagnetic $[\alpha\text{-}AsW_6O_{26}]^{11-}$ fragment resulting in two asymmetric sandwich-type $[(\alpha\text{-}AsW_6O_{26})Ni_6(OH)_2(H_2O)_3(en)\ (B\text{-}\alpha\text{-}AsW_9O_{34})]^{10-}$ subunits (Fig. 1d). Moreover, two $[(\alpha\text{-}AsW_6O_{26})Ni_6(OH)_2(H_2O)_3(en)(B\text{-}\alpha\text{-}AsW_9O_{34})]^{10-}$ subunits are separated by the nonmagnetic $[W_4O_{16}]^{8-}$ fragment. As a result, the magnetic couplings between two hexa-Ni^{II} $[Ni_6(OH)_2\ (H_2O)_3(en)]^{10+}$ clusters are very weak so as to be negligible, therefore, the magnetic behavior of two $[(\alpha\text{-}AsW_6O_{26})Ni_6\ (OH)_2(H_2O)_3(en)(B\text{-}\alpha\text{-}AsW_9O_{34})]^{10-}$ subunits can be viewed as the addition of the magnetic behaviors of two hexa-Ni^{II} $[Ni_6(OH)_2(H_2O)_3(en)]^{10+}$ clusters. In the hexa-Ni^{II} $[Ni_6(OH)_2(H_2O)_3(en)]^{10+}$ cluster, the $Ni_{ex}\cdots Ni_{ex}$ distances among Ni7, Ni9 and Ni12 cations range from 6.183(3) to 6.256(3) Å while the $Ni_{in}\cdots Ni_{in}$ / $Ni_{ex}\cdots Ni_{in}$ separations among Ni7, Ni8, Ni9, Ni10, Ni11 and Ni12 cations are 3.074(3)–3.323(3) Å. The Ni–O–Ni bond angles are in the range of 94.1(4)–106.2(4)°. Such distribution motif of the six octahedral Ni^{II} ions has been observed in the previous studies.[1,2] In these studies, the magnetic behaviors of the hexa-Ni^{II} clusters have been deeply investigated and the experimental and theoretical results have proved that the hexa-Ni^{II} clusters show the weak ferromagnetic coupling interactions.[3] For example, in $[\{Ni_6(\mu_3\text{-}OH)_3(en)_3(H_2O)_6\}(B\text{-}\alpha\text{-}PW_9O_{34})]\cdot 7H_2O$ [$d_{Niex\cdots Niex}$: 6.232(3)–6.260(5) Å, $d_{Niin\cdots Niin/\ Niex\cdots Niin}$: 3.108(5)–4.144(3) Å, $\angle Ni\text{-}O\text{-}Ni$: 91.7(2)–102.4(2)°], the magnetic exchange constant between Ni_{ex} and Ni_{in} centers is 0.63 cm^{-1} and the magnetic exchange constant between Ni_{in} and Ni_{in} centers is 1.10 cm^{-1}.[3a] In $[Ni(en)_2]_{0.5}[\{Ni_6(\mu_3\text{-}OH)_3(en)_3(H_2O)_6\}(B\text{-}\alpha\text{-}GeW_9O_{34})]\cdot 3$

H_2O [$d_{Niex\cdots Niex}$: 6.185(3)–6.203(3) Å, $d_{Niin\cdots Niin/Niex\cdots Niin}$: 3.079(3)–3.122(3) Å, $\angle Ni–O–Ni$: 93.2(4)–100.4(5)°], the magnetic exchange constant between Ni_{ex} and Ni_{in} centers is 0.68 cm^{-1} and the magnetic exchange constant between Ni_{in} and Ni_{in} centers is 1.48 cm^{-1}.[3b] Because of the same distribution motif of the six octahedral Ni^{II} ions and the similar $Ni\cdots Ni$ distances and Ni–O–Ni angles in **1** to those in the reported hexa-Ni^{II} substituted POMs, we can conclude that the hexa-Ni^{II} $[Ni_6(OH)_2(H_2O)_3(en)]^{10+}$ clusters in **1** also displays the ferromagnetic coupling interactions. Thus, the magnetic behavior of two asymmetric sandwich-type $[(\alpha-AsW_6O_{26})Ni_6(OH)_2(H_2O)_3(en)(B-\alpha-AsW_9O_{34})]^{10-}$ subunits should be the ferromagnetic coupling interactions. On the other hand, the Ni4, Ni5, Ni6 group and Ni4A, Ni5A, Ni6A group form two symmetrically equivalent tri-Ni^{II} $[Ni_3(en)(H_2O)_2]^{6+}$ clusters, which respectively graft to two sides of the nonmagnetic $[W_4O_{16}]^{8-}$ fragment generating the centric symmetric $\{[W_4O_{16}][Ni_3(H_2O)_2(en)]_2\}^{4+}$ subunit (Fig. 1e). Notably, two tri-Ni^{II} $[Ni_3(en)(H_2O)_2]^{6+}$ clusters are also separated by the nonmagnetic $[W_4O_{16}]^{8-}$ fragment, therefore, the magnetic exchange interactions between two tri-Ni^{II} $[Ni_3(en)(H_2O)_2]^{6+}$ clusters are negligible, so the magnetic behavior of the symmetric $\{[W_4O_{16}][Ni_3(H_2O)_2(en)]_2\}^{4+}$ subunit can be also viewed as the addition of the magnetic behaviors of two tri-Ni^{II} $[Ni_3(en)(H_2O)_2]^{6+}$ clusters. The $[Ni_3(en)(H_2O)_2]^{6+}$ cluster is built by three edge-sharing $Ni(O/N)_6$ octahedra in the triangle fashion. The $Ni\cdots Ni$ distances are in the range of 3.037(3)–3.203(3) Å and the Ni–O–Ni angles vary in 92.7(4)–100.3(4)°. Such distribution motif of the tri-Ni^{II} clusters have been previously encountered.[4,5] Magnetic experimental and theoretical results of these tri-Ni^{II} clusters have proved that the tri-Ni^{II} clusters show the ferromagnetic coupling interactions.[4,5] For example, in $Na_{11}[Ni_3Na(H_2O)_2(AsW_9O_{34})_2]\cdot30.5H_2O$ [$d_{Ni\cdots Ni}$: 3.175(6)–3.255(6) Å, $\angle Ni–O–Ni$: 96.0(8)–100.8(8)°], the magnetic exchange constant between Ni^{II} and Ni^{II} centers is 4.2 cm^{-1}.[4] In $K_6Na[Ni_3(H_2O)_3PW_{10}O_{39}H_2O]\cdot12H_2O$ [$d_{Ni\cdots Ni}$: 3.172–3.178 Å, $\angle Ni–O–Ni$: 91.9–101.0°], the magnetic exchange constant between Ni^{II} and Ni^{II} centers is 3.9 cm^{-1}.[5] Due to the similar distribution motif of three octahedral Ni^{II} ions and the similar $Ni\cdots Ni$ distances and Ni–O–Ni angles in **1** to those in the reported tri-Ni^{II} substituted POMs, we can also conjecture that the tri-Ni^{II} $[Ni_3(en)(H_2O)_2]^{6+}$ clusters in **1** also exhibit the ferromagnetic coupling interactions. Thus, the magnetic behavior of the $\{[W_4O_{16}][Ni_3(H_2O)_2(en)]_2\}^{4+}$ subunit should be the ferromagnetic coupling interactions. From the connection mode between $[(\alpha-AsW_6O_{26})Ni_6(OH)_2(H_2O)_3(en)$ $(B-\alpha-AsW_9O_{34})]^{10-}$ subunit and $\{[W_4O_{16}][Ni_3(H_2O)_2(en)]_2\}^{4+}$

subunit in **1**, we can presume that the magnetic coupling interactions between $[(\alpha\text{-}AsW_6O_{26})Ni_6(OH)_2(H_2O)_3(en)(B\text{-}\alpha\text{-}AsW_9O_{34})]^{10-}$ and $\{[W_4O_{16}][Ni_3(H_2O)_2(en)]_2\}^{4+}$ subunits are very weak so as to be negligible. Therefore, the magnetic behavior of **1** should be the addition of the magnetic behaviors of two $[(\alpha\text{-}AsW_6O_{26})Ni_6(OH)_2(H_2O)_3(en)(B\text{-}\alpha\text{-}AsW_9O_{34})]^{10-}$ subunit**,** one $\{[W_4O_{16}][Ni_3(H_2O)_2(en)]_2\}^{4+}$ subunit and the paramagnetic cations ($[Ni2(en)]^{2+}$, $[Ni2A(en)]^{2+}$, $[Ni1(en)_2]^{2+}$, $[Ni1A(en)_2]^{2+}$, $[Ni3(H_2O)_4]^{2+}$ and $[Ni3A(H_2O)_4]^{2+}$), the ferromagnetic coupling interactions of **1** are able to be predicted. Furthermore, according to the magnitude of the magnetic exchange constants in the reported hexa-Ni^{II} clusters[3] and tri-Ni^{II} clusters[4,5], the magnetic exchange interactions within Ni^{II} centers in **1** are very weak, which is also confirmed by the result of the Curie-Weiss law ($\theta = 4.42$ K).

1. B. Keita, I. M. Mbomekalle, L. Nadjo, T. M. Anderson and C. L. Hill, *Inorg. Chem.,* 2004, **43**, 3257.

2. (*a*) J. M. Clemente-Juan, E. Coronado, J. R. Galán-Mascarós and C. J. Gómez-García, *Inorg. Chem.,* 1999, **38**, 55; (*b*) Z. Zhang, J. Liu, E. Wang, C. Qin, Y. Li, Y. Qi and X. Wang, *Dalton Trans.,* 2008, 463; (*c*) J.-W. Zhao, B. Li, S.-T. Zheng and G.-Y. Yang, *Cryst. Growth Des.,* 2007, **7**, 2658.

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5. J. M. Clemente-Juan, E. Coronado, J. R. Galán-Mascarós and C. J. Gómez-García, *Inorg. Chem.,* 1999, **38**, 55.
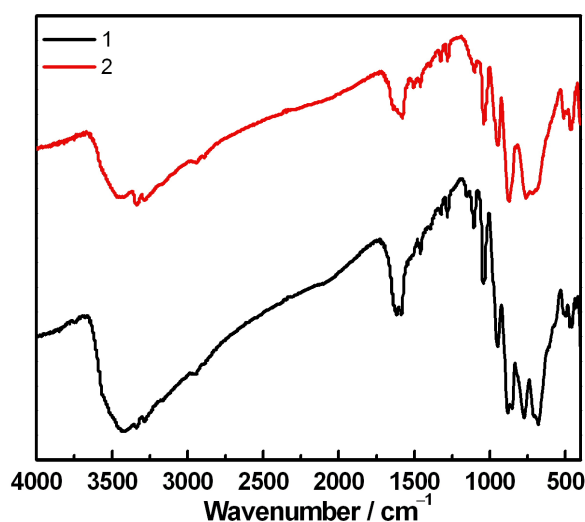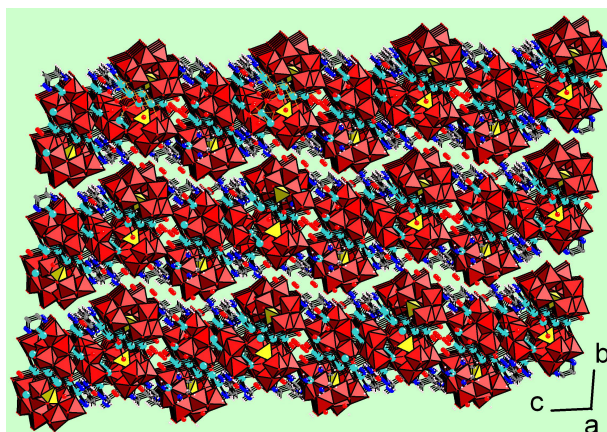
Fig. S1 IR spectra of **1** and **2.**

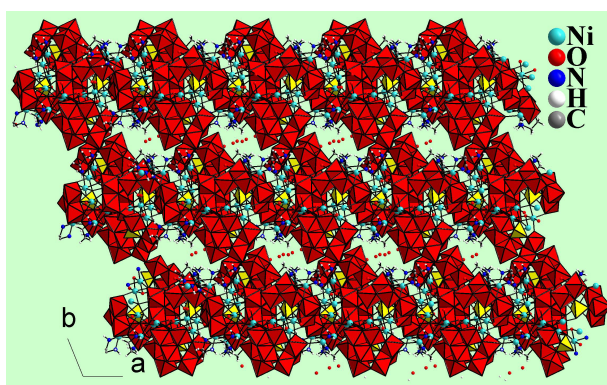**Fig. S2** The packing arrangement of 1D chains in **1**.

Fig. S3 The packing arrangement of **1** along the crystallographical *ab* plane.
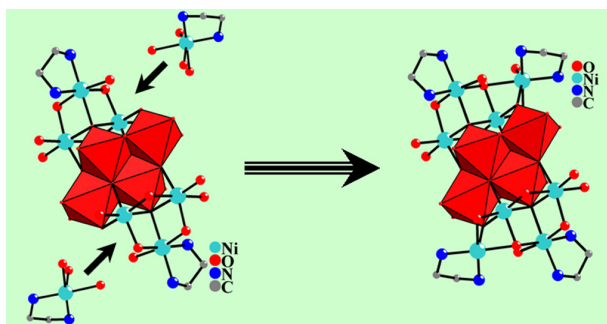

Fig. S4 Relationship of the $\{[W_4O_{16}][Ni_3(H_2O)_2(en)]_2\}^{4+}$ subunit in **1** and the $\{[W_4O_{16}][Ni_4(H_2O)_2(en)_2]_2\}^{8+}$ subunit in **2**.
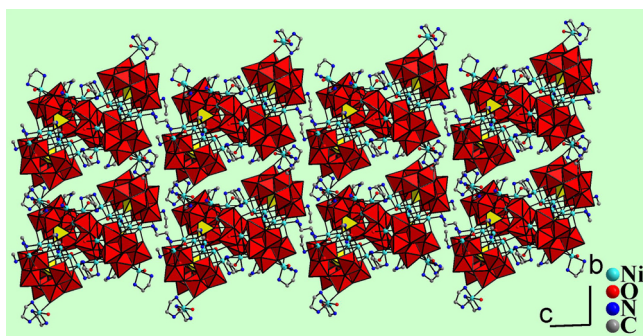
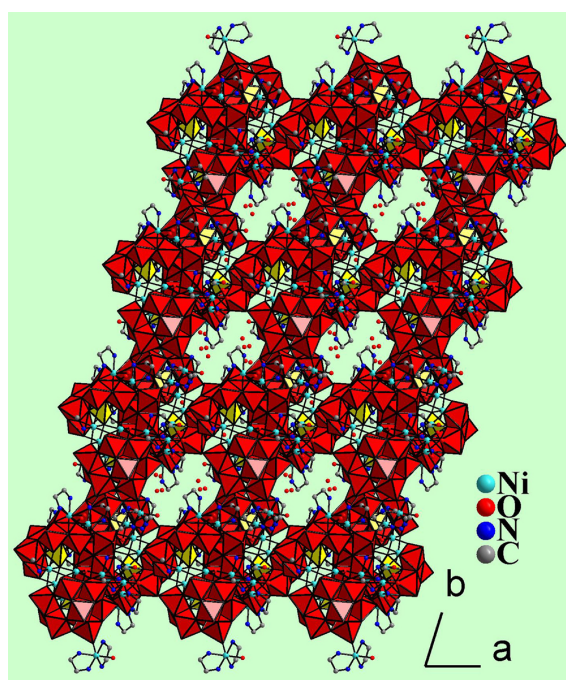**Fig. S5** The packing arrangement of 1D chains in **2**.

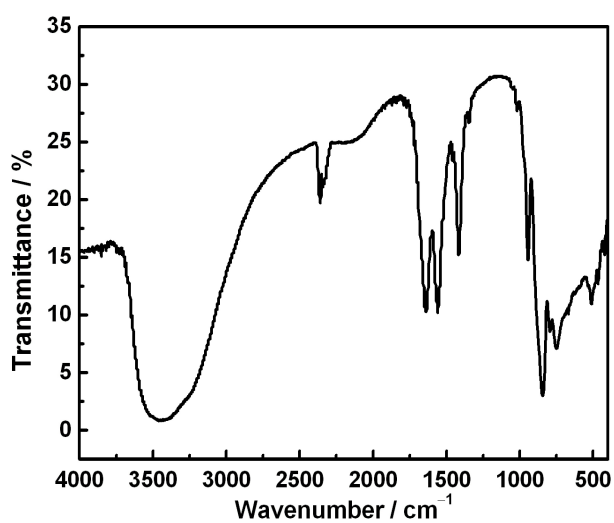**Fig. S6** The packing arrangement of **2** along the crystallographical *ab* plane.

Fig. S7 IR spectrum of $Na_8[A-\alpha-HAsW_9O_{34}]\cdot 11H_2O$.
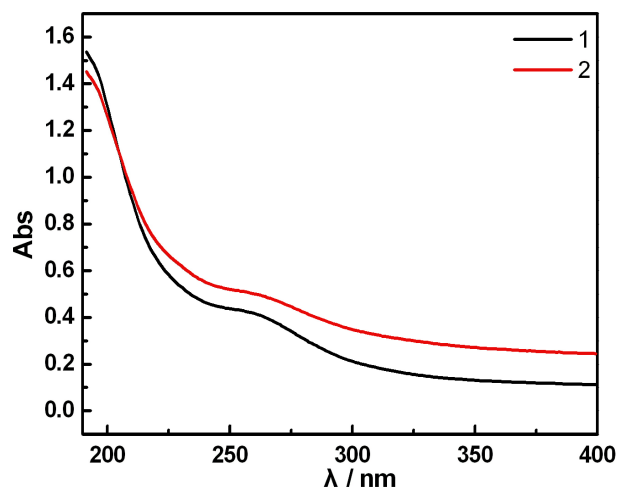
Fig. S8 UV spectra of **1** and **2**.

Fig. S9 Field dependence of magnetization for **1** at 1.8 K.

Table S1 The BVS values of all the oxygen atoms except the lattice water molecules in **2**.

Atoms	BVS values	Atoms	BVS values	Atoms	BVS values
O1, O1A	1.80	O28, O28A	1.81	O55, O55A	1.73
O2, O2A	1.85	O29, O29A	1.85	O56, O56A	1.62
O3, O3A	1.86	O30, O30A	1.70	O57, O57A	1.65
O4, O4A	2.07	O31, O31A	1.93	O58, O58A	1.92
O5, O5A	1.97	O32, O32A	1.71	O59, O59A	1.64

O6, O6A	1.98	O33, O33A	1.88	O60, O60A	1.89
O7, O7A	1.75	O34, O34A	2.03	O61, O61A	1.77
O8, O8A	2.08	O35, O35A	1.10	O62, O62A	2.02
O9, O9A	1.89	O36, O36A	1.07	O63, O63A	1.95
O10, O10A	1.81	O37, O37A	1.93	O64, O64A	2.01
O11, O11A	2.01	O38, O38A	1.92	O65, O65A	1.77
O12, O12A	1.76	O39, O39A	2.05	O66, O66A	1.58
O13, O13A	2.08	O40, O40A	1.62	O67, O67A	1.86
O14, O14A	1.85	O41, O41A	1.97	O68, O68A	1.66
O15, O15A	1.89	O42, O42A	1.84	O69, O69A	1.79
O16, O16A	1.65	O43, O43A	1.87	O70, O70A	1.87
O17, O17A	1.88	O44, O44A	1.95	O1W, O1WA	0.26
O18, O18A	1.89	O45, O45A	2.06	O2W, O2WA	0.33
O19, O19A	1.93	O46, O46A	1.89	O3W, O3WA	0.23
O20, O20A	1.77	O47, O47A	1.96	O4W, O4WA	0.34
O21, O21A	1.86	O48, O48A	1.19	O5W, O5WA	0.38
O22, O22A	1.77	O49, O49A	1.68	O6W, O6WA	0.26
O23, O23A	1.68	O50, O50A	1.82	O7W, O7WA	0.29
O24, O24A	1.81	O51, O51A	1.83		
O25, O25A	1.92	O52, O52A	1.85		
O26, O26A	1.92	O53, O53A	2.00		
O27, O27A	1.85	O54, O54A	1.61		

Symmetry transformations used to generate equivalent atoms: A: $-x$, $1-y$, $1-z$