Two types of novel tetra-iron substituted sandwich-type arsenotungastates with supporting lanthanide pendants

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Electronic Supplementary Information

The refinement details in 1-13

Fig. S1 The IR spectra of **1**–**13.**

Fig. S2 The $Pr1^{3+}$ cation splitting to two positions.

The refinement details in 1-13:

Thanks to the large structures of **1-13** and the existence of a large amount of weight atoms, their intensity data are not very good, leading to the ADP max/min ratio of some atoms, and it is very difficult to refine these large structures, therefore, some unit-occupancy atoms have been refined isotropically and restrainedly refined.

For **1**: The K^+ and La^{3+} cations are disordered with the site occupancy of 0.5, which are determined according to the mass percentages of K^+ and La^{3+} cations from inductively coupled plasma atomic emission spectrometry and their magnitude of anisotropic displacement parameters. The ISOR instruction is used for O1W, O2, O3, O8, O10, O13, O18, O25, O28, O32, O33, O1, O6, O27, O29, O30, O15, O9, O17, O19, O24 and O5. The DFIX instruction is used for Na1 and O24W. O13W is disordered over two positions (O13W and O13A) and O21W is disordered over two positions (O21W and O21A). The O6W, O7W, O8W, O9W, O10W, O11W, O13W, O13A, O14W, O15W, O17W, O20W, O21W, O21A, O23W and O24W are refined isostropicallly. 582 parameters and 133 restraints are used in the refinement.

For **2**: The K^+ and Pr^{3+} cations are disordered with the site occupancy of 0.5, which are determined according to the mass percentages of K^+ and Pr^{3+} cations from inductively coupled plasma atomic emission spectrometry and their magnitude of anisotropic displacement parameters. The ISOR instruction is used for O12, O16, O17, O21 and Na1. The DFIX instruction is used for Na1 and O24W. O13W is disordered over two positions (O13W and O13A) and O21W is disordered over two positions (O21W and O21A). The O6W, O7W, O8W, O9W, O10W, O11W, O13W, O13A, O14W, O15W, O17W, O20W, O21W, O21A, O23W and O24W are refined isostropicallly. 582 parameters and 31 restraints are used in the refinement.

For **3**: The K^+ and Nd^{3+} cations are disordered with the site occupancy of 0.5, which are determined according to the mass percentages of K^+ and Nd^{3+} cations from inductively coupled plasma atomic emission spectrometry and their magnitude of anisotropic displacement parameters. The ISOR instruction is used for O3, O12, O24, O5, O18, O15, O4, O17, O25, O31, O22W, O30 and O23. The DFIX instruction is used for Na1 and O24W. O13W is disordered over two positions (O13W and O13A) and O21W is disordered over two positions (O21W and O21A). The O6W, O7W, O8W, O9W, O10W, O11W, O13W, O13A, O14W, O15W, O17W, O20W, O21W, O21A, O23W and O24W are refined isostropicallly. 577 parameters and 79 restraints are used in the refinement.

For **4**: The K^+ and Sm^{3+} cations are disordered with the site occupancy of 0.5, which are determined according to the mass percentages of K^+ and Sm^{3+} cations from inductively coupled plasma atomic emission spectrometry and their magnitude of anisotropic displacement parameters. The ISOR instruction is used for O23. The DFIX instruction is used for Na1 and O24W. O13W is disordered over two positions (O13W and O13A) and O21W is disordered over two positions (O21W and O21A). The O6W, O7W, O8W, O9W, O10W, O11W, O13W, O13A, O14W, O15W, O17W, O20W, O21W, O21A, O23W and O24W are refined isostropicallly. 582 parameters and 7 restraints are used in the refinement.

For **5**: Its structure contains a chiral L-thr ligand, theoretically its structure should be chiral. However, its structure is pseudo-centrosymmetric, i.e. most of the structure fits space group *P*–1, therefore, its structure was solved and refined in centrosymmetric space group *P*–1. Such phenomena are rather common. An attempt to refine the structure in *P*–1 shows the disorder around the chiral centre of L-thr (because we impose inversion on a chiral entity), as a result, C1, C2, N1, O35 and O36 atoms on L-thr are disordered over two positions. In addition, some coordination water molecules on La^{3+} cations are disordered over two positions. The ISOR instruction is used for O5, O6 and O12. The SADI instruction is used for C2' C1' C2 C1, O34 C1' O34 C1, O35' C1' O35 C1, N1' C2' N1 C2, C3 C2' C3 C2, O36 C3 O36' C3, N1' C2' N1 C2. The EADP instruction is used for C2 and C2', N1 and N1', O36 and O36'. The O7W, O7M, O8W, O10W, O10M, O11W, O11M, O12W, O12M, O13W, O14W, O15W, O16W, O16M, O18W, O18M, O22W, O35, O35', O36, O36', C1, C1', C2, C2', N1 and N1' are refined isostropicallly. 656 parameters and 24 restraints are used in the refinement.

For **6**: Its structure contains a chiral L-thr ligand, theoretically its structure should be chiral. However, its structure is pseudo-centrosymmetric, i.e. most of the structure fits space group *P*–1, therefore, its structure was solved and refined in centrosymmetric space group *P*–1. Such phenomena are rather common. An attempt to refine the structure in *P*–1 shows the disorder around the chiral centre of L-thr (because we impose inversion on a chiral entity), as a result, C1, C2, N1, O35 and O36 atoms on L-thr are disordered over two positions. In addition, some coordination water molecules on Pr^{3+} cations are disordered over two positions. The ISOR instruction is used for O2, O3, O13, O18, O10, O16, O33, O21, O23, O24 and O29. The DELU instruction is used for Pr1 and O5W. The SADI instruction is used for C2' C1' C2 C1, O34 C1' O34 C1, O35' C1' O35 C1, N1' C2' N1 C2, C3 C2' C3 C2, O36 C3 O36' C3, N1' C2' N1 C2. The EADP instruction is used for C2 and C2', N1 and N1', O36 and O36'. The O7W, O7M, O8W, O10W, O10M, O11W, O11M, O12W, O12M, O13W, O14W, O15W, O16W, O16M, O18W, O18M, O22W, O35, O35', O36, O36', C1, C1', C2, C2', N1 and N1' are refined isostropicallly. 656 parameters and 79 restraints are used in the refinement.

For **7**: Its structure contains a chiral L-thr ligand, theoretically its structure should be chiral. However, its structure is pseudo-centrosymmetric, i.e. most of the structure fits space group *P*–1, therefore, its structure was solved and refined in centrosymmetric space group *P*–1. Such phenomena are rather common. An attempt to refine the structure in *P*–1 shows the disorder around the chiral centre of L-thr (because we impose inversion on a chiral entity), as a result, C1, C2, N1, O35 and O36 atoms on L-thr are disordered over two positions. In addition, some coordination water molecules on Nd^{3+} cations are disordered over two positions. The ISOR instruction is used for O3, O11, O30, O16, O19, O12, O13, O14 and O9. The DELU instruction is used for C3 and C4. The SADI instruction is used for C2' C1' C2 C1, O34 C1' O34 C1, O35' C1' O35 C1, N1' C2' N1 C2, C3 C2' C3 C2, O36 C3 O36' C3, N1' C2' N1 C2. The EADP instruction is used for C2 and C2', N1 and N1', O36 and O36'. The O7W, O7M, O8W, O10W, O10M, O11W, O11M, O12W, O12M, O13W, O14W, O15W, O16W, O16M, O18W, O18M, O22W, O35, O35', O36, O36', C1, C1', C2, C2', N1 and N1' are refined isostropicallly. 655 parameters and 73 restraints are used in the refinement.

For **8**: Its structure contains a chiral L-thr ligand, theoretically its structure should be chiral. However, its structure is pseudo-centrosymmetric, i.e. most of the structure fits space group *P*–1, therefore, its structure was solved and refined in centrosymmetric space group *P*–1. Such phenomena are rather common. An attempt to refine the structure in *P*–1 shows the disorder around the chiral centre of L-thr (because we impose inversion on a chiral entity), as a result, C1, C2, N1, O35 and O36 atoms on L-thr are disordered over two positions. In addition, some coordination water molecules on Sm^{3+} cations are disordered over two positions. The ISOR instruction is used for O2, O12, O18, O25, O26, O29, O30, O33, C4, O17, O14, O24, O5, O28, O34, O22, O23, O13, O34 and O21. The SADI instruction is used for C2' C1' C2 C1, O34 C1' O34 C1, O35' C1' O35 C1, N1' C2' N1 C2, C3 C2' C3 C2, O36 C3 O36' C3, N1' C2' N1 C2. The EADP instruction is used for C2 and C2', N1 and N1', O36 and O36'. The O7W, O7M, O8W, O10W, O10M, O11W, O11M, O12W, O12M, O13W, O14W, O15W, O16W, O16M, O18W, O18M, O22W, O35, O35', O36, O36', C1, C1', C2, C2', N1 and N1' are refined isostropicallly. 656 parameters and 120 restraints are used in the refinement.

For **9**: Its structure contains a chiral L-thr ligand, theoretically its structure should be chiral. However, its structure is pseudo-centrosymmetric, i.e. most of the structure fits space group *P*–1, therefore, its structure was solved and refined in centrosymmetric space group *P*–1. Such phenomena are rather common. An attempt to refine the structure in *P*–1 shows the disorder around the chiral centre of L-thr (because we impose inversion on a chiral entity), as a result, C1, C2, N1, O35 and O36 atoms on L-thr are disordered over two positions. In addition, some coordination water molecules on Eu^{3+} cations are disordered over two positions. The ISOR instruction is used for O1, O20, O30, O11, O12, O5, O21W, O1W, N1, C4, O7, O26, O29, O30, O2, O16, O21, O27, O33, O25, O9, O24, W2, O10, O23, O4, O8, O18, O22, O16 and O6. The SADI instruction is used for C2' C1' C2 C1, O34 C1' O34 C1, O35' C1' O35 C1, N1' C2' N1 C2, C3 C2' C3 C2, O36 C3 O36' C3, N1' C2' N1 C2. The EADP instruction is used for C2 and C2', N1 and N1', O36 and O36'. The As1, O7W, O7M,

O8W, O10W, O10M, O11W, O11M, O12W, O12M, O13W, O14W, O15W, O16W, O16M, O18W, O18M, O22W, O35, O35', O36, O36', C1, C1', C2, C2', N1 and N1' are refined isostropicallly. 651 parameters and 186 restraints are used in the refinement.

For **10**: Its structure contains a chiral L-thr ligand, theoretically its structure should be chiral. However, its structure is pseudo-centrosymmetric, i.e. most of the structure fits space group *P*–1, therefore, its structure was solved and refined in centrosymmetric space group *P*–1. Such phenomena are rather common. An attempt to refine the structure in *P*–1 shows the disorder around the chiral centre of L-thr (because we impose inversion on a chiral entity), as a result, C1, C2, N1, O35 and O36 atoms on L-thr are disordered over two positions. In addition, some coordination water molecules on Gd^{3+} cations are disordered over two positions. The ISOR instruction is used for O1W, C3, C4, O8, O33, O12 and O18. The SADI instruction is used for C2' C1' C2 C1, O34 C1' O34 C1, O35' C1' O35 C1, N1' C2' N1 C2, C3 C2' C3 C2, O36 C3 O36' C3, N1' C2' N1 C2. The EADP instruction is used for C2 and C2', N1 and N1', O36 and O36'. The O7W, O7M, O8W, O10W, O10M, O11W, O11M, O12W, O12M, O13W, O14W, O15W, O16W, O16M, O18W, O18M, O22W, O35, O35', O36, O36', C1, C1', C2, C2', N1 and N1' are refined isostropicallly. 655 parameters and 37 restraints are used in the refinement.

For **11**: Its structure contains a chiral L-thr ligand, theoretically its structure should be chiral. However, its structure is pseudo-centrosymmetric, i.e. most of the structure fits space group *P*–1, therefore, its structure was solved and refined in centrosymmetric space group *P*–1. Such phenomena are rather common. An attempt to refine the structure in *P*–1 shows the disorder around the chiral centre of L-thr (because we impose inversion on a chiral entity), as a result, C1, C2, N1, O35 and O36 atoms on L-thr are disordered over two positions. In addition, some coordination water molecules on Tb^{3+} cations are disordered over two positions. The ISOR instruction is used for O3, O9W, O8, O13, O15, O22, O12, O33, O24, O9, O17, O4, O23, O14 and O29. The SADI instruction is used for C2' C1' C2 C1, O34 C1' O34 C1, O35' C1' O35 C1, N1' C2' N1 C2, C3 C2' C3 C2, O36 C3 O36' C3, N1' C2' N1 C2. The EADP instruction is used for C2 and C2', N1 and N1', O36 and O36'. The O7W, O7M, O8W, O10W, O10M, O11W, O11M, O12W, O12M, O13W, O14W, O15W, O16W, O16M, O18W, O18M, O22W, O35, O35', O36, O36', C1, C1', C2, C2', N1 and N1' are refined isostropicallly. 654 parameters and 96 restraints are used in the refinement.

For **12**: Its structure contains a chiral L-thr ligand, theoretically its structure should be chiral. However, its structure is pseudo-centrosymmetric, i.e. most of the structure fits space group *P*–1, therefore, its structure was solved and refined in centrosymmetric space group *P*–1. Such phenomena are rather common. An attempt to refine the structure in *P*–1 shows the disorder around the chiral centre of L-thr (because we impose inversion on a chiral entity), as a result, C1, C2, N1, O35 and O36 atoms on L-thr are disordered over two positions. In addition, some coordination water molecules on Dy^{3+} cations are disordered over two positions. The ISOR instruction is used for C4, O23, O24, O18 and O14. The DELU instruction is used for C3 and C4. The SADI instruction is used for C2' C1' C2 C1, O34 C1' O34 C1, O35' C1' O35 C1, N1' C2' N1 C2, C3 C2' C3 C2, O36 C3 O36' C3, N1' C2' N1 C2. The EADP instruction is used for C2 and C2', N1 and N1', O36 and O36'. The O7M, O8W, O10W, O10M, O11W, O11M, O12W, O12M, O13W, O14W, O15W, O16W, O16M, O18W, O18M, O22W, O35, O35', O36, O36', C1, C1', C2, C2', N1 and N1' are refined isostropicallly. 654 parameters and 37 restraints are used in the refinement.

For **13**: Its structure contains a chiral L-thr ligand, theoretically its structure should be chiral. However, its structure is pseudo-centrosymmetric, i.e. most of the structure fits space group *P*–1, therefore, its structure was solved and refined in centrosymmetric space group *P*–1. Such phenomena are rather common. An attempt to refine the structure in *P*–1 shows the disorder around the chiral centre of L-thr (because we impose inversion on a chiral entity), as a result, C1, C2, N1, O35 and O36 atoms on L-thr are disordered over two positions. In addition, some coordination water molecules on Er^{3+} cations are disordered over two positions. The ISOR instruction is used for O15W, O8, O9, O13, O16, O7, O1W, O27, O21, O22, O23, O32, O33, O34, C4, O18W, O13,

O29, W1, W4 ,As1, O2, O3, O4, O14, O18, O28, O6, W9, O12, O17, O20 and O26. The SADI instruction is used for C2' C1' C2 C1, O34 C1' O34 C1, O35' C1' O35 C1, N1' C2' N1 C2, C3 C2' C3 C2, O36 C3 O36' C3, N1' C2' N1 C2. The EADP instruction is used for C2 and C2', N1 and N1', O36 and O36'. The O7W, O7M, O8W, O10W, O10M, O11W, O11M, O12W, O12M, O13W, O14W, O15W, O16W, O16M, O18W, O18M, O22W, O35, O35', O36, O36', C1, C1', C2, C2', N1 and N1' are refined isostropicallly. 654 parameters and 192 restraints are used in the refinement.

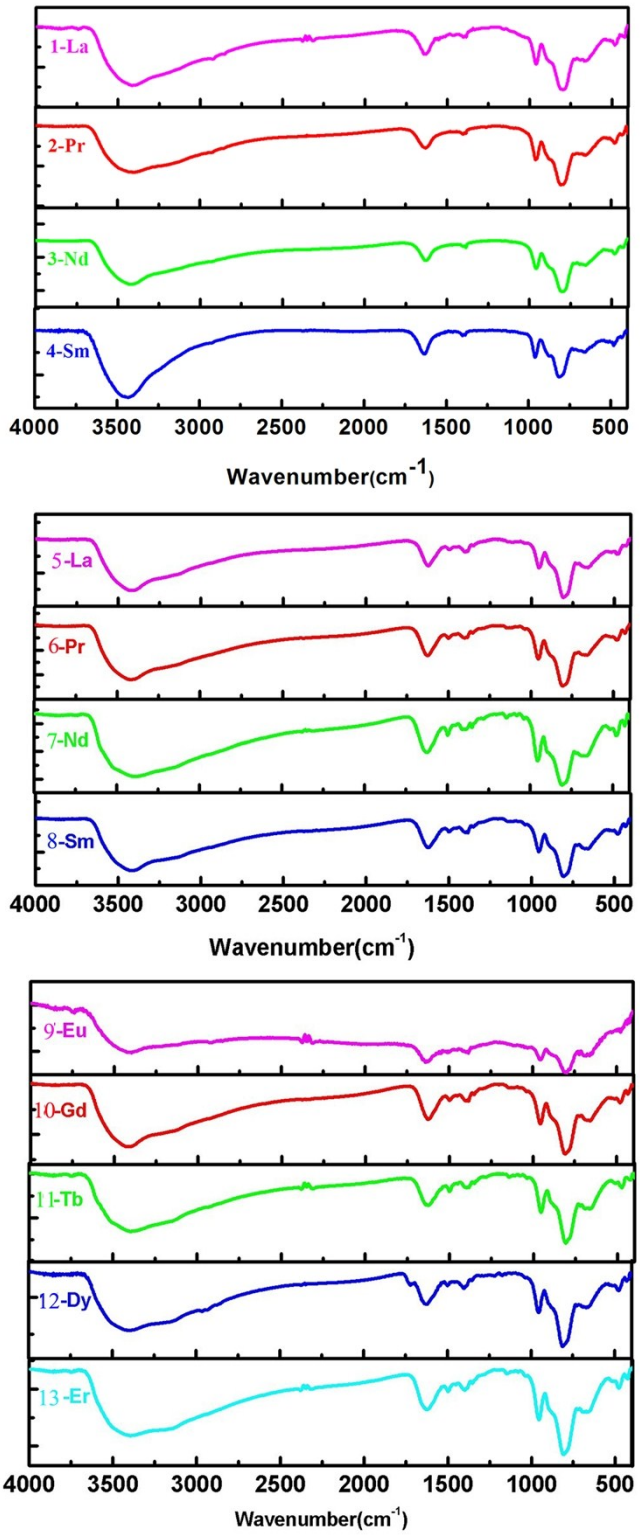

Fig. S1 The IR spectra of **1–13.**

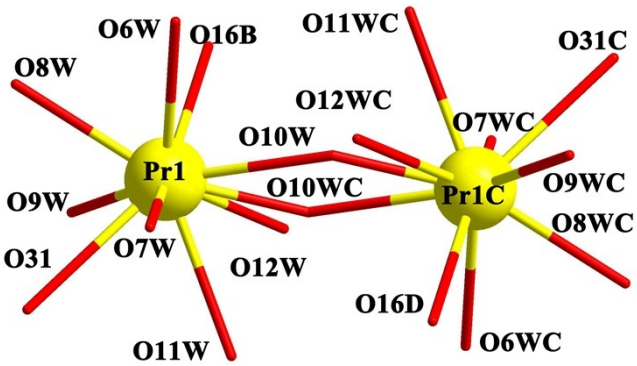

Fig. S2 The $Pr1^{3+}$ cation splitting to two positions.