Heterometallic 3d–4f cubane clusters inserted in polyoxometalate matrices

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Supplementary Information

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Experimental section

Synthesis

The hydrothermal syntheses were carried out in polytetrafluoroethylene lined stainless steel containers under autogenous pressure. The 23 mL vessel was filled to approximatively 20% volume capacity (V_i = 5 mL). Commercially available reagents were used as received without further purification. All reactants were stirred briefly before heating. The mixture was heated to 140°C over a period of 4h, kept at 140°C for 40h and cooled down to room temperature over a period of 44h. The pH of the mixture was measured before (pH_i) and after the reaction (pH_f). The products were isolated by filtration and washed with ethanol.

General procedure: A mixture of 1 eq. of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]$ $19H_2O$ (0.300 g, 0.107 mmol), 3.5 eq. of $Cu(CH_3COO)_2$ (0.068 g, 0.374 mmol), 1 eq. of $Ln(NO_3)_3$ (0.107 mmol), 3 eq. of ethylenediamine (21 μL, 0.321 mmol), and H_2O (5 mL) or NaOAc/HOAc buffer 1M (pH = 4.8) were stirred and the pH was adjusted to 4.8 (pH_i) with 2M HCl (pH_f= 4.6). Single crystals suitable for X-ray diffraction study were collected after filtration. Attempts to obtain the compounds **1a**, **1b** and **3**, respectively, following this general procedure but using the monovacant $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ precursor instead of the $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ ligand have only led to the obtaining of purple powders instead of blue crystals. It has not been possible to determine the nature of these precipitates.

Preparation of compound 1a: Following the general procedure, a mixture of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]$ $19H_2O$ (0.300 g, 0.107 mmol), $Cu(CH_3COO)_2$ (0.068 g, 0.374 mmol), $Gd(NO_3)_3$ (0.048 g, 0.107 mmol), 3 eq. of ethylenediamine (21 μL, 0.321 mmol), and H_2O (5 mL) were stirred and the pH was adjusted to 4.8 (pH_i) with 2M HCl. Single blue crystals suitable for X-ray diffraction study were collected after filtration. (0.145 g, 19% based on SiW_9O_{34}).

IR (KBr pellets, ν/cm^{-1}): 3476 (s), 3281 (s), 3240 (s), 3137 (sh), 1627 (w), 1586 (m), 1391 (m), 1283 (w), 1175 (w), 1104 (w), 1047 (m), 996 (m), 944 (s), 888 (s), 801 (s), 762 (sh), 685 (s), 525 (m). Anal Calcd for $C_{20}H_{130}Cu_8Gd_2N_{20}O_{106}Si_2W_{22}$ (7270.1): C, 3.29; H, 1.79; N, 3.85; Cu, 6.98; Gd, 4.33; W, 55.62. Found: C, 3.14; H, 1.49; N, 3.43; Cu, 6.76; Gd, 4.71; W, 53.51.

Preparation of compound 1b: Following the general procedure, a mixture of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]$ $19H_2O$ (0.300 g, 0.107 mmol), $Cu(CH_3COO)_2$ (0.068 g, 0.374 mmol), $Eu(NO_3)_3$

(0.045 g, 0.107 mmol), 3 eq. of ethylenediamine (21 µL, 0.321 mmol), and H_2O (5 mL) were stirred and the pH was adjusted to 4.8 (pH_i) with 2M HCl. Single blue crystals suitable for X-ray diffraction study were collected after filtration. (0.102 g, 13% based on SiW_9O_{34}).

IR (KBr pellets, ν/cm^{-1}): 3440 (s), 3296 (s), 3225 (s), 3132 (sh), 1622 (w), 1586 (m), 1468 (w), 1273 (w), 1109 (w), 1057 (m), 1001 (m), 950 (s), 878 (s), 790 (s), 762 (sh), 682 (s), 534 (m), 483 (sh). Anal Calcd for $C_{20}H_{130}Cu_8Eu_2N_{20}O_{106}Si_2W_{22}$ (7260.3): C, 3.31; H, 1.80; N, 3.86; Cu, 6.99; Eu, 4.19; W, 55.71. Found: C, 3.15; H, 1.55; N, 3.41; Cu, 6.81; Eu, 4.27; W, 53.41. Crystal data for **1b**: monoclinic, a = 13.36, b = 23.86, c = 18.68 Å, β = 92.68°, V = 6215.6 Å^3.

Preparation of compound 2: Following the general procedure, a mixture of Na_{10}[A-α-SiW_9O_{34}] $19H_2O$ (0.300 g, 0.107 mmol), $Cu(CH_3COO)_2$ (0.068 g, 3.74 mmol), $Gd(NO_3)_3$ (0.048 g, 0.107 mmol), ethylenediamine (21 µL, 3.21 mmol), and (5 mL) of NaOAc/HOAc buffer 1M (pH = 4.8) were stirred. Single purple crystals suitable for X-ray diffraction study were collected after filtration. (0.147 g, 19% based on SiW_9O_{34}).

IR (KBr pellets, ν/cm^{-1}): 3435 (s), 3312 (s), 3255 (s), 3157 (sh), 1638 (w), 1586 (m), 1530 (w), 1047 (w), 991 (w), 939 (w), 883 (m), 811 (m), 688 (w), 667 (sh), 508 (w). Anal Calcd for $C_{28}H_{118}Cu_6Gd_2N_{24}O_{108}Si_2W_{22}$ (7315.8): C, 4.61; H, 1.63; N, 4.59; Cu, 5.21; Gd, 4.30; W, 55.28. Found: C, 4.56; H, 1.81; N, 4.56; Cu, 5.13; Gd, 5.14; W, 53.56.

Preparation of compound 3: Following the general procedure, a mixture of Na_{10}[A-α-SiW_9O_{34}] $19H_2O$ (0.300 g, 0.107 mmol), $Cu(CH_3COO)_2$ (0.068 g, 0.374 mmol), $La(NO_3)_3$ (0.040 g, 0.107 mmol), 3 eq. of ethylenediamine (21 µL, 0.321 mmol), and H_2O (5 mL) were stirred and the pH was adjusted to 4.8 (pH_i) with 2M HCl. Single blue crystals suitable for X-ray diffraction study were collected after filtration. (0.128 g, 19% based on SiW_9O_{34}).

IR (KBr pellets, ν/cm^{-1}): 3440 (s), 3311 (s), 3296 (s), 3245 (s), 3132 (sh), 2936 (sh), 1622 (m), 1555 (m), 1463 (w), 1124 (w), 1032 (m), 996 (m), 944 (s), 872 (s), 800 (s), 780 (sh), 693 (s), 528 (m), 472 (sh). Anal Calcd for $C_{20}H_{130}Cu_8La_2N_{20}O_{106}Si_2W_{22}$ (7234.2): C, 3.34; H, 1.76; N, 3.89; Cu, 7.06; La, 3.86; W, 56.18. Found: C, 3.11; H, 1.37; N, 3.38; Cu, 6.80; La, 3.97; W, 56.25.

X-ray crystallography. For all compounds, intensity data collections were carried out with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using the monochromatized wavelength λ(Mo Kα) = 0.71073 Å. All the data were recorded at room temperature. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program[1] based on the method of Blessing.[2] The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package.[3] In all the structures there is a discrepancy between the formulae determined by elemental analysis and the formulae deduced from the crystallographic atom list because of the difficulty in locating all the disordered water molecules. Several disordered water molecules have been refined with partial occupancy factors.

Elemental analysis was performed by the Service Central d'Analyse of CNRS, 69390 Vernaison, France.

Infrared spectra (KBr pellets) were recorded on a IRFT Nicolet 550 apparatus.

Magnetic measurements. Magnetic susceptibility measurements were carried out with a Quantum Design SQUID Magnetometer with an applied field of 1000 G using powder samples pressed in pellets to avoid preferential orientation of the crystallites. The independence of the susceptibility value with regard to the applied field was checked at room temperature. The susceptibility data were corrected from the diamagnetic contributions as deduced by using Pascal's constant tables and from Temperature Independent Paramagnetism considering -60.10^{-6} cm^3 mol^{-1} per Cu^{II} center. All the magnetic data have been simulated using MAGPACK.[4]

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[1] G. M. Sheldrick, SADABS, program for scaling and correction of area detector data, University of Göttingen, Germany, 1997.

[2] R. Blessing, *Acta Crystallogr.*, 1995, **A51**, 33.

[3] G. M. Sheldrick, SHELX-TL version 5.03, Software Package for the Crystal Structure Determination, Siemens Analytical X-ray Instrument Division , Madison, WI USA, 1994.

[4] Borras-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *J. Comput. Chem.* **2001**, *22*, 985.

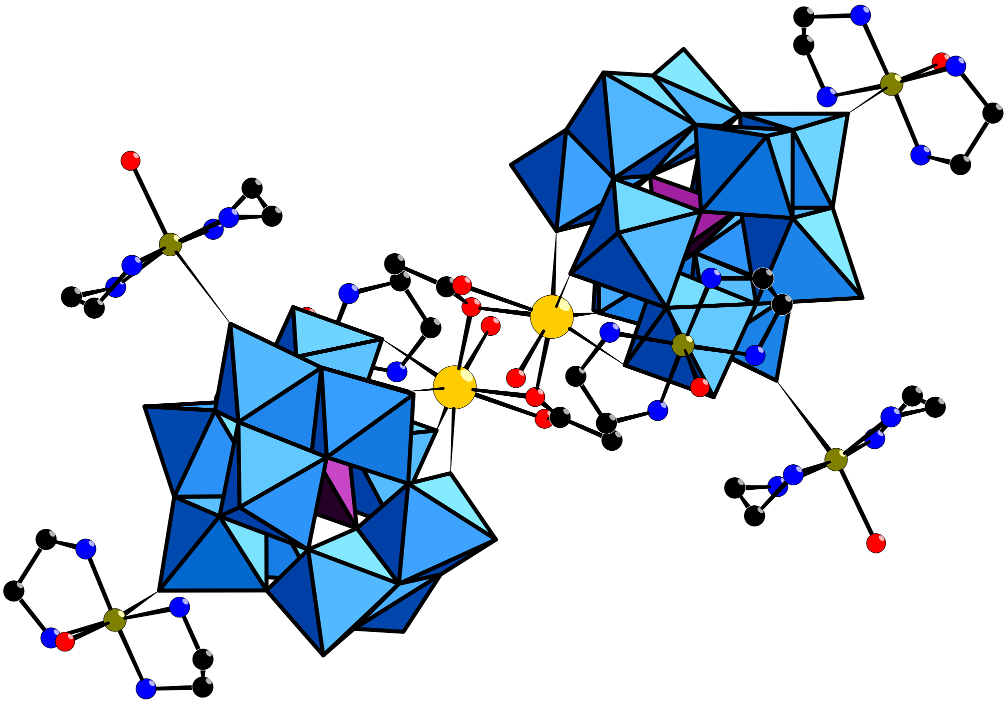
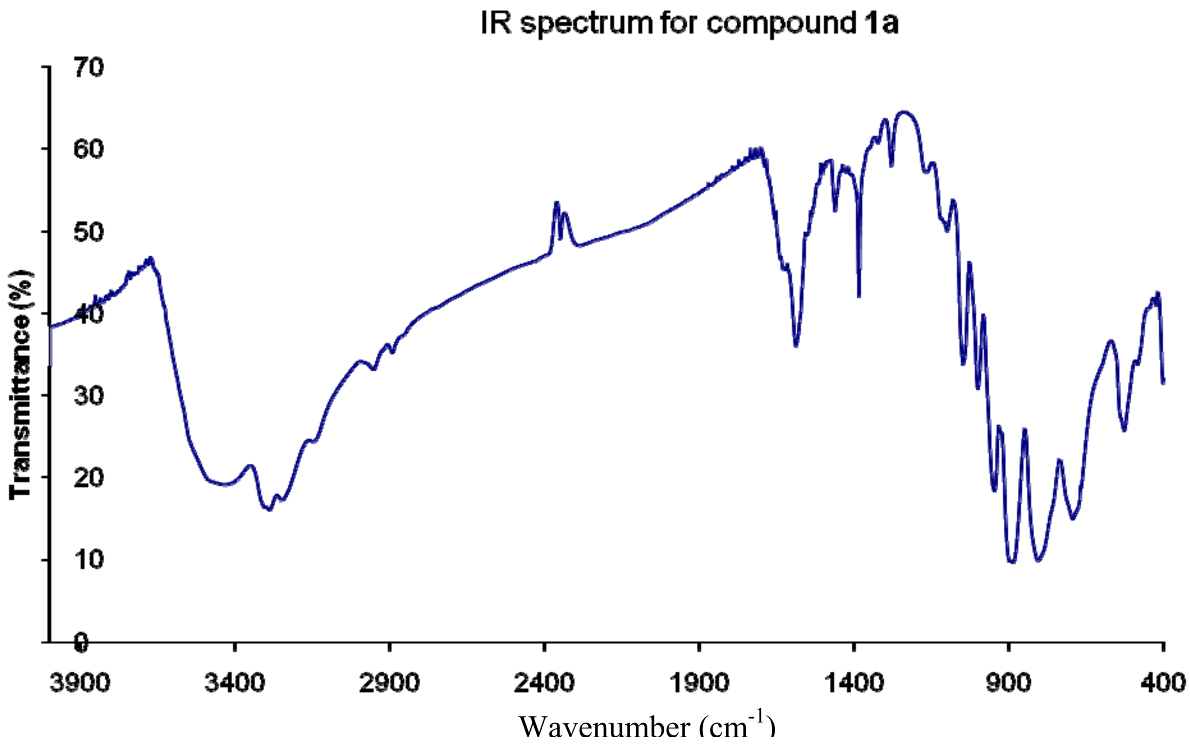


Fig. SI1 : Ball-and-stick and polyhedral representation of the dimeric POM $[(Gd(SiW_{11}O_{39})(CH_3COO)(H_2O))_2(Cu(en)_2(H_2O))_4]^{4-}$ constituting **2**. Yellow spheres, Gd; green spheres, Cu; red spheres, O; blue spheres, N; black spheres, C; blue octahedra, WO_6; purple tetrahedra, SiO_4.



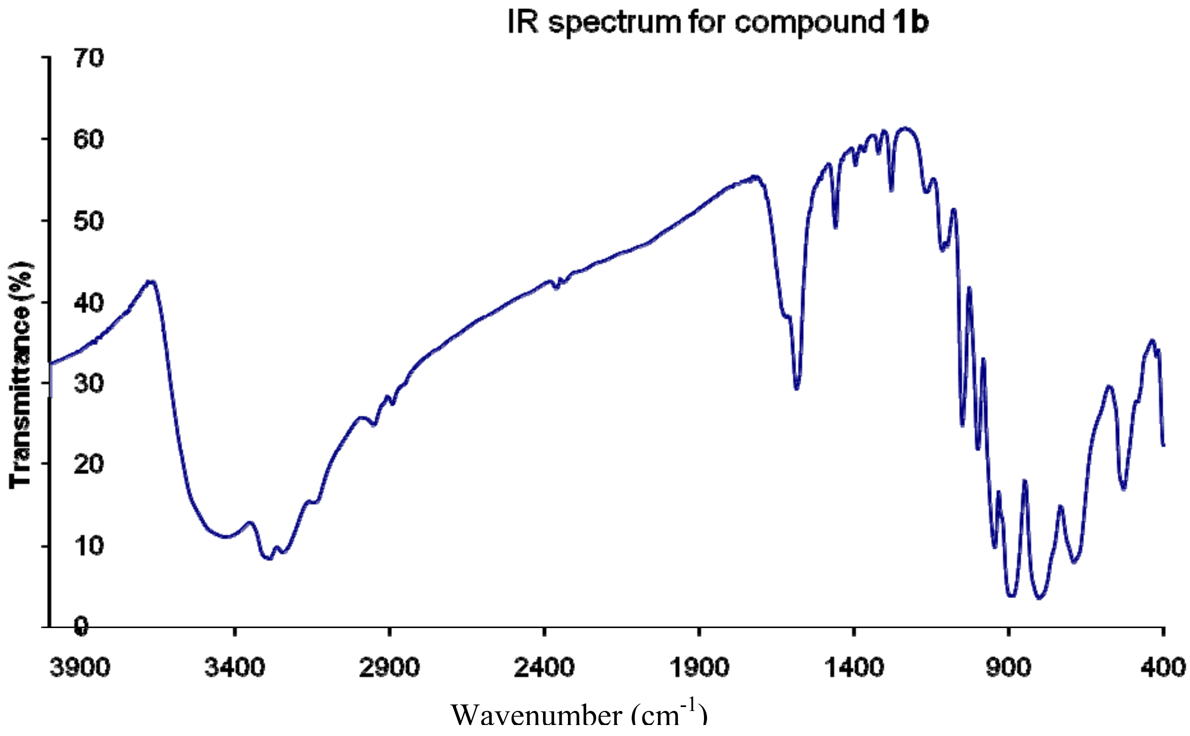
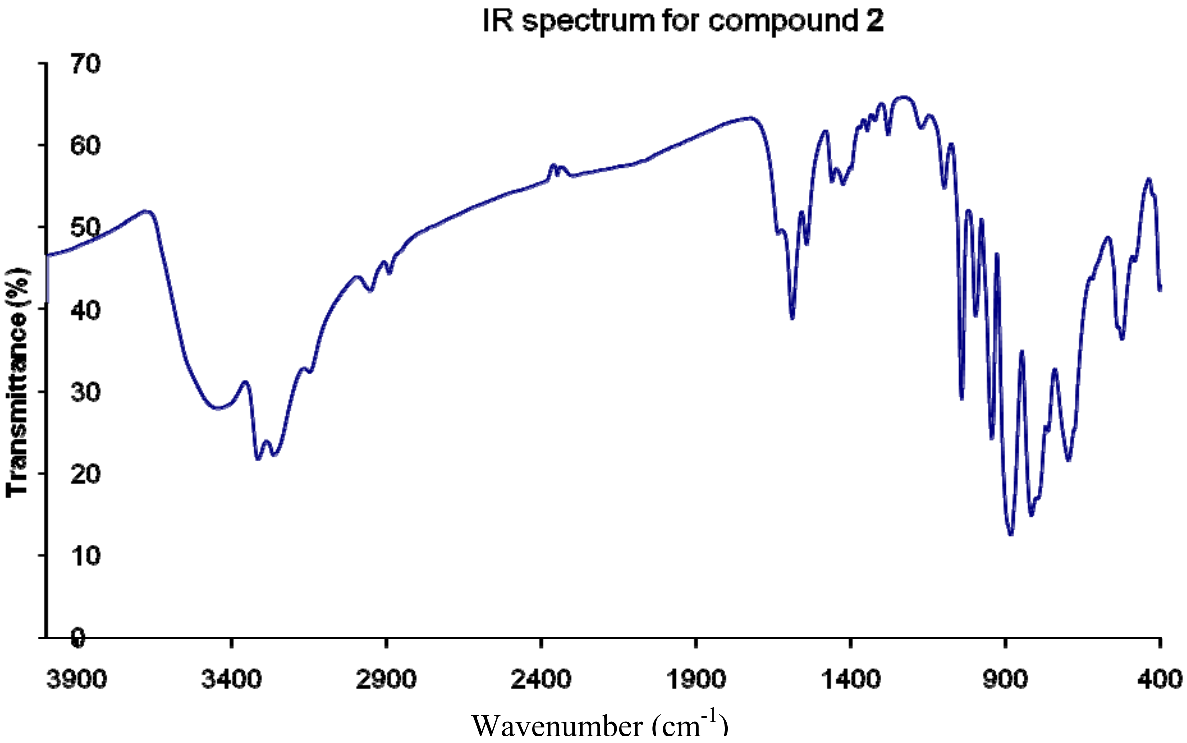


Fig. SI 2 : IR spectra of compounds **1a** and **1b**.



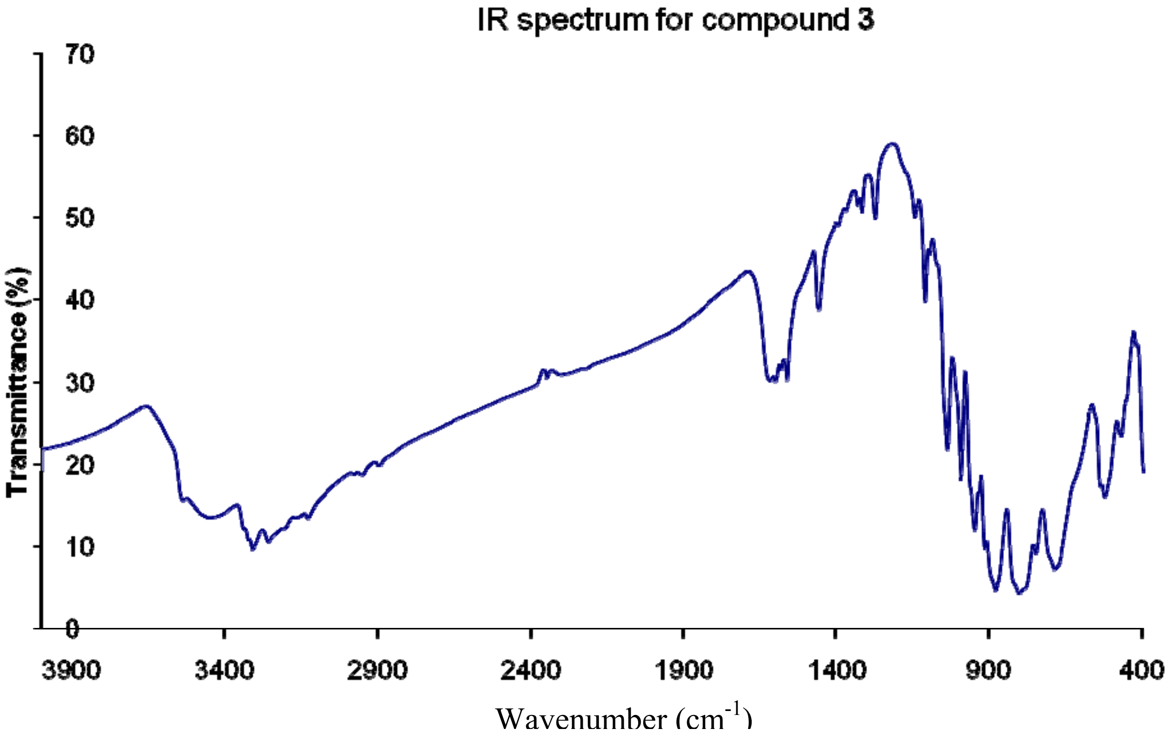


Fig. SI 3 : IR spectra of compounds **2** and **3**.