Extended framework materials incorporating cyanide cluster complexes: structure of the first 3D architecture accommodating organic molecules†

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Hexadentate cluster anions $[Re_6S_8(CN)_6]^{4-}$ coordinate to Mn(II) centers to give a neutral 3D coordination network topologically related to the structure of Prussian Blue; the residual space is filled with isopropyl alcohol molecules, both ligated to Mn(II) and guest-solvated.

For three centuries, polydimensional metal cyanides have intrigued chemists with their diversity and unique properties.[1] Representatives include the oldest synthetic coordination compound Prussian Blue‡[2,3] which gives rise to a wide family of 'blues' and 'greens',[1–4] Hofmann and related clathrates,[5] and inclusion compounds formed by cadmium cyanide.[6] Today, cyanide complexes are important elements in crystal engineering.[7] Very recently, the cyanide cluster complexes $[Re_6X_8(CN)_6]^{4-}$ (X = S, Se, Te)[8] capable of acting as octahedral hexadentate ligands have become available. The first structural studies were performed for salts (usually hydrated) of these cluster anions, where pure ionic packing or H-bonded systems were found.[8] Incorporation of M(II) cations (Mn, Fe, Co, Zn, Cd)[9–12] resulted in layered coordination polymers. With M(II) (Mn, Co, Ni) and tetrapropylammonium cations 0D, 1D and 2D structures were obtained.[13] Salts reported with negatively charged 3D coordination frameworks include $Cs_2Mn_3[Q]_2\cdot15H_2O$ [Q = $Re_6Se_8(CN)_6$], $(H_3O)_2Co_3[Q]_2\cdot14.5H_2O$,[14] $Cs_2[trans\text{-}Fe(H_2O)_2]_3[Q]_2\cdot18H_2O$ and its Mn, Co, Ni and Cd analogs,[9] $(H_3O)_2Zn_3[Q]_2\cdot20H_2O$[15] and others,[11,12,16] with plenty of water molecules as well as metal or H_3O^+ cations filling the space of the open pore system.

In the course of our efforts to design novel porous materials with a high propensity for absorbing organic species[17] we have exploited cyanide cluster complexes as prospective building units. For this purpose the capability of the cluster anions to create weakly charged or electrically neutral 3D-bonded networks seems essential. The 3D phase $[Zn(H_2O)]_2[Re_6S_8(CN)_6]\cdot7H_2O$ has been reported[9] but is of low inclusion capacity as it contains two interpenetrating neutral frameworks. Dehydrated $Ga_4[Re_6Se_8(CN)_6]_3\cdot xH_2O$ and $Fe_4[Re_6Te_8(CN)_6]_3\cdot xH_2O$,[16] $[Cd_2(H_2O)_4][Re_6S_8(CN)_6]_3\cdot14H_2O$,[18] have been reported to absorb alcohols; $[Co_2(H_2O)_4][Re_6S_8(CN)_6]\cdot10H_2O$ and $[Co(H_2O)_3]_4[Co_2(H_2O)_4][Re_6Se_8(CN)_6]_3\cdot44H_2O$ have demonstrated vapochromic behavior during exposure to organic solvents. Structural studies showing included organic species are not available so far, however. We report here, for the first time, on a 3D polymer formed from Mn(II) cations bound to $[Re_6S_8(CN)_6]^{4-}$ cluster anions in molar ratio of 2 : 1 where the residual space is filled with organic molecules, in this case isopropyl alcohol.

Red octahedral crystals of the compound were grown in the course of slow diffusion of isopropyl alcohol vapor into a solution of 70 mg $K_4[Re_6S_8(CN)_6]$ [0.04 mmol; see ref. 8(*c*) for synthesis], 25 mg $MnSO_4\cdot5H_2O$ (0.10 mmol), and 7 mL of water. A single crystal was maintained inside a sealed capillary filled with supernatant solution and studied by X-ray diffraction.§ The chemical formula derived therefrom was $\{[Mn(Pr^iOH)_2(H_2O)]_2[Re_6S_8(CN)_6]\}\cdot2Pr^iOH$. A fine crystalline product was prepared by mixing saturated solutions of 170 mg $K_4[Re_6S_8(CN)_6]$ (0.1 mmol) and of 70 mg $MnSO_4\cdot5H_2O$ (*ca.* 0.3 mmol) in water–isopropyl alcohol (1 : 3 v/v). A powder diffractogram of the bulky fresh product corresponded well to that calculated from single-crystal X-ray diffraction data, but the elemental analysis was not satisfactory because the compound readily lost isopropyl alcohol when exposed to air. The position of the ν(CN) band at 2143 cm^{-1} in the IR spectrum (in liquid paraffin) corresponded to a bridging cyanide group, values close to 2134–2138 cm^{-1} were found previously for cyanides bridging the 'Re_6S_8' core with Mn(II), Fe(II), Co(II) and Cd(II).[10]

The geometry of the anion fragment $[Re_6S_8(CN)_6]^{4-}$ found in the structure [Fig. 1(a)] is similar to those previously reported.[9–11,13,18] The Re_6 cluster is an almost ideal octahedron with Re–Re distances of 2.598–2.602 Å, the sulfur atoms capping each triangular face at Re–S distances of 2.399–2.414 Å. Six cyanide ligands coordinate to rhenium atoms through carbon with C–N distances of 2.117–2.118 Å, sticking out in pairs in a mutually perpendicular fashion.

The Mn(II) center has an 'N_3O_3' octahedral environment [Fig. 1(b)]. Three mutually perpendicular bonds extend to cyanide nitrogens, connecting each center to three neighboring cluster anions with Mn–N distances of 2.16–2.19 Å. The coordination octahedron is completed by three oxygen atoms from one water [at 2.220(7) Å] and two isopropyl alcohol molecules [2.230(7) and 2.259(6) Å for molecules A and B, respectively]. There is one further isopropyl alcohol molecule which is not chemically bound to the metal center, as it is H-bonded to ligand water with an O(water)–O(Pr^iOH) distance of 2.65(2) Å.

In the crystal structure, two Mn(II) centers are located about the inversion center, with an Mn–Mn distance of ≈5.3 Å. Isopropyl alcohol molecules attached to one center penetrate between isopropyl alcohol molecules attached to another center. The resulting packing associate $\{[Mn(Pr^iOH)_2(H_2O\cdots$

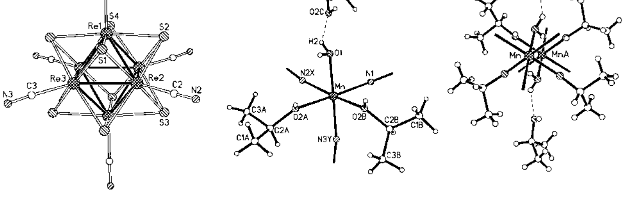

Fig. 1 The structure of the $[Re_6S_8(CN)_6]^{4-}$ cluster anion (a), coordination environment of Mn(II) (b), and the $\{[Mn(Pr^iOH)_2(H_2O\cdots Pr^iOH)]_2\}^{4+}$ associate. Hydrogen bonds are shown with dashes. N2X and N3Y arise from N2 and N3 atoms through (−1/2 + *x*, 1/2 − *y*, 1 − *z*) and (3/2 − *x*, −*y*, −1/2 + *z*) operations, respectively; the MnA atom rises from Mn through centrosymmetry.

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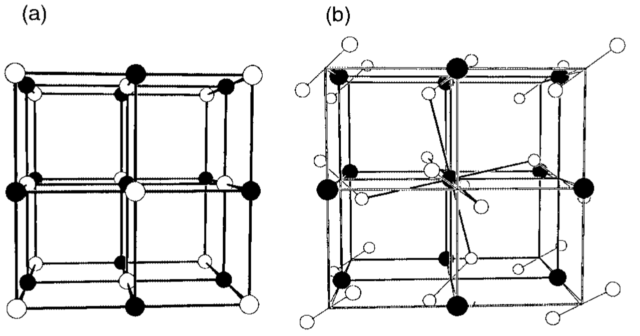

Fig. 2 3D coordination motif in Prussian Blue (a) [one unit cell is shown; black spheres show Fe(III) and open spheres show Fe(II) cations] compared to the 3D framework of the title compound (b) (one unit cell, schematic drawing: black spheres replace the cluster anions [Fig. 1(a)] and pairs of open spheres connected by single lines represent the associates [Fig. 1(c)]; coordination to manganese atoms is shown by solid lines for only the central cyanide cluster.

$Pr^iOH)]_2\}^{4+}$ is shown in Fig. 1(c). It should be noted that this fragment is complementary to the $[Re_6S_8(CN)_6]^{4-}$ cluster as it bears an equal but opposite charge and possesses six octahedrally disposed acceptor coordination sites (three about each Mn).

The 3D coordination framework in the structure shows profound parallels with the main structural motif of Prussian Blue; the latter is shown in Fig. 2(a).[2,3] In the structure of our work the $[Re_6S_8]^{10-}$ and $\{[Mn(Pr^iOH)_2(H_2O\cdots Pr^iOH)]_2\}^{4+}$ units play the role of Fe centers of two different types; each unit has six neighbors of another type attached approximately octahedrally through six cyanide bridges [Fig. 2(b)]. The unit cell of Prussian Blue is cubic with an *a*-parameter of 10.2 Å. The inner space within the smaller cubes is large enough to accommodate alkali metal cations and water molecules. The 3D framework of our structure also has a cubic motif distorted to orthorhombic. But the average unit cell parameter of 16.8 Å is dramatically larger than that in Prussian Blue. From the estimated volume of the $\{Mn_2[Re_6S_8(CN)_6]\}$ the framework occupies not more than 34% of the overall structure, with the residual empty space of 3120 Å^3 concentrated mainly in the eight smaller cubes of the unit cell. Moreover, the neutral charge of the framework makes it more hydrophobic. Such factors explain the filling of the inner space with isopropyl alcohol molecules, both as ligands and as solvating species. A cut-away layer of the 3D framework is shown in Fig. 3(a) and the packing of isopropyl alcohol solvate species inside the smaller cubes is shown in Fig. 3(b).

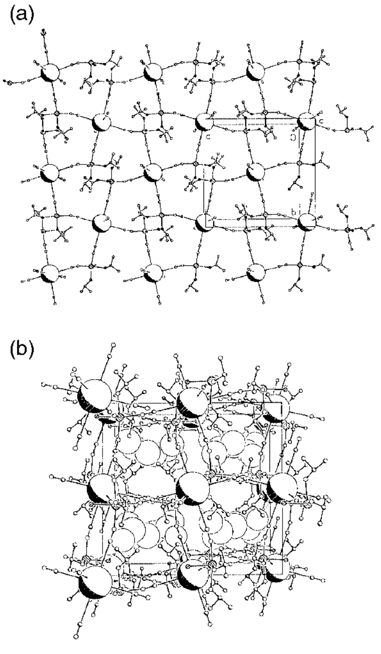

Fig. 3 Cut-away layer of the 3D framework in the title material (a) (coordinated water and isopropyl alcohol molecules are also shown) and packing of guest-solvated isopropyl alcohol molecules (van der Waals dimensions) in the small cube cavities (b). For clarity, cluster cores Re_6S_8 are replaced with 1.5 Å spheres.

Prussian Blue and related compounds form an extensive class of 3D coordination polymers revealing a remarkable stability of the main architecture and the ability to include small molecules and cations. This study demonstrates how utilization of cluster cyanides makes it possible to design analogous polymers but displaying a propensity to include species of larger size and lower polarity, thus making these useful materials for absorbing common organics.

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Notes and references

‡ Discovered in 1704 by a Berlin painter [see ref. 1(*a*)].

§ *Crystal data* for $\{[Mn(Pr^iOH)_2(H_2O)]_2[Re_6S_8(CN)_6]\}\cdot 2Pr^iOH$: $C_{24}H_{52}Mn_2N_6O_8Re_6S_8$, M = 2036.3, orthorhombic, a = 16.501(3), b = 16.633(3), c = 17.208(3) Å, U = 4723(2) Å^3, T = 298 K, space group *Pbca* (no. 61), Z = 4, D_c = 2.86 g cm^{-3}, μ(Mo-Kα) = 16.2 mm^{-1}, 51564 reflections collected, 5961 unique (R_{int} = 0.066) which were used in solution and refinement. The final R-values were 0.053 (all data) and 0.033 [for 4397 intense ($I > 2\sigma_I$) data]. CCDC 149441. See http://www.rsc.org/suppdata/cc/b0/b008040n/ for crystallographic data in .cif or other electronic format.

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