

# Octahedral metal clusters as building units in a neutral layered honeycomb network, $[\text{Zn}(\text{en})]_2[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^\dagger$

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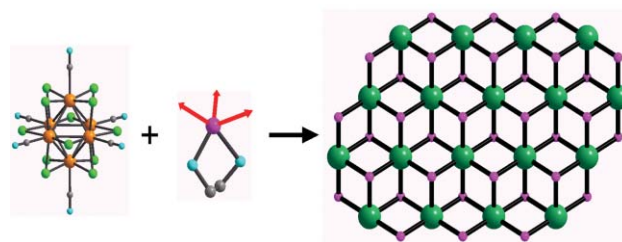
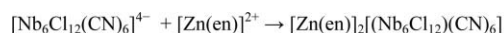
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A polymeric hybrid cluster-based compound with a double-layered honeycomb framework built of octahedral niobium cyanochloride clusters and  $\{\text{Zn}(\text{en})\}^{2+}$  metal complexes was designed and synthesized at room temperature, and structurally characterized by single crystal X-ray diffraction.

Hybrid organic–inorganic solid-state materials have received considerable interest recently due to their potential applications in catalysis, gas storage, chemical separation, and ion exchange.<sup>1</sup> Inorganic cluster units have been used as building blocks of solid materials with extended structures in which clusters are linked through organic or inorganic ligands, transition metal ions or metal complexes.<sup>2</sup> The use of coordination complexes instead of simple metal ions as the linking tethers between clusters offers the possibility of rational design and should, in principle, allow for better control over the structural and physical properties of these extended solids. In particular, the incorporation of metal complexes as linkers between nanosize building blocks may modify the physical properties and enhance the catalytic properties of the metal complexes. Recently, there have been extensive studies on utilizing face-capped octahedral  $[\text{Re}_6\text{Q}_8]^{2+}$  (Q = S, Se) clusters as the building blocks to create a wide variety of extended architectures.<sup>2a–c,3</sup> However, the use of edge-bridged octahedral metal clusters  $[\text{M}_6\text{X}_{12}]^{n+}$  as building units, and their assembly into cluster-based hybrid organic–inorganic extended frameworks remains largely unexplored except for the recently reported Prussian blue analogue  $[\text{NMe}_4]_2[\text{MnNb}_6\text{Cl}_{12}(\text{CN})_6]$ .<sup>4</sup> Octahedral metal clusters possess a number of advantages compared to simple metal ions. For example, it has been shown that the larger size of octahedral metal clusters can potentially lead to porous materials with larger pore sizes.<sup>4,5</sup> Furthermore, the electronic flexibility of these clusters would endow the novel materials with redox catalytic activities or magnetic properties.<sup>6</sup>

In this report, we describe how the combination of anisotropic coordination requirements of metal complexes and octahedral coordination environment of niobium clusters affords an especially effective implementation of the assembly of a designed solid-state coordination network—a layered honeycomb  $[\text{Zn}(\text{en})]_2(\text{Nb}_6\text{Cl}_{12})(\text{CN})_6$  (**2**). As illustrated in Scheme 1, the complex  $[\text{Zn}(\text{en})]^{2+}$  has three free sites available for coordination to three cyanide ligands of the cluster units  $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$  while the cluster can connect to six  $[\text{Zn}(\text{en})]^{2+}$  through its six terminal cyanide ligands.

The cluster precursor material,  $\text{Na}_4[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6] \cdot 13\text{H}_2\text{O}$  (**1**)<sup>†</sup> was prepared by reaction of  $[\text{Nb}_6\text{Cl}_{12}(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 4\text{H}_2\text{O}$ <sup>7</sup> with excess NaCN in MeOH–H<sub>2</sub>O. **1** crystallizes in the tetragonal system (space group,  $I4_1/amd$ ) and has an unusual and complex three-dimensional framework in which anionic cluster units  $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$  are linked to sodium cations by cyanide ligands.‡ Six cyanide ligands occupy apical positions of the octahedral cluster core  $[\text{Nb}_6\text{Cl}_{12}]^{2+}$  consisting of Nb<sub>6</sub> octahedron whose edges are bridged by 12 chloride ligands. The cluster core  $[\text{Nb}_6\text{Cl}_{12}]^{2+}$  in **1** is essentially the same as that found in other octahedral niobium cyanochloride clusters.<sup>4,8</sup> The intracenter bond lengths are similar to those found in other niobium chloride clusters with 16 valence

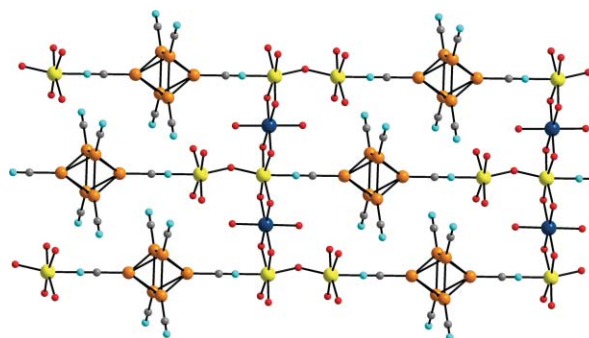


**Scheme 1** Schematic representation of the design of  $[\text{Zn}(\text{en})]_2[(\text{Nb}_6\text{Cl}_{12})(\text{CN})_6]$ . Green large spheres represent  $[\text{Nb}_6\text{Cl}_{12}]^{2+}$  cluster core; pink spheres (Zn); dark black lines represent CN linkages.

electrons per cluster.<sup>9</sup> The Nb–C bond length is comparable to that found in other cyanochloride niobium clusters, but slightly shorter than those found in cyano-oxychloride niobium clusters.<sup>10</sup> IR spectra of **1** show a shift to high frequency of the  $\nu(\text{C}\equiv\text{N})$  band ( $2118\text{ cm}^{-1}$ ), compared to those found in ionic cyanide salts ( $2040\text{--}2080\text{ cm}^{-1}$ ).<sup>11</sup> The structure of **1** may be described as formed of cluster units linked to each other *via* sodium dimers to form one-dimensional chains along  $[1\ 1\ 0]$ . Each dimer is formed of two  $\text{Na}(2)(\text{H}_2\text{O})_5\text{N}$  octahedra sharing one aquo ligand. Adjacent chains are connected by  $\text{Na}(1)(\text{H}_2\text{O})_6$  octahedra to form layers paralleled to the  $(-1\ 1\ 1)$  plane (Fig. 1). The layers are linked by additional  $\text{Na}(1)(\text{H}_2\text{O})_6$  octahedra to form the 3D network.

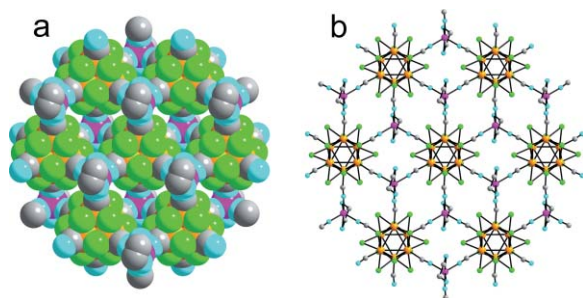
Reaction of **1** with  $[\text{Zn}(\text{en})][\text{ClO}_4]_2$  in EtOH–H<sub>2</sub>O results in the formation of the new layered compound  $[\text{Zn}(\text{en})]_2[(\text{Nb}_6\text{Cl}_{12})(\text{CN})_6]$  (**2**)<sup>†</sup>, which crystallizes in the trigonal system (space group,  $P\bar{3}$ ). Compound **2** is not soluble in common solvents such as methanol, ethanol and water, but can be dissolved in concentrated NaCN aqueous solution. Thermogravimetric analysis showed that **2** is stable up to  $300\text{ }^\circ\text{C}$ . The observed weight loss of 19.2% in the temperature range  $300\text{--}380\text{ }^\circ\text{C}$  can be attributed to decomposition of (en) and cyanide ligands (calculated 19.85%).

The structure of **2** consists of neutral layers built of octahedral



**Fig. 1** View of a layer parallel to the  $(-1\ 1\ 1)$  plane in the 3D structure of **1**. Chlorine ligands have been omitted for clarity. Nb: orange; Na(1): blue; Na(2): yellow; C: gray; N: cyan. Selected bond lengths (Å): Nb–Nb: 2.9243(6), 2.9287(7); Nb–Cl: 2.464(1)–2.466(1); Nb–C: 2.278(9), 2.266(6); Na–O: 2.328(1)–2.438(6); Na–N: 2.319(9).

<sup>†</sup> Electronic supplementary information (ESI) available: syntheses of **1** and **2**. See <http://www.rsc.org/suppdata/cc/b4/b408000a/>



**Fig. 2** (a) Space-filling representation of the layer in **2**. (b) A view of the structure of **2** along the *c* axis, illustrating the linkage of  $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$  building units via the metal complex  $[\text{Zn}(\text{en})]^{2+}$  into a honeycomb-like layered framework parallel to the *ab* plane. Nb: orange; Zn: pink; Cl: green; C: gray; N: cyan.

$[\text{Nb}_6\text{Cl}_{12}]^{2+}$  cluster units and  $[\text{Zn}(\text{en})]^{2+}$  linked by cyanide ligands (Fig. 2). The cluster unit  $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$  in **2** consists of a slightly distorted  $\text{Nb}_6$  octahedron in which every edge is bridged by a chloride ligand, and six CN ligands located in apical positions. The cluster has the same ligand arrangement and similar bond distances (Nb–Nb 2.917(1), 2.920(1); Nb–Cl: 2.426(5)–2.505(5); Nb–C: 2.260(8) Å) as those found in the precursor **1**. The IR spectra of **2** exhibit the characteristic C≡N vibration peak ( $\nu_{\text{C}=\text{N}}$ ) = 2167  $\text{cm}^{-1}$ , increased by 49  $\text{cm}^{-1}$  compared to that for **1**, which confirms the coordination of zinc to the nitrogen end of the cyanide ligand.

Each cluster unit  $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$  connects to six  $[\text{Zn}(\text{en})]^{2+}$  groups, and each  $[\text{Zn}(\text{en})]^{2+}$  connects to three cluster units to form layers parallel to the *ab* plane. Six-membered rings are formed by three  $[\text{Zn}(\text{en})]^{2+}$  groups and three  $[\text{Nb}_6\text{Cl}_{12}]^{2+}$  clusters linked by CN groups. These fused six-member rings form two honeycomb layers that share a common octahedral cluster. Four-member rings are also formed within the layer by two  $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$  and two  $[\text{Zn}(\text{en})]^{2+}$ . Adjacent layers are stacked perfectly on top of each other and interact through weak Van der Waals interactions only.

Layered structures similar to **2** have been observed in  $[\text{Zn}(\text{H}_2\text{O})_2][\text{Fe}(\text{CN})_6] \cdot 0.5\text{H}_2\text{O}$ <sup>12</sup> and in  $[\text{Zn}(\text{H}_2\text{O})_2][\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 13\text{H}_2\text{O}$ .<sup>13</sup> Interestingly, the structure of **2** can be viewed as formed by replacing  $\text{Fe}^{3+}$  ions in  $[\text{Zn}(\text{H}_2\text{O})_2][\text{Fe}(\text{CN})_6] \cdot 0.5\text{H}_2\text{O}$  with  $[\text{Nb}_6\text{Cl}_{12}]^{2+}$  cluster units. However, the coordination geometry of  $\text{Zn}^{2+}$  in **2** is different from that in these two analogues.  $\text{Zn}^{2+}$  in **2** is coordinated by two nitrogen atoms from (en) (Zn–N: 2.08(3), 2.37(2) Å) and three nitrogen atoms from three cyanide ligands of three different  $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$  clusters (Zn–N: 2.051(8) Å) forming distorted square pyramid  $\text{ZnN}_5$ . The basal plane of the pyramid is formed by two nitrogen atoms from an (en) molecule and two nitrogen atoms from two CN ligands while the apical position is occupied by a nitrogen atom from a CN group. In contrast to **2**,  $\text{Zn}^{2+}$  adopts a tetrahedral geometry in  $[\text{Zn}(\text{H}_2\text{O})_2][\text{Fe}(\text{CN})_6] \cdot 0.5\text{H}_2\text{O}$  and in  $[\text{Zn}(\text{H}_2\text{O})_2][\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 13\text{H}_2\text{O}$ . The  $[\text{Zn}(\text{en})]^{2+}$  complex with an anisotropic coordination environment plays an important role in the formation of the two-dimensional network of **2**. The coordination of an (en) to the  $\text{Zn}^{2+}$  ions prevents the formation of three-dimensional structures like those observed in  $\text{Na}_2[\text{Zn}_3\{\text{Re}_6\text{Se}_8(\text{CN})_6\}_2]^{13}$  or  $[\text{NMe}_4][\text{MnNb}_6\text{Cl}_{12}(\text{CN})_6]$ .<sup>4</sup> Reaction of  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  with **1** in solution led to the formation of a new phase, which is not soluble in water and methanol.<sup>†</sup>

Compound **2** represents the first hybrid layered structure consisting of octahedral niobium cyanochloride clusters. The layered structure of **2** illustrates the feasibility of using the coordination environment of metal complexes to control the topology and dimension of novel cluster materials. It should be possible to use a similar approach to control the structure and properties of cluster materials by proper design and synthesis of cluster units containing a combination of ditopic and blocking ligands in apical positions such as  $\text{Nb}_6\text{Cl}_{12}(\text{CN})_2(\text{B})_4$  (B = triphenylphosphine).

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## Notes and references

† Crystal data for **1**:  $\text{C}_6\text{H}_{26}\text{Cl}_{12}\text{N}_6\text{Na}_4\text{Nb}_6\text{O}_{13}$ , tetragonal, space group *I4<sub>1</sub>/amd*, *a* = 14.231(1), *c* = 19.413(2) Å, *V* = 3931.7(6) Å<sup>3</sup> at *T* = 193(2) K, *Z* = 4, *D*<sub>calcd</sub> = 2.475  $\text{g cm}^{-3}$  and *R*<sub>1</sub>(*wR*<sub>2</sub>) = 0.0489 (0.0936). Crystal data for **2**:  $\text{C}_{10}\text{H}_{16}\text{Cl}_{12}\text{N}_{10}\text{Zn}_2\text{Nb}_6$ , trigonal, space group *P* $\bar{3}$ , *a* = 10.891(1), *c* = 8.685(2) Å, *V* = 892.2(2) Å<sup>3</sup> at *T* = 193(2) K, *Z* = 1, *D*<sub>calcd</sub> = 2.587  $\text{g cm}^{-3}$  and *R*<sub>1</sub>(*wR*<sub>2</sub>) = 0.0568 (0.1154). CCDC 240364 and 240365. See <http://www.rsc.org/suppdata/cc/b4/b408000a/> for crystallographic data in .cif or other electronic format.

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