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Crystal structure of the two-dimensional framework $[Mn(salen)]_{4n}[Re_6Te_8(CN)_6]_n$ [salen = *N*,*N′*-ethylenebis(salicylideneaminato)]

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The first complex-bridged cyano–rhenium cluster framework material $[Mn(salen)]_{4n}[Re_6Te_8(CN)_6]_n$, with a two-dimensional layered structure is prepared by the reaction of a methanol solution of $[Mn(salen)]ClO_4$ with an aqueous solution of $Na_4[Re_6Te_8(CN)_6]$.

The design of extended structures based on molecular complexes has received much attention. Recently, there have been many studies on developing engineered-supramolecular networks in an effective manner and designing highly dimensional molecular systems with adjustable structures.[1,2] One way to obtain an extended structure is to utilize a molecular precursor that consists of multi-binding sites such as hexacyanoiron(III). For example, in MnL^+ (L = 3-MeO-salen,[3] 5-Cl-salen[4,5] or acacen[6]) linkage occurs *via* hexacyanoiron(III) to form two-dimensional layers. These cyano-bridged mixed-metal compounds with ferromagnetic and antiferromagnetic interactions are two-dimensional network structures. There have also been extensive studies on the face-capped octahedral rhenium cluster, $[Re_6Te_8(CN)_6]^{4-}$, which is analogous to hexacyanoiron(III). Cluster-expanded materials such as $Fe_4[Re_6Te_8(CN)_6]_3{\cdot}27H_2O$, $Ga_4[Re_6Se_8(CN)_6]_3{\cdot}38H_2O$, $[Cd_2(H_2O)_4][Re_6S_8(CN)_6]{\cdot}14H_2O$, and $Cs_2[trans\text{-}Fe(H_2O)_2]_3[Re_6Se_8(CN)_6]_2{\cdot}18H_2O$, where simple metal ions link the Re clusters to form bigger cavities, resemble the Prussian Blue $Fe_4[Fe(CN)_6]_3{\cdot}14H_2O$.[7–9] These three-dimensional frameworks include plenty of water molecules as well as metal ions within their cavities. $[Re_6S_8(CN)_6]^{4-}$ also coordinates to Mn(II) centers to form a neutral three-dimensional framework with isopropyl alcohol molecules.[10] In order to develop new framework materials with a potential to create new spatial or chemical functions, we designed a new extended solid system based on the Re cluster. For our linking material, we chose the $[Mn(salen)]^+$ complex instead of a simple metal ion since $[Mn(salen)]^+$ is paramagnetic with a high-spin d^4 electronic configuration of Mn(III). Futhermore, it also has axial sites to which the cyano–rhenium clusters can link up. We report here the preparation of the first cyano–rhenium cluster which is linked to an Mn complex to provide an extended framework with a unique layered structure.

The face-capped octahedral rhenium cluster $Na_4[Re_6Te_8(CN)_6]$ was prepared by a previous procedure.[11] The orange-red solid $Na_4[Re_6Te_8(CN)_6]$ was purified by recrystallization using methanol–diethyl ether. After an aqueous solution of $Na_4[Re_6Te_8(CN)_6]$ was carefully layered with a methanol solution of $[Mn(salen)]ClO_4$, black crystals of $[Mn(salen)]_{4n}[Re_6Te_8(CN)_6]_n$ **1** formed directly at the interface. A quantitative yield[12] of **1** was obtained by mixing an aqueous solution of $Na_4[Re_6Te_8(CN)_6]$ with a methanol solution of $[Mn(salen)]ClO_4$. Compound **1** was not soluble in common solvents such as methanol, ethanol, water, diethyl ether, acetone, acetonitrile, or THF. The structure of **1** was determined by X-ray crystallography.[13]

The asymmetric unit contains half of an Re cluster, a bridged $[Mn(salen)]^+$ unit, and a dangling $[Mn(salen)]^+$ unit. The complete two-dimensional layered structure is generated by the symmetry operations, $(-x + 3/2, y - 1/2, -z + 1/2)$, $(-x + 2, -y + 2, -z + 1)$, and $(-x + 3/2, y + 1/2, -z + 1/2)$. Four cyano groups of the Re cluster with C–N distances of 1.17(2)–1.18(2) Å are linked to $[Mn(salen)]^+$ units, forming a two-dimensional layer. The remaining two cyano groups with C–N distance of 1.13(2) Å are bound to a $[Mn(salen)]^+$ unit dangling outside the layer. The IR spectrum (KBr) of this compound showed two CN stretching peaks at 2073 and 2090 cm^{-1}, whereas the starting Re cluster had only one CN stretching peak at 2081 cm^{-1}. This result is consistent with the X-ray crystallographic data which shows two different types of cyano groups. Fig. 1(a) shows the rhenium cluster $[Re_6Te_8(CN)_6]^{4-}$, surrounded by six $[Mn(salen)]^+$ units. The Re–Re and Re–Te bonds range from 2.6842(7) to 2.7004(7) Å and from 2.685(1) to 2.703(1) Å, respectively. These are not significantly different from the starting rhenium cluster [The mean values of the Re–Re and Re–Te distances of the cyano–rhenium cluster are 2.681(3) and 2.694(2) Å, respectively]. The Mn(bridging

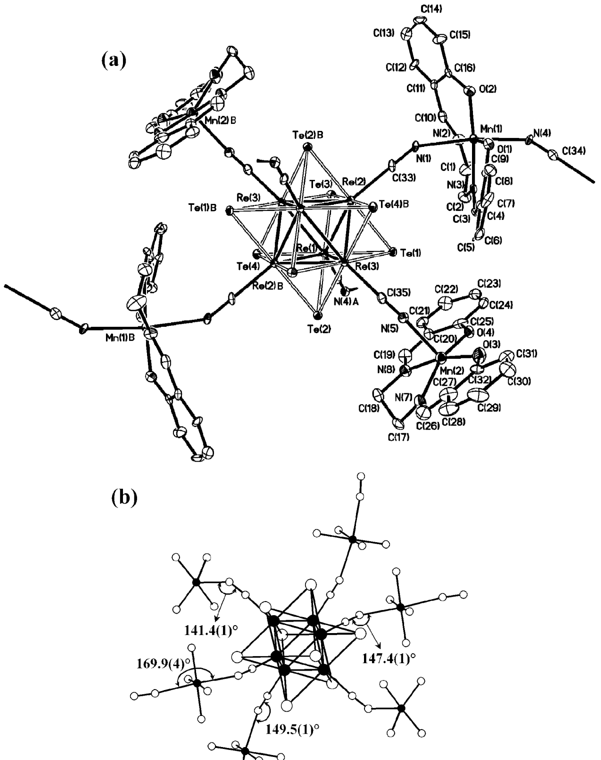

Fig. 1 (a) ORTEP drawing of the rhenium cluster $[Re_6Te_8(CN)_6]^{4-}$ surrounded by six $Mn(salen)^+$ units. Among the six $Mn(salen)^+$ units bound to six rhenium atoms, only four are shown. (b) A simplified drawing with some bond angles around the rhenium cluster. All carbon atoms of the salen molecules have been omitted for clarity. Symmery operations: A $(-x + 3/2, y - 1/2, -z + 1/2)$, B $(-x + 2, -y + 2, -z + 1)$.

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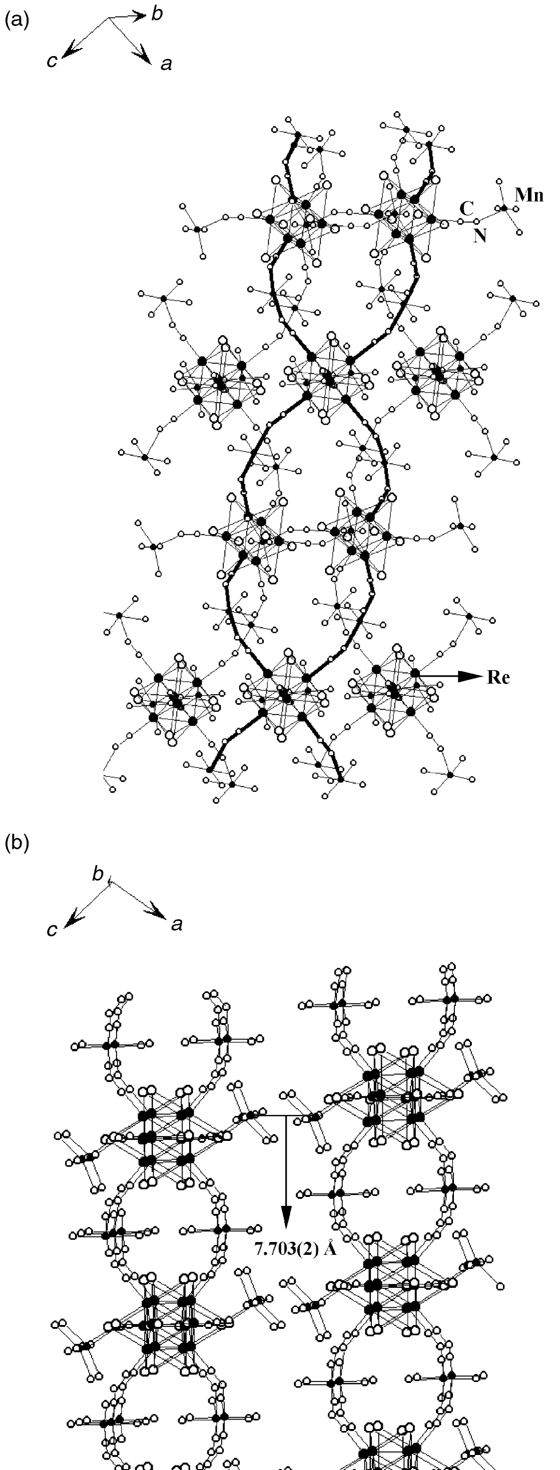

Fig. 2 (a) A two-dimensional layer containing $[Mn(salen)]^+$ units linked by cyano–rhenium clusters. The twisted ropes interconnected by Re_6Te_8 clusters are shown. (b) Side view of two layers. All carbon atoms of the salen molecules are omitted for clarity.

Mn unit)–N(cyano group) distances are 2.27(1) and 2.28(1) Å, while the Mn(dangling Mn unit)–N(cyano group) distance is 2.14(1) Å. Fig. 2(a) shows a two-dimensional layer containing $[Mn(salen)]^+$ units linked by cyano–rhenium clusters, while Fig. 2(b) shows a side view of two layers stacked perpendicular to the (1 0 1) direction. This layer is not a flat sheet, since the angle of the bridging elements N(cyano group)–Mn–N(cyano group) is 169.9(4)° and the angles C(cyano group)–N(cyano group)–Mn are 147.4(1) and 149.5(1)°. The unlinked dangling $[Mn(salen)]^+$ units are directed toward the outside of the layers, and the C(cyano group)–N(cyano group)–Mn(dangling Mn unit) angle is 141.4(1)° [Fig. 1(b)]. Two neighboring chains of –Mn(salen)–NC–Re_6Te_8–CN–Mn(salen)– run akin to a twisted rope, such ropes being interconnected by Re_6Te_8 clusters forming two-dimensional sheets. The intermolecular distances between the Mn units *via* the Re cluster are 14.490(9) and 14.38(1) Å, while the distance between the dangling Mn units *via* the Re cluster is 13.788(8) Å. The interlayer distance between the neighboring Mn (dangling Mn unit) atoms is 7.703(2) Å.

This system with cyano–rhenium clusters linked by Mn(salen) complexes is the first complex-bridged cyano–rhenium cluster framework material. Remarkably, this compound shows a unique thick-layered structure which opens the possibility of developing a new class of materials through crystal engineering of appropriate molecular complexes. We are currently investigating other transition metal complexes with high-spin systems which could provide extended network structures with cyano–rhenium clusters.

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12 Yield: 39.1%. Anal. Calc. for $C_{70}H_{56}Mn_4N_{14}O_8Re_6Te_8$: C, 23.49; H, 1.58; N, 5.48. Found: C, 23.48; H, 1.51; N, 5.42%.

13 The X-ray diffraction data were collected on a Nonius Kappa-CCD diffractometer using Mo-Kα radiation (λ = 0.71071 Å) at 150 K; crystal size 0.40 × 0.12 × 0.06 mm. The CCD data were integrated and scaled using the DENZO-SMN software package, and the structure was solved and refined using SHEXTL V5.0. All non-hydrogen atoms were located in the calculated positions. *Crystal data*: $C_{70}H_{56}Mn_4N_{14}O_8Re_6Te_8$, M = 3579.05, monoclinic, space group $P2_1/n$ (no. 14) a = 15.8104(7), b = 13.5732(7), c = 18.9822(5) Å, β = 101.738(3)°, V = 3988.4(3) Å^3, Z = 2, μ(Mo-Kα) = 12.603 mm^{-1}, 34426 reflections measured, 7847 unique (R_{int} = 0.115) which were used in all calculations, final R = 0.0552 (R_w = 0.1241) with reflections having intensities greater than 2σ, GOF(F^2) = 1.030. CCDC reference number 152818. See http://www.rsc.org/suppdata/cc/b1/b104276a/ for crystallographic data in CIF or other electronic format.