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Novel octahedral tungsten sulfidocyanide cluster anion $[W_6S_8(CN)_6]^{6-}$†

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Novel tungsten octahedral sulfidocyanide cluster compounds $Na_6[W_6S_8(CN)_6]\cdot 18DMSO$ 1 and $K_6[W_6S_8(CN)_6]$ 2 have been synthesized and characterized by X-ray crystallography and NMR spectroscopy.

Chevrel phases,[1] $M_xMo_6Q_8$, (M = metal, Q = chalcogen) are a class of cluster compounds extensively studied for their superconductivity,[2] fast ion conductivity[3] and catalytic activity.[4] The building block of the Chevrel phases is an octahedral molybdenum cluster face-capped by eight chalcogenide atoms (Q). Although no tungsten analogues of the Chevrel phases are known, the molecular tungsten clusters $W_6Q_8L_6$ (L = neutral Lewis base ligand) have been synthesized in solution,[5–10] as have the $Mo_6S_8L_6$ clusters.[11,12] Our investigation of $W_6S_8L_6$ clusters,[10,13–15] particularly the finding of strong bonding to the W_6S_8 cluster by isocyanide,[15] suggested cyanide might also be a good ligand. It would be interesting to explore such chemistry, given the diverse structural chemistry of cyanides,[16] in particular, $[Re_6Q_8(CN)_6]^{4-}$ clusters have been exploited to prepare a number of extended structure coordination compounds.[17,18] It was reported recently that molecular $[Mo_6Se_8(CN)_6]^{7-/6-}$ clusters could be synthesized through 'excision' of clusters from the Chevrel phase with molten KCN,[19] however, such synthesis could be achieved from simple non-cluster starting materials as well.[20] We report here the synthesis and characterization of the first W_6S_8 cluster compounds with anionic cyanide ligand: $Na_6[W_6S_8(CN)_6]\cdot 18DMSO$ **1** and $K_6[W_6S_8(CN)_6]$ **2**. Our preliminary study indicates that $[W_6S_8(CN)_6]^{6-}$ have different redox behavior from $[Mo_6Se_8(CN)_6]^{6-}$.

Reaction of $W_6S_8(4\text{-Bu}^t\text{py})_6$[10] with NaCN (slightly more than 1 : 6 equiv.) in DMSO at 100 °C for 1 day resulted in a brown-red crystalline precipitate which was filtered off as product **1**‡ from a brown–red solution (yield of the product: 84%). Slow cooling of a hot DMSO solution of **1** yielded suitable single crystals for X-ray structural analysis.§ The identity of the cluster anion is apparent and shown in Fig. 1(a). The W_6S_8 cluster core is a quite regular octahedron with an average W–W distance of 2.685(3) Å, similar to that found in $W_6S_8(C{\equiv}NBu^t)_6$ [2.681(3) Å].[15] The N terminal of each CN^- ligand is coordinated to a Na^+ ion in a roughly collinear fashion and each Na^+ ion is also coordinated by 3 O atoms from DMSO solvent molecules [Fig. 1(b)]. The overall crystal structure can be described as approximately "ABC" close packing of the cluster complexes including Na^+ ions and DMSO [Fig. 1(c)]. Based on the stoichiometry, the charge of the cluster anion is −6 and the metal electron count (MEC) of the cluster is 20.

Reaction of $W_6S_8(4\text{-Bu}^t\text{py})_6$ with $K^{13}CN$ (slightly more than 1:6 equiv.) in DMSO at 100 °C for 1 day resulted in a lustrous crystalline precipitate which was filtered off as product **2**¶ from a nearly colorless solution (yield of the product: 91%). Insoluble in any organic solvents, **2** is apparently not isostructural to **1** as the PXRDs are different. Layering deoxygenated water solutions of **2** with methanol yielded dark red single crystals suitable for X-ray structural analysis.§ Shown in Fig. 2, the refined cubic structure of $K_6[W_6S_8(CN)_6]\cdot 10H_2O$ ($\mathbf{2}\cdot 10H_2O$) shows *fcc* packing of the $[W_6S_8(CN)_6]^{6-}$ cluster anion. The K^+ ions and solvent water molecules reside, often with partial occupancies, in octahedral, tetrahedral and other interstitial sites. The cluster has the ideal O_h symmetry with a slightly shorter W–W distance [2.6772(7) Å] than that of **1**.

These syntheses are facilitated by the sparing solubility of both $W_6S_8(4\text{-Bu}^t\text{py})_6$ and NaCN (or KCN) in DMSO and simplified by the insolubility of product **2** or the low solubility of **1** at RT. Cyanide can replace the more weakly bonded ligands (L) on $W_6S_8L_6$ clusters, such as *n*-butylamine,[13] more readily, but phosphine ligands on $W_6S_8(PEt_3)_6$[10] can not be completely replaced by cyanide even in considerable excess. Therefore, the binding free energy of CN^- is estimated to be, not surprisingly, close to that of *tert*-butyl isocyanide.[15]

The PXRD of the bulk sample of **1** is identical to the simulated pattern from the single crystal structure (both

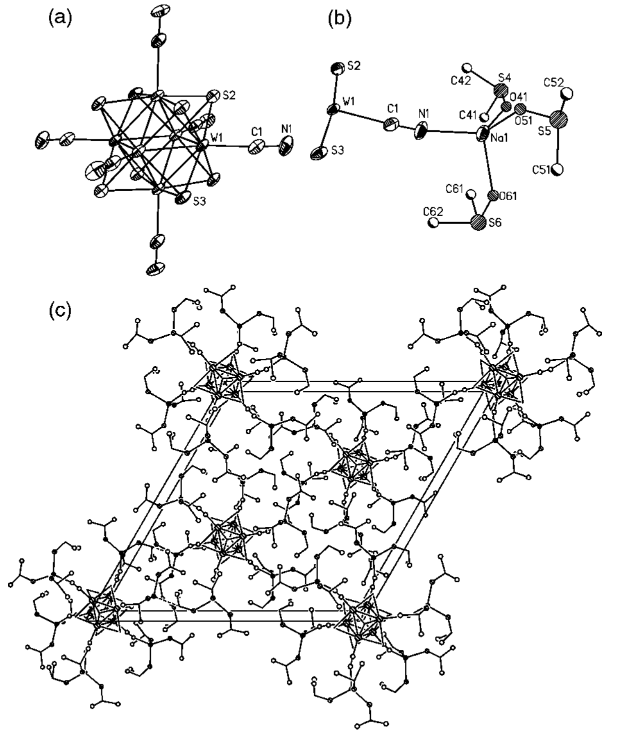

Fig 1 (a) ORTEP drawing of the $[W_6S_8(CN)_6]^{6-}$ cluster anion in **1** at 50% probability level; (b) asymmetric unit in **1** emphasizing the tetrahedral environment around the Na^+ cation (DMSO molecules are disordered, but not shown for clarity); (c) packing diagram of $Na_6[W_6S_8(CN)_6]\cdot 18DMSO$ **1** along the *c* axis. Selected bond lengths (Å) and angles (°): W1–W1A 2.6875(4), W1–W1C 2.6818(4), W1–S2 2.4518(15), W1–S3 2.4571(12), W1–S3A 2.4587(11), W1–S3B 2.4667(11), W1–C1 2.196(5), C1–N1 1.158(6), N1–Na1 2.327(4), Na1–O range 2.118(13)–2.378(8); W1–C1–N1 176.6(4), C1–N1–Na1 164.2(4). Symmetry transformations used to generate equivalent atoms: A *y*, −*x* + *y*, −*z* + 2; B *x* −*y*, *x*, −*z* + 2; C −*y*, *x* −*y*, *z*.

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† Electronic supplementary information (ESI) available: Fig. S1: observed and simulated XRPD patterns for **1**. Fig. S2: observed XRPD pattern for **2**. Fig. S3: TGA for **1**. See http://www.rsc.org/suppdata/cc/b1/b104161b/

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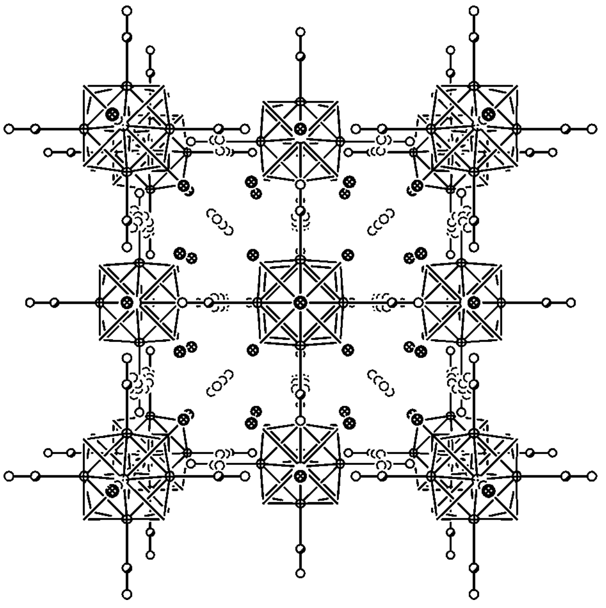

Fig 2 Unit cell (*fcc*) packing structure of $K_6[W_6S_8(CN)_6]\cdot 10H_2O$ (**2**·$10H_2O$). The circles of S atoms are omitted for clarity, K^+ ions are shown as cross-hatched circles, oxygen atoms of solvent water are shown as open circles with dotted boundaries. Selected bond lengths (Å): W–W 2.6772(7), W–S 2.452(2), W–C 2.152(16), C–N 1.162(19), N–K 2.447(13), 3.139(5).

available as ESI†). The stoichiometry was also confirmed by elemental analysis‡ and TGA analysis in which all of the DMSO solvent molecules (46 wt%) were lost upon heating. For **2**, the crystallographic refinements alone can not determine the stoichiometry or cluster oxidation state since K^+ and H_2O are disordered. Interestingly, the reported *blue* crystal of $K_7[Mo_6Se_8(CN)_6]\cdot 8H_2O$[19] is isotypic to this structure. However, elemental analysis¶ and ^{13}C NMR (*vide infra*) of the as prepared compound **2** establishes the 6− charge for the cluster anion.

It proved to be extremely difficult to observe the ^{13}C NMR signal from $[W_6S_8(CN)_6]^{6-}$ anions due to the low receptivity and tertiary nature of ^{13}C in CN^-.[21] Using ^{13}C labeled KCN enabled such observation and thus provides convenient means to monitor the chemistry in solution. A ^{13}C NMR spectrum of cluster **2** in D_2O is shown in Fig. 3. The chemical shift, δ 146.8, is different from that of free CN^- in water (δ 165) and falls into the general range for C-bonded cyanide ligands.[21] Satellite peaks with $J_{W\text{-}C}$ 107 Hz caused by coupling to ^{183}W isotope (14.3%)[21] confirms C terminal bonding to the W atom in the cyanide. The *sharp* NMR signal indicates a closed shell electron configuration. *If* the cluster was oxidized or reduced, the paramagnetic cluster would have severely broadened the NMR peak(s).[14]

In deoxygenated D_2O, the NMR spectrum of the clear brown–red solution of **2** does not change for at least a week. Upon exposure to air, the solution becomes darker and the ^{13}C NMR peak diminishes to half of the original intensity within 20 days accompanied by some new upfield peaks, suggesting that the cluster has been oxidized. This behavior is different from that of $[Mo_6Se_8(CN)_6]^{7-/6-}$ anions: the *reduced* cluster $[Mo_6Se_8(CN)_6]^{7-}$ (MEC = 21) was found to be the product of reactions with molten KCN (though the reducing agent has yet to be identified) and this cluster is oxidized in air to the *'normal'* closed shell cluster $[Mo_6Se_8(CN)_6]^{6-}$.[19,20] The stability of the $[W_6S_8(CN)_6]^{6-}$ cluster in deoxygenated water should allow the exploration of its aqueous solution chemistry.

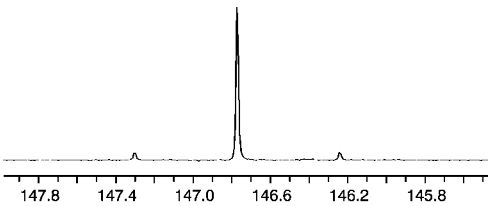

Fig 3 ^{31}C NMR spectrum of $K_6[W_6S_8(CN)_6]$ **2** in deoxygenated D_2O with dioxane as internal reference.

When excess NaCN is present in the DMSO solutions, the $[W_6S_8(CN)_6]^{6-}$ cluster anion is stable at least up to 180 °C. This suggests that $[W_6S_8(CN)_6]^{6-}$ might be synthesized by direct reaction of NaCN, W and S.

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Notes and references

‡ Elemental analysis for **1**: found (calc.): C 16.58 (16.49), H 3.37 (3.56), N 2.86 (2.91), W 35.84 (36.05), Na 4.37 (4.51)%. IR: ν(C≡N), 2083; DMSO, 2990, 1435, 1313, 1037, 954 cm^{-1}.

§ *Crystal data*: for **1**: $C_{42}H_{108}N_6Na_6O_{18}S_{26}W_6$, M = 3059.94, rhombohedral, space group $R\bar{3}$ (no. 148), a = 26.497(3), c = 12.1761(19) Å, U = 7403.3(15) Å^3, T = 165 K, Z = 3, D_c = 2.059 g cm^{-3}, μ(Mo-Kα) = 7.593 mm^{-1}, $F(000)$ = 4416, 17304 reflections measured, 3370 unique (R_{int} = 0.0328) which were used in refinements, 166 parameters. The final refinements converge to R_1 = 0.0249, wR_2 = 0.0563 [for $I > 2\sigma(I)$] and R_1 = 0.0314, wR_2 = 0.0576 for all data.

For **2**·$10H_2O$: $C_6H_{20}K_6N_6O_{10}S_8W_6$, M = 1930.46, cubic, space group $Fm\bar{3}m$ (no. 225), a = 15.3084(15) Å, U = 3587.5(6) Å^3, T = 165 K, Z = 4, D_c = 3.574 g cm^{-3}, μ(Mo-Kα) = 20.369 mm^{-1}, $F(000)$ = 3456, 2749 reflections measured, 327 unique (R_{int} = 0.0445) which were used in refinements, 27 parameters. The final refinements converge to R_1 = 0.0348, wR_2 = 0.0453 [for $I > 2\sigma(I)$] and R_1 = 0.0385, wR_2 = 0.0457 for all data.

CCDC reference numbers 163699 and 163700. See http://www.rsc.org/suppdata/cc/b1/b104161b/ for crystallographic data in CIF or other electronic format.

¶ Elemental analysis for **2**: found (calc.): C 4.48 (4.13), H 0.58 (0), N 4.77 (4.78), W 62.86 (62.81), K 13.28 (13.35)%. IR: ν(C≡N), 2038 cm^{-1}.

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