Synthesis and structures of a triply-fused incomplete-cubane cluster $[\{(\eta^5\text{-}C_5Me_5)WS_3\}_3Cu_7(MeCN)_9](PF_6)_4$ and a 2D polymer $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3Cl(MeCN)(pz)]PF_6$ (pz = pyrazine)

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Received (in Cambridge, UK) 27th July 1999, Accepted 8th October 1999

The reaction of $PPh_4[(\eta^5\text{-}C_5Me_5)WS_3]$ with 3 equiv. of $[Cu(MeCN)_4]PF_6$ in MeCN yielded an unusual high nuclearity W/Cu/S cluster $[\{(\eta^5\text{-}C_5Me_5)WS_3\}_3Cu_7(MeCN)_9](PF_6)_4$ 1, which in turn gave rise to a 2D polymer $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3Cl(MeCN)(pz)]PF_6$ 2 upon treatment with pyrazine in MeCN in the presence of LiCl.

The transition metal-mediated self-assembly of inorganic clusters and extended macromolecular structures is of intense interest to chemists, and a remarkable range of polynuclear structures have emerged.[1–4] Homoleptic acetonitrile complexes $[M(MeCN)_m]^{n+}$ have often been used as convenient precursors for such molecular ensembles of transition metal compounds, since they undergo facile substitution of MeCN and adduct formation with N-donor ligands.[5] On the other hand, we have been interested in construction of new heterometallic sulfide clusters based on the organometallic trisulfide complex anions of group 5 and 6 metals, $[(\eta^5\text{-}C_5Me_5)MS_3]^{2-}$ (M = Nb, Ta)[6,7] and $[(\eta^5\text{-}C_5Me_5)MS_3]^-$ (M = Mo, W).[8,9] As a part of such a study, a series of $(\eta^5\text{-}C_5Me_5)$M/M′/S clusters, consisting of tungsten and coinage metal atoms (M′), have been synthesized.[10–16] For instance, treatment of $[(\eta^5\text{-}C_5Me_5)WS_3]^-$ with CuNCS, CuBr, CuCl and $[Cu(PPh_3)_2]NO_3$ resulted in the formation of various $(\eta^5\text{-}C_5Me_5)$W/Cu/S clusters with the nuclearity varying from WCu_3 to W_3Cu_9.[12–16]

In an attempt to expand the scope of the cluster syntheses, we examined the reaction of $PPh_4[(\eta^5\text{-}C_5Me_5)WS_3]$ with $[Cu(MeCN)_4]PF_6$, and isolated a triply-fused incomplete-cubane cluster $[\{(\eta^5\text{-}C_5Me_5)WS_3\}_3Cu_7(MeCN)_9](PF_6)_4$ **1**. Furthermore, we constructed a 2D polymeric structure $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3Cl(MeCN)(pz)]PF_6$ **2** by treating **1** with pyrazine (pz) in the presence of LiCl. We report herein the synthesis and structures of these cluster/polymer compounds.

Compounds **1** and **2** were synthesized by the following procedures. When $[Cu(MeCN)_4]PF_6$ (0.17 g, 0.45 mmol) was added to a red MeCN (20 ml) solution of $PPh_4[(\eta^5\text{-}C_5Me_5)WS_3]$ (0.11 g, 0.15 mmol) under Ar, the solution darkened immediately. After stirring the solution overnight at room temperature, it was concentrated and layered by Et_2O, from which dark red cubic crystals of **1** were obtained in 76% yield. Complex **1** (0.052 g, 0.02 mmol) was then treated with 1 equiv. of LiCl in MeCN for 1 h at room temperature. 1 equiv. of pyrazine was added to the resulting homogenous solution which was stirred for 10 min. Subsequent work-up similar to that used for crystallization of **1** generated dark red plates of **2** in 67% yield. Compounds **1** and **2** are both stable toward oxygen and moisture and soluble in MeCN and DMSO.†

X-Ray analysis of **1**‡ revealed that a discrete cluster complex $[\{(\eta^5\text{-}C_5Me_5)WS_3\}_3Cu_7(MeCN)_9]^{4+}$ is accompanied by four PF_6^- counter anions. Being tetracationic, the cluster is considered as composed of three W(VI) and seven Cu(I) metal ions, and thus no redox process occurred during the cluster forming reaction. As shown in Fig. 1, the tetracationic cluster contains three $(\eta^5\text{-}C_5Me_5)WS_3$ units linked by two copper atoms, Cu(3) and Cu(5), and five more coppers chelate the sulfur ends to form a $W_3Cu_7S_9$ core. While the bridging coppers are tetrahedrally surrounded by four sulfurs, a total of nine acetonitrile molecules further coordinate to the latter five coppers to complete their coordination geometries. Alternatively, the core geometry of **1** can be viewed as a corner-shared triply-fused WCu_3S_3 incomplete cubane cluster. Interestingly, the resulting cluster structure is unsymmetric in that Cu(2) coordinates only one acetonitrile while each of the other coppers coordinates two acetonitrile molecules. It is rather surprising that one copper, Cu(2), assumes a trigonal planar coordination geometry with N(MeCN) and two μ_3-S atoms, despite the fact that the cluster was synthesized and recrystallized using MeCN as a solvent. The geometry of each incomplete WS_3Cu_3 cube of **1** is similar to those of the related double incomplete cubane clusters $[PPh_4]_2[(\eta^5\text{-}C_5Me_5)WS_3Cu_3X_3]_2$ (X = Br, Cl), as are the W–(μ_3-S) bond lengths.[12,14] It is noteworthy here that the W–Cu distances of **1** can be classified into three groups; a short W(1)–Cu(2) bond of 2.620(3) Å, long W–Cu(3,5) bonds of 2.759(3)–2.779(3) Å, and the remainder of W–Cu bonds with intermediate distances of 2.695(3)–2.720(4) Å. The observed trend of W–Cu bond lengths correlates with the number of bonding interactions at the Cu centers. The long W–Cu distances occur at Cu atoms, Cu(3) and Cu(5), each of which interacts with four S ligands and two W atoms, while the short W–Cu distance is observed for Cu(2) which interacts with three ligands and one W atom.

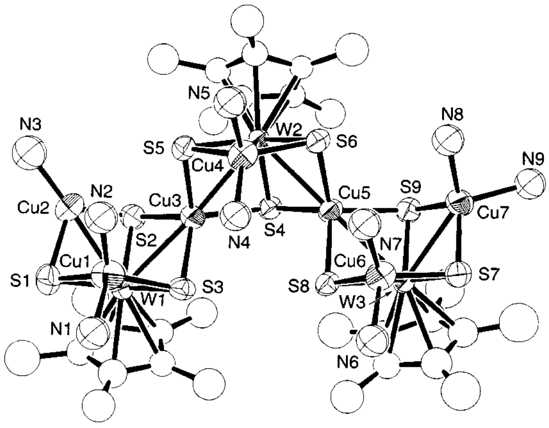

Fig. 1 Structure of the complex tetracation of **1**, with labelling scheme and 50% thermal ellipsoids. The MeCN molecules coordinated at the Cu atoms are represented by the pivotal N atoms only for clarity.

Compound **2**‡ has a 2D sheet structure in the crystalline state as shown in Fig. 2, which stacks along the crystallographic *b* axis. Fig. 3 displays the repeating unit of the 2D network and its connectivity. The cluster components, $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3(MeCN)]$, are linked by pyrazine through interactions with Cu(1) and Cu(2′), to form zigzag chains extending along the *a* axis where the orientation of the $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3(MeCN)]$ unit is alternating. The chains are then connected by μ-Cl at Cu(2*) and Cu(3) along the *c* axis. In the pyrazine linkage, two Cu–N bond distances are virtually the same, Cu(1)–N1 1.96(1)

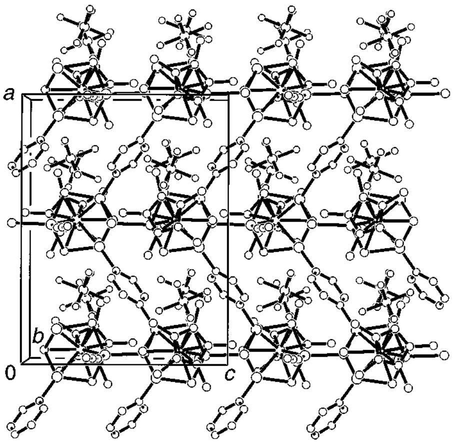

Fig. 2 Extended 2D layer structure of **2** looking down the *b* axis.

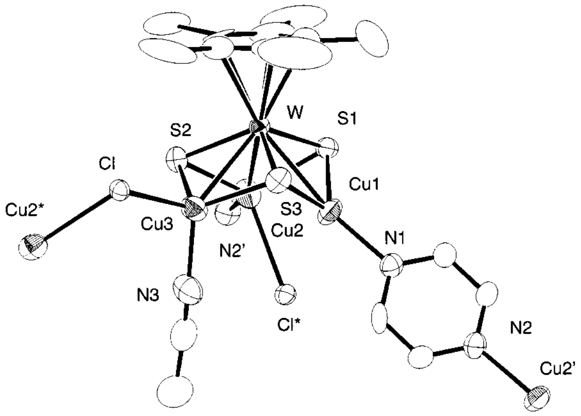

Fig. 3 Structure of a repeating unit of **2** with 50% thermal ellipsoids.

Å *cf.* Cu(2′)–N2 1.99(1) Å, while the μ-Cl bridge occurs in a less symmetric fashion with a Cu(2*)–Cl–Cu(3) angle of 106.8°, and the bonding with Cu(3) is substantially stronger, Cu(2*)–Cl 2.584(4) Å *cf.* Cu(3)–Cl 2.418(4) Å. The resulting 2D network forms a parallelogrammic mesh, and each cavity is filled by a PF_6^- anion. The surfaces of each layer are covered with η^5-C_5Me_5 rings, and the thickness of the layers is estimated to be *ca.* 9.9 Å. The layers are separated by *ca.* 3.5 Å, and no inter-layer bonding interactions were observed. The W(VI) and Cu(I) oxidation states are again retained in **2**, and the geometry of the WS_3Cu_3 incomplete cubane unit resembles closely those of **1** and $[PPh_4]_2[(\eta^5\text{-}C_5Me_5)WS_3Cu_3X_3]_2$.[12,14] Of the three copper atoms, Cu(1) is coordinated by three ligands, N(pz) and two μ_3-S atoms, and the W–Cu(1) distance is relatively short [2.654(2) Å]. On the other hand, Cu(2) and Cu(3) are coordinated by four ligands, N(pz or MeCN), μ-Cl and two μ_3-S atoms, and the W–Cu interactions are slightly weaker [2.673(2) and 2.722(2) Å].

The triply-fused incomplete-cubane $W_3S_9Cu_7$ framework of **1** is broken during the reaction with LiCl and pyrazine, providing a WS_3Cu_3 incomplete-cubane cluster as a building block of the stacked sheet structure of **2**. A key factor of this transformation is coordination of labile MeCN molecules at Cu in **1**. The formation of the intriguing 2D layer structure of **2** suggests that the construction of various types of 2D/3D extended structures will be made possible by reactions of **1** with appropriate hooking ligands such as 4,4′-bipyridine and dicyanoquinodiimine, *etc.*

Notes and references

† Synthetic manipulations were carried out under an argon atmosphere. *Spectroscopic data*: for **1**: IR (KBr, cm^{-1}): ν(C≡N) 2312m, 2279m; ν(P–F) 839vs, 558s; ν(W–S_{br}) 432w, 408m, 410m. UV–VIS (MeCN): λ_{max}/nm (ε/M^{-1} cm^{-1}) 405 (13 000). ^1H NMR (DMSO-d_6, 500 MHz), δ 2.18 (s, 45H, η^5-C_5Me_5), 2.08 (s, 27H, MeCN) (Found: C, 21.89; H, 2.71; N, 5.03; S, 10.27. Calc. for $C_{48}H_{72}Cu_7F_{24}N_9P_4S_9W_3$: C, 21.84; H, 2.75; N, 4.78; S, 10.93%). For **2**: IR (KBr, cm^{-1}): ν(C≡N) 2307m, 2287m; ν(P–F) 838vs, 558s; ν(W–S_{br}) 429w, 407m. UV–VIS (MeCN): λ_{max}/nm (ε/M^{-1} cm^{-1}) 421 (4100). ^1H NMR (DMSO-d_6, 500 MHz), δ 8.83 (s, 4H pz), 2.17 (s, 15H, η^5-C_5Me_5), 2.07 (s, 3H, MeCN) (Found: C, 21.23; H, 2.48; N, 4.75; S, 10.23. Calc. for $C_{16}H_{22}ClCu_3F_6PS_3W$: C, 21.17; H, 2.45; N, 4.63; S, 10.60%).

‡ *Crystal data* for **1**: $C_{48}H_{72}Cu_7F_{24}N_9P_4S_9W_3$, M = 2639.93, orthorhombic, space group *Pbca*, a = 25.23(1), b = 31.84(1), c = 20.951(8) Å, V = 16835(11) $Å^3$, Z = 8. Of 8574 reflections collected (Mo-Kα, $2\theta_{max}$ = 45.0°) on a Rigaku AFC7R diffractometer, 5252 [$I > 3.00\sigma(I)$] were observed. The structure was solved by direct methods and expanded using Fourier techniques with the TEXSAN program package. W, Cu, S and P atoms were refined anisotropically while F, N and C atoms were refined isotropically. H atoms were put on the calculated positions without refinement. The R values are $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ = 0.054 and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ = 0.064. For **2**: $C_{16}H_{22}N_3ClCu_3F_6PS_3W$, M = 907.46, orthorhombic, space group *Pbca*, a = 16.055(3), b = 26.78(1), c = 12.295(5) Å, V = 5285(3) $Å^3$, Z = 8. Of 5203 reflections collected (Mo-Kα, $2\theta_{max}$ = 50.1°), 2830 [$I > 3.00\sigma(I)$] were observed. The structure was solved by the Patterson method. All nonhydrogen atoms were refined anisotropically, and H positions were idealized. The final R values are R = 0.046 and R_w = 0.050.

CCDC 182/1443. See http://www.rsc.org/suppdata/cc/1999/2315/ for crystallographic files in .cif format.

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Communication 9/06081B