First complexes with cuboidal-type M_4Te_4 (M = Mo, W) cluster cores: synthesis and structure of $K_7[Mo_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 11H_2O$ and $K_6[W_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 5H_2O$

Vladimir P. Fedin,*[a] Irina V. Kalinina,[a] Alexander V. Virovets,[a] Nina V. Podberezskaya[a] and A. Geoffrey Sykes*[b]

[a] *Institute of Inorganic Chemistry, Russian Academy of Sciences, pr. Lavrentjeva 3, Novosibirsk 630090, Russia*
[b] *Department of Chemistry, The University of Newcastle, Newcastle-upon-Tyne, UK NE1 7RU*

High-temperature reactions of $Mo_3Te_7I_4$ or WTe_2 with KCN at 450 °C produce M_4Te_4 cubane-type complexes, isolated here as $K_7[Mo_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 11H_2O$ and $K_6[W_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 5H_2O$ in high yields, and characterized by X-ray crystallography.

Homo- and heterometallic cuboidal cluster complexes with bridging chalcogenide ligands are known for a wide variety of transition metals, and appear to be one of the most important common basic structures of transition metal cluster complexes. Homometallic Mo_4S_4 cubane-type clusters have been known for some 20 years.[1–6] They have the general formula $[Mo_4Y_4L_{12}]$, where L denotes the ligating atoms, either neutral or anionic. Cubane-type molecular cluster complexes $[Mo_4Se_4(H_2O)_{12}]^{4+/5+/6+}$ have been reported.[7,8] Solid-state compounds $Mo_4S_4X_4$ (X = Cl, Br, I) and MMo_4Y_8 (M = Al, Ga, Y = S; M = Ga, Y = Se) containing Mo_4Y_4 clusters, with Mo atoms coordinated octahedrally by either three chalcogen and three halogen atoms or six chalcogen atoms have been isolated.[9–12]

Preparative routes to $[Mo_4Y_4(H_2O)_{12}]^{4+/5+/6+}$ (Y = S, Se) clusters by dimerization of chalcogenide Mo^V_2 complexes under reducing conditions, and from Mo_3Y_7 and Mo_3Y_4 cores, have been reported. Self-assembly routes have also been developed.[13] There are as yet no examples of cuboidal $[W_4Y_4(H_2O)_{12}]^{4+/5+/6+}$ clusters and the number of W_4 chalcogenide complexes is limited. Examples are (*i*) the raft-type complex $[W_4S_6(SH)_2(PMe_2Ph)_6]$,[14] (*ii*) the tetrahedral complex $[W_4S_6(PMe_2Ph)_4]$[14] having a $W_4(\mu_2\text{-}S)_6$ adamantane-like core, and (*iii*) $[W_4S_8(H_2NCH_2CH_2NH_2)_4]S$[15] which has a cuboidal $W_4S_4^{10+}$ core.

No Mo and W cubes, M_4Y_4 with Y = telluride, have as yet been prepared. Many of the traditional reagents used in the development of the sulfide/selenide chemistry, *e.g.* H_2Y or $[MY_4]^{2-}$ (M = Mo, W; Y = S, Se), are simply not known in the case of Y = Te.[16,17] Our recent research has therefore focused on the development of high-temperature techniques to synthesize solid-state molybdenum/tungsten tellurides as starting materials for the preparation of molecular telluride containing complexes.[18,19] The first complex having an M_3Te_7 core $Mo_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3^{4+}$, was synthesized by extrusion of the polymeric solid-state product $Mo_3Te_7I_4$ from the high-temperature reaction of molybdenum, tellurium and iodine, with cyanide.[19]

Here we report the high-yield synthesis and crystal structure determination of the first complexes with Mo_4Te_4 and W_4Te_4 cluster cores. Cuboidal M_4Te_4 complexes are known for transition metals M = Mn, Re, Fe, Ru, Rh, Ir, Ni and Pt, but with the exception of Fe these do not have as highly developed M_4S_4 and M_4Se_4 chemistry as in the case of Mo.[20]

We have used a simple procedure starting from the elements for the synthesis of the title telluride cluster complexes of molybdenum and tungsten. Dark red–brown crystals of $K_7[Mo_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 11H_2O$ **1** and $K_6[W_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 5H_2O$ **2** were obtained in high yields by the high-temperature reaction of $Mo_3Te_7I_4$ or WTe_2 with KCN at 450 °C and further crystallization from aqueous solutions.† Complete X-ray structural determinations have revealed that the structures of **1** and **2** consist of discrete cluster anions of $[Mo_4(\mu_3\text{-}Te)_4(CN)_{12}]^{7-}$‡ or $[W_4(\mu_3\text{-}Te)_4(CN)_{12}]^{6-}$‡ and K^+ cations, and solvent water molecules. Fig. 1 and 2 show perspective views of the cluster units with important bond distances. The cluster anions display a cubane-like geometry, with the M_4Te_4 (M = Mo, W) cores constituted by two concentric interpenetrating tetrahedra of molybdenum/tungsten and tellurium. The tellurium atoms cap in a symmetrical manner the triangular faces of the molybdenum/tungsten tetrahedron [the mean Mo–Te distance is 2.674(1) Å; the mean W–Te distance is 2.686(2) Å]. The octahedral coordination of each molybdenum/tungsten center is completed by three cyanide ligands. For **1**, the distortion of the Mo_4 tetrahedron from ideal T_d symmetry is irregular, giving a relatively narrow range of Mo–Mo distances from 2.967(1) to 3.002(1) Å. Some notable differences, however, can be found for W–W bond distances: the W(1)–W(4) distance of 2.839(1) Å is significantly shorter than the W(2)–W(4) distance of 3.054(1) Å. The average oxidation state of the molybdenum atoms in **1** is 3.25 and the complex has one unpaired electron. The average oxidation state of the tungsten atoms in **2** is 3.5 and the complex is diamagnetic. The M_4Te_4 clusters of 5+ and 6+ charges, respectively, provide interesting comparisons with $[Mo_4Y_4]^{5+}$ and $[Mo_4Y_4]^{6+}$ (Y = S, Se) clusters.[8,13,21,22] The higher charge on the W_4Te_4

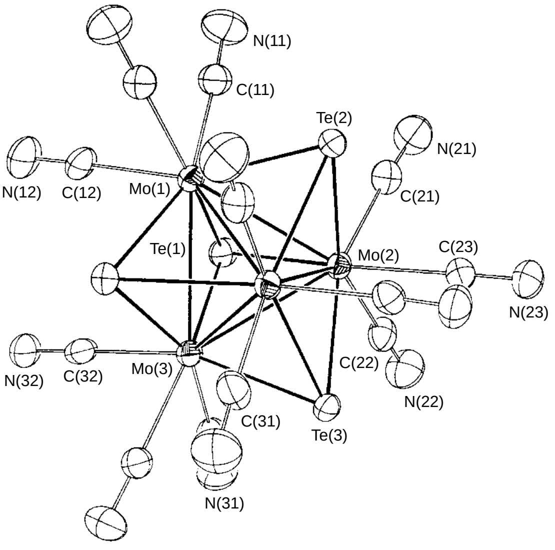

Fig. 1 Anion in **1** (thermal ellipsoids at 50% probability level). Some geometrical parameters (Å): Te–Mo 2.6663(8)–2.686(1), av. 2.674(1); Mo–Mo 2.967(1)–3.002(1), av. 2.993; Mo–C 2.14(1)–2.176(8), av. 2.162(9); C–N 1.13(1)–1.17(1), av. 1.15(1).

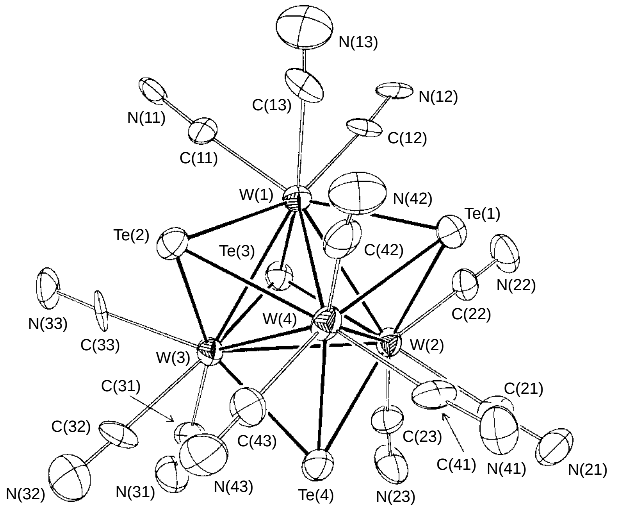

Fig. 2 Anion in **2** (thermal ellipsoids at 50% probability level). Some geometrical parameters (Å): W(1)–W(2) 2.957(1), W(1)–W(3) 2.923(1), W(1)–W(4) 2.839(1), W(2)–W(3) 3.054(1), W(2)–W(4) 3.008(1), W(3)–W(4) 2.991(2), W–Te 2.674(2)–2.704(2), av. 2.686(2); W–C 2.10(3)–2.20(3), av. 2.15(3); C–N 1.07(3)–1.20(3), av. 1.16(3).

cluster is consistent with the greater difficulty in reducing W to its lower oxidation states.

The cluster compounds **1** and **2** are stable indefinitely in air at 95 °C, and dissolve in aqueous solution, with no tendency to lose core atoms. Further studies on the reactivities of the telluride clusters, including an investigation of NMR and EPR spectra, and magnetic properties are in progress.

This work was supported by the Russian Foundation for Basic Research (research grant no. 96-03-33018), and an EU INTAS collaboration (research grant no. 96-1256).

Footnotes and References

† *General method* for preparation of $K_7[Mo_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 11H_2O$ **1** and $K_6[W_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 5H_2O$ **2**: a mixture of $Mo_3Te_7I_4$ (3.00 g) and KCN (3 g) or a mixture of WTe_2 (5.00 g) and KCN (5 g) was heated (450 °C; 2 days) in a sealed quartz tube. The product of the reaction was added to 50 ml of water and the mixture was refluxed for 3 h. After filtration, the solution was kept at 80 °C. During this time, the volume was decreased to 10 ml. After allowing to stand at 20 °C for 1 day, dark red–brown crystals were filtered off, washed with cold water and dried in air. Yield: 1.86 g of $K_7[Mo_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 11H_2O$ (83%), 4.73 g of $K_6[W_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 5H_2O$ (88%). Satisfactory elemental analyses (C, H, N, Mo, W and Te) were obtained. In order to ensure product homogeneity, the X-ray powder diffraction diagrams of **1** and **2** were obtained, and found to be identical with diagrams calculated from the single-crystal data. The UV–VIS absorption spectrum of **1** in H_2O gave peak positions $[\lambda/\text{nm}\ (\varepsilon/\text{M}^{-1}\ \text{cm}^{-1}\ \text{per}\ M_4)]$ at 382 (6100), 535 (2080), 769 (420). The UV–VIS absorption spectrum of **2** in H_2O gave peak positions at 357 (8000), 382 (sh), 474 (3140), 869 (440). IR (KBr pellet): ν(CN) 2086 cm^{-1} (**1**); ν(CN) 2108, 2097 cm^{-1} (**2**). The magnetic susceptibility of **1** was measured at 77 K: μ = 2.03 μ_B. The magnetic susceptibility of **2** was measured at 300 K: $\chi_M = -360 \times 10^{-5}$ cm^3 mol^{-1}.

‡ *Crystallography*: **1**: single crystal (0.14 × 0.38 × 0.44 mm) obtained by recrystallisation from an aqueous solution of KCN. *Crystal data*: orthorhombic, space group *Pnma*, $a = 12.112(1)$, $b = 21.736(2)$, $c = 16.109(1)$ Å, $U = 4241.0(6)$ Å^3, $Z = 4$, $D_c = 2.632$ g cm^{-3}. Total 5874 reflections [in which 4707 $F_o > 4\sigma(F)$] were collected using standard techniques at room temperature on an Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation (λ = 0.710 69 Å) up to $2\theta_{max}$ = 60°. The structure was solved by direct methods and refined in anisotropic approximation by full-matrix least-squares on F_o^2 using the SHELX-97[23] package. Absorption corrections were made using five azimuthal scan curves. Some hydrogen atoms of the solvent water molecules were found on Fourier map, but our attempts to refine these were unsuccessful. Final *R* values: $R(F) = 0.0473$, $wR(F^2) = 0.1239$ for 4707 $F_o > 4\sigma(F)$, $R(F) = 0.0612$, $wR(F^2) = 0.1276$, GOF = 1.153 for all data.

2: Single crystal (0.26 × 0.32 × 0.76 mm) obtained by recrystallisation from an aqueous solution of KCN. *Crystal data*: triclinic, space group $P\bar{1}$, $a = 12.399(1)$, $b = 13.187(1)$, $c = 13.496(1)$ Å, $\alpha = 83.712(8)$, $\beta = 66.575(8)$, $\gamma = 63.223(9)$°, $U = 1801.1(2)$ Å^3, $Z = 2$, $D_c = 3.471$ g cm^{-3}. Total 8464 reflections (in which 8103 unique, $R_{int} = 0.0594$) were collected using standard techniques at room temperature on an Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation (λ = 0.710 69 Å) up to $2\theta_{max}$ = 56°. The structure was solved by direct methods and refined in anisotropic approximation by full-matrix least-squares on F_o^2 using the SHELX-97[23] package. Absorption corrections were made using six azimuthal scan curves. Hydrogen atoms of solvate water molecules were not located. Final *R* values: $R(F) = 0.0696$, $wR(F^2) = 0.2151$ for 6752 $F_o > 4\sigma(F)$, $R(F) = 0.0796$, $wR(F^2) = 0.2213$, GOF = 1.143 for all unique data. CCDC 182/712.

1 T. Shibahara, *Adv. Inorg. Chem.*, 1991, **37**, 143.
2 T. Shibahara, *Coord. Chem. Rev.*, 1993, **123**, 73.
3 T. Saito, in *Early Transition Metal Clusters with π-Donor Ligands*, ed. M. H. Chisholm, VCH, New York, 1995, p. 63.
4 R. H. Holm, *Adv. Inorg. Chem.*, 1992, **38**, 1.
5 S. Harris, *Polyhedron*, 1989, **8**, 2843.
6 T. Saito, *Adv. Inorg. Chem.*, 1996, **44**, 45.
7 M. Nasreldin, G. Henkel, G. Kampmann, B. Krebs, G. J. Lamprecht, C. A. Routledge and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1993, 737.
8 W. McFarlane, M. Nasraldin, D. M. Saysell, Z.-S. Jia, W. Clegg, M. R. J. Elsegood, K. S. Murray, B. Moubaraki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1996, 363 and references therein.
9 C. Perrin, R. Chevrel and M. Sergent, *Compt. Rend.*, 1975, **280**, 949.
10 J. M. Vandenberg and D. Brasen, *J. Solid State Chem.*, 1975, **14**, 203.
11 C. Perrin, R. Chevrel and M. Sergent, *Compt. Rend.*, 1975, **281**, 23.
12 A. Lebeuze, M. C. Zerrovski, H. Loirat and R. Lissillour, *J. Alloys Compd.*, 1992, **190**, 1.
13 T. Shibahara, H. Kyroya, H. Akashi, K. Matsumoto and S. Ooi, *Inorg. Chim. Acta*, 1993, **212**, 251 and references therein.
14 S. Kuwata, Y. Mizobe and M. Hidai, *J. Chem. Soc., Chem. Commun.*, 1995, 1057.
15 P. T. Wood, W. T. Pennington, J. W. Kolis, B. Wu and C. J. O'Connor, *Inorg. Chem.*, 1993, **32**, 129.
16 J. Beck, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 163.
17 L. C. Roof and J. W. Kolis, *Chem. Rev.*, 1993, **93**, 1037.
18 V. P. Fedin, H. Imoto and T. Saito, *J. Chem. Soc., Chem. Commun.*, 1995, 1559.
19 V. P. Fedin, H. Imoto, T. Saito, W. McFarlane and A. G. Sykes, *Inorg. Chem.*, 1995, 5097.
20 Mn_4Te_4: H.-O. Stephan and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2322; Re_4Te_4: Y. V. Mironov, T. E. Albrecht-Schmitt and J. A. Ibers, *Inorg. Chem.*, 1997, **36**, 944; Fe_4Te_4: H.-O. Stephan, Changneng Chen, G. Henkel, K. Griesar and W. Haase, *J. Chem. Soc., Chem. Commun.*, 1993, 886; P. Barbaro, A. Bencini, I. Bertini, F. Briganti and S. Midollini, *J. Am. Chem. Soc.*, 1990, **112**, 7238; M. L. Steigerwald, T. Siegrist, S. M. Stuczynski and Y. U. Kwon, *J. Am. Chem. Soc.*, 1992, **114**, 3155; M. L. Steigerwald, T. Siegrist, E. M. Gyorgy, B. Hessen, Y.-U. Kwon and S. M. Tanzler, *Inorg. Chem.*, 1994, **33**, 3389; H.-O. Stephan, Changneng Chen, G. Henkel, K. Griesar and W. Haase, *J. Chem. Soc., Chem. Comm.*, 1993, 886; Ru_4Te_4: E. J. Houser, T. B. Rauchfuss and S. R. Wilson, *Inorg. Chem.*, 1993, **32**, 4069; Rh_4Te_4: S. Schulz, M. Andruh, T. Pape, T. Heinze, H. W. Roesky, L. Haming, A. Kuhn and R. Herbst-Irmer, *Organometallics*, 1994, **13**, 4004; Ir_4Te_4: S. Schulz, M. Andruh, T. Pape, T. Heinze, H. W. Roesky, L. Haming, A. Kuhn and R. Herbst-Irmer, *Organometallics*, 1994, **13**, 4004; Ni_4Te_4: J. M. McConnachie, M. A. Ansari and J. A. Ibers, *Inorg. Chim. Acta*, 1992, **198**–**200**, 85; J. M. McConnachie, J. S. Bollinger and J. A. Ibers, *Inorg. Chem.*, 1993, **32**, 3923; Pt_4Te_4: J. M. McConnachie, J. C. Bollinger and J. A. Ibers, *Inorg. Chem.*, 1993, **32**, 3923.
21 F. A. Cotton, M. P. Diebold, Z. Dori, R. Llusar and W. Schwotzer, *J. Am. Chem. Soc.*, 1985, **107**, 6735.
22 A. Müller, W. Eltzner, W. Clegg and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 536.
23 G. M. Sheldrick, SHELX-93, Göttingen University, 1997.

Received in Cambridge, UK, 6th November 1997; 7/07995H