A Three-Dimensional, Cyano-Bridged Cluster−Metal Coordination Compound with Large Cavities

Vladimir P. Fedin,*[a] Alexander V. Virovets,[a] Irina V. Kalinina,[a] Vladimir N. Ikorskii,[a] Mark R. J. Elsegood,[b] and William Clegg[b]

Keywords: Tungsten / Tellurium / Cobalt / Cyanides / Crystal engineering

By very slow diffusion of aqueous solutions of $CoCl_2 \cdot 6H_2O$ and $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$ through silica gel, single crystals of $[Co(H_2O)_4]_3[W_4Te_4(CN)_{12}] \cdot 15.38H_2O$ were obtained. A complete X-ray structure determination reveals an extremely porous, three-dimensional neutral cluster-expanded framework structure with large water-filled cuboidal cavities.

Introduction

Reactions of mononuclear aquo- and cyano-transition metal complexes lead to the formation of an extensive family of cyanide-bridged metal−metal coordination polymers.[1,2] This class of compounds has the potential for use in molecular separation because large cavities are formed in some cases.[3,4] Recently, octahedral $[Re_6E_8(CN)_6]^{4-}$ (E = S, Se, Te) cluster complexes with an outer ligand topologically equivalent to hexacyanometallates have been shown to react with transition metal ions to precipitate a range of framework solids with unprecedented structures.[5] Cluster-expanded Prussian blue analogues of the composition $M_4[Re_6E_8(CN)_6] \cdot nH_2O$ (M = Ga, Fe)[6] and $[Cd_2(H_2O)_4][Re_6S_8(CN)_6] \cdot 14H_2O$[7] with large, water-filled cavities have been obtained. In the Cd compound the volume of each water-filled cavity is 345 Å^3, and the cavities represent 62% of the total volume of the structure. Another example of a porous compound based on a cyanide cluster is $(H_5O_2)_2Zn_3[Re_6Se_8(CN)_6] \cdot 18H_2O$[8] with a hexagonal cavity of ca. 11 × 11 × 5 Å filled by hydroxonium cations and water molecules.

The synthesis and crystallization of cyanide-bridged coordination polymers with structural and functional similarity to inorganic zeolites continues to be a challenging problem. Recently we have described the syntheses, X-ray structure determination and properties of cubane-type M_4E_4 (M = Mo, W; E = S, Se, Te) water-soluble cyano complexes.[9] Here we report for the first time that cuboidal cluster complexes of T_d symmetry can be used for the preparation of framework solids with voluminous cavities.[10]

[a] Institute of Inorganic Chemistry, Russian Academy of Sciences, pr. Lavrentjeva 3, Novosibirsk 630090, Russia
E-mail: cluster@che.nsk.su
[b] Department of Chemistry, The University of Newcastle upon Tyne,
Newcastle upon Tyne NE1 7RU, UK

Results and Discussion

An aqueous solution of $CoCl_2 \cdot 6H_2O$ was added slowly to an aqueous solution of mixed-valence (3.5) $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$ to give, in quantitative yield, well-formed cuboidal dark red-brown crystals of composition $[Co(H_2O)_4]_3[W_4Te_4(CN)_{12}] \cdot 8H_2O$ (**1**). The compound is X-ray amorphous after drying in air (XRD, Philips APD 1700). The compound was characterized by elemental analysis, IR spectroscopy, thermogravimetry and magnetochemical measurements. The FT-IR spectrum of **1** clearly shows the presence of H_2O and two types of cyanide ligands: the terminal W−CN fragments exhibit a sharp, intense band at 2100 cm^{-1} {compared with ν(CN) = 2097 cm^{-1} for $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$},[9] whereas the W−CN−Co bridges exhibit a broader line shifted to higher frequency (2127 cm^{-1}). The effective magnetic moment of 4.72 μB calculated per Co atom is reasonable for three isolated high-spin Co^{2+} ions per formula unit. The N end of the cyanide ligand is a weak field ligand and thus stabilizes a high-spin state. Thermogravimetric analysis in Ar revealed complete dehydration of **1** by 150 °C, with no further significant weight loss below 450 °C. The FT-IR spectra of **1** and a dehydrated sample (150 °C, vacuum, 1 h) confirm that only minor perturbation occurs in the arrangement of the framework upon complete dehydration. The structure of X-ray amorphous compound **1** is still unknown.

Further attempts were made to prepare single crystals from the system $Co^{2+}/[W_4Te_4(CN)_{12}]^{6-}$. Very slow diffusion of aqueous solutions of $[W_4Te_4(CN)_{12}]^{6-}$ and $[Co(H_2O)_6]^{2+}$ through silica gel for eight weeks resulted in cuboidal dark red-brown crystals (**2**) suitable for an X-ray single-crystal analysis. The composition of compound **2**, according to diffraction data, is $[Co(H_2O)_4]_3[W_4Te_4(CN)_{12}] \cdot 15.38H_2O$, the calculated density being approximately half of that measured for **1**.

The local coordination environment of the Co atom and the structure of the $[W_4Te_4(CN)_{12}]^{6-}$ cluster complex are shown in Figure 1. Each Co^{2+} ion exhibits pseudo-octahedral coordination, with four water ligands and two nitrogen atoms of the cyanide ligands bound in a *trans* arrangement.

  1434−1948/00/1111−2341 $ 17.50+.50/0

The arrangement of water around Co^{2+} is disordered over two symmetrically equivalent positions. A structure determination revealed a cubic three-dimensional neutral framework of cuboidal $[W_4Te_4]^{6+}$ and $[Co(H_2O)_4]^{2+}$ fragments linked through bridging cyanide ligands (Figure 2). There are 12 cobalt atom positions around each W_4Te_4 cluster. These positions are statistically half-occupied, and therefore each cluster is linked to six cobalt atoms to give a primitive cubic lattice of ReO_3 type with clusters and cobalt atoms in the Re and O positions, respectively. The centres of the cluster anions follow a primitive cubic motif, although not face-centred as in Prussian blue. The large cavities are filled by highly disordered water molecules. Our attempts to resolve the disorder by assuming lower symmetry space groups were unsuccessful.

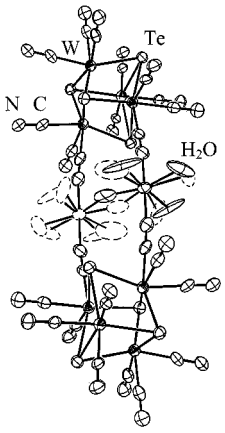

Figure 1. Fragment of structure of **2** showing the $[Co(H_2O)_4]^{2+}$ bridges between $[W_4Te_4(CN)_{12}]^{6-}$ anions, 30% probability ellipsoids; the W−W bonds are omitted for clarity; the disordered positions of Co atoms and water molecules are shown by dashed lines; main bond lengths (Å): W−W, 2.952(2), W−Te, 2.6889(17), W−C, 2.078(19), C−N, 1.20(2), Co−N, 2.096(17), Co−O, 2.15(4)−2.19(5).

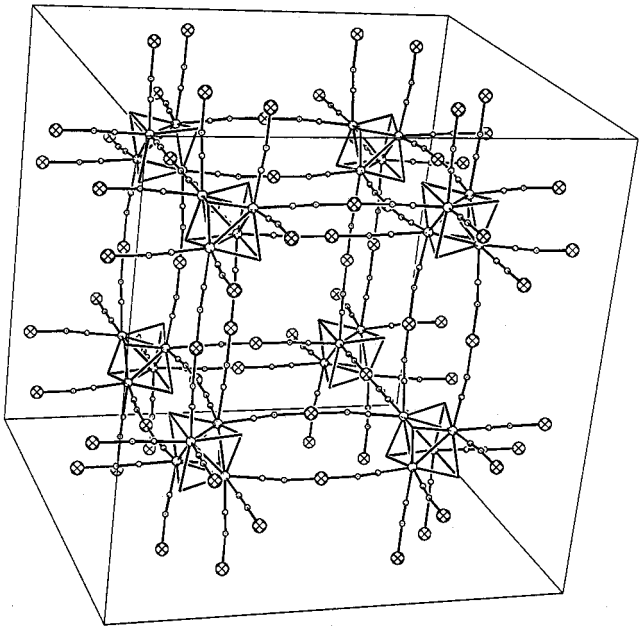

Figure 2. Crystal packing of **2**; all water molecules are omitted for clarity; all disordered positions of Co^{2+} ions are shown, but only one half of them are occupied.

The cavity in **2** of O_h symmetry has the centre at the point with coordinates (1/2, 1/2, 1/2). The O(3) atoms coordinated to the cobalt atoms form a cubic cubeoctahedron (the coordination polyhedron in the *ccp* structure) around the centre of the cavity. The diameter of the cubeoctahedron is 10.05 Å and the edges are of 5.05 Å. The calculated packing coefficient of **2** is unusually low at 0.354. The framework occupies only 27.3% of the unit cell, which means that the total Van der Waals volume of cavities and portals is 1520.1 $Å^3$ per formula unit of **2**. For comparison, the calculated void volumes per formula unit of $Na_{12}[Al_{12}Si_{12}O_{48}]$ (zeolite A) and $H_2[Al_2Si_{94}O_{192}]\cdot 24H_2O$ (zeolite ZSM-5) are 557 $Å^3$ and 2365 $Å^3$, respectively.

Our experiments show that crystals of compound **2** are very unstable. Water loss happens within a few minutes at room temperature resulting in an amorphous product which is identical to **1** according to the chemical analysis and physical measurement data. Crystals of **2** can be kept in native silica gel for a long time.

Investigations probing the electrochemistry and inclusion properties of this and related cyano-bridged cuboidal M_4E_4 (M = Mo, W; E = S, Se, Te) cluster-metal framework solids are in progress.

Experimental Section

Preparation of $[Co(H_2O)_4]_3[W_4Te_4(CN)_{12}]\cdot 8H_2O$ (1): Diffusion of 3 mL of an aqueous solution of $CoCl_2\cdot 6H_2O$ (0.076 g, 0.319 mmol) through silica gel in a narrow-diameter tube into 15 mL of an aqueous solution of $K_6[W_4Te_4(CN)_{12}]\cdot 5H_2O$ (0.100 g, 0.053 mmol) for two weeks resulted in a dark red-brown compound which was isolated by filtration, washed with water, and dried in air. Yield 0.108 g of $[Co(H_2O)_4]_3[W_4Te_4(CN)_{12}]\cdot 8H_2O$ (97%). Satisfactory elemental analyses (C, H, N, W, Te, Co) were obtained. − IR (KBr pellet): $\tilde{\nu}$ = 2127 s, ν(CN), 2100 s, ν(CN), 1600 s, br, δ(HOH), 450 m, ν(WC)/δ(WCN) cm^{-1}. − The magnetic susceptibility was measured at 300 K: $2.78\cdot 10^{-2}$ $cm^{-3}\cdot mol^{-1}$. The density of **1** was measured by microburette method: 3.34 gcm^{-3}.

Preparation of 2: Diffusion of aqueous solutions of $K_6[W_4Te_4(CN)_{12}]\cdot 5H_2O$ (0.05 $mol\cdot L^{-1}$) and $CoCl_2\cdot 6H_2O$ (0.1 $mol\cdot L^{-1}$) through silica gel in a U-tube for eight weeks resulted in cuboidal single crystals of **2** suitable for X-ray single crystal analysis.

X-ray Crystal Structure Determination of 2: The X-ray structural analysis was carried out at 160 K on a Bruker SMART CCD diffractometer (Mo-K_α, λ = 0.71073 Å, graphite monochromator, standard techniques, narrow frames of 0.3°, 40 s/frame). The crystal was covered by a frozen drop of oil to prevent decomposition. *Crystal data*: $C_{12}H_{54.76}Co_3N_{12}O_{27.38}Te_4W_4$, mol. Wt. 2228.0, cubic, space group $Fm\bar{3}m$, a = 25.577(6) $Å^3$, U = 16732(7) $Å^3$, Z = 8, D_c = 1.769 gcm^{-3}. A total of 25728 reflections were collected up to θ_{max} = 28.6°, of which 1103 were unique (R_{int} = 0.0768). Absorption corrections (μ = 7.476 mm^{-1}) were applied by the SADABS program with transmission factors ranging from 0.417 to 0.604. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 in an anisotropic approximation using the SHELX-97 set of programs.[11] Hydrogen atoms were not located. It was found that the Co atom position has half occupancy, along with the water molecules attached to it. Some of

the uncoordinated water molecules are also disordered, and their occupancy factors and displacement parameters were refined to reasonable values. Final *R* values: *R1* = 0.0418 for 422, $F_o \geq 4\sigma(F)$, *wR2* = 0.1438, GOF = 0.931 for all unique data. The packing coefficient and the volume of the framework were calculated by the KPACK program[12] using 600 test points per 1 Å^3 and the following atomic radii (Å): C, 1.71, O, 1.40, N, 1.55, Te, 2.15, W, 1.37 (metallic).

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144302. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by RFBR (99−03−32788) and INTAS (96−1256). AVV thanks the Royal Society for financial support. The authors thanks S. V. Belaya for density measurements, and the EPSRC (UK) for equipment funding.

[1] K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem*. **1997**, *45*, 283 and references therein.
[2] T. Iwamoto, in *Comprehensive Supramolecular Chemistry, Solid-state Supramolecular Chemistry: Crystal Engineering*, Vol. 6 (Eds.: D. D. MacNicol, F. Toida, R. Bishop), Pergamon, Oxford, **1996**, p. 643 and references therein.
[3] O. M. Yaghi, G. Li, H. Li, *Nature* **1995**, *378*, 703.
[4] T. Niu, X. Wang, A. J. Jacobson, *Angew. Chem. Int. Ed.* **1999**, *38*, 1934; P. Schwarz, E. Siebel, R. D. Fischer, N. A. Davies, D. C. Apperley, R. K. Harris, *Chem. Eur. J.* **1998**, *4*, 919; A. M. A. Ibrahim, E. Siebel, R. D. Fischer, *Inorg. Chem*. **1998**, *37*, 3521; T. Niu, J. Lu, X. Wang, J. D. Korp, A. J. Jacobson, *Inorg. Chem*. **1998**, *37*, 5324; J. Lu, W. T. A. Harrison, A. J. Jacobson, *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 2557; J. Lu, W. T. A. Harrison, A. J. Jacobson, *Inorg. Chem*. **1996**, *35*, 4271.
[5] N. G. Naumov, A. V. Virovets, M. N. Sokolov, S. B. Artemkina, V. E. Fedorov, *Angew. Chem. Int. Ed.* **1998**, *37*, 1943; L. G. Beauvais, M. P. Shores, J. R. Long, *Chem. Mater*. **1998**, *10*, 3783.
[6] M. P. Shores, L. G. Beauvais, J. R. Long, *J. Am. Chem. Soc*. **1999**, *121*, 775.
[7] M. P. Shores, L. G. Beauvais, J. R. Long, *Inorg. Chem*. **1999**, *38*, 1648.
[8] N. G. Naumov, A. V. Virovets, V. E. Fedorov, *Inorg. Chem. Commun.* **2000**, *3*, 71.
[9] V. P. Fedin, I. V. Kalinina, A. V. Virovets, N. V. Podberezskaya, A. G. Sykes, *Chem. Commun.* **1998**, 237; V. P. Fedin, I. V. Kalinina, D. G. Samsonenko, Y. V. Mironov, M. M. Sokolov, S. V. Tkachev, A. V. Virovets, N. V. Podberezskaya, M. R. J. Elsegood, W. Clegg, A. G. Sykes, *Inorg. Chem*. **1999**, *38*, 1956; A. Müller, R. Jostes, W. Eltzner, C.-S. Nie, E. Diemann, H. Bögge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, S. Che, S. J. Cyvin, B. N. Cyvin, *Inorg. Chem*. **1985**, *24*, 2872.
[10] Tetrahedral $[Ge_4S_{10}]^{4-}$ clusters have been used to construct porous three-dimensional frameworks: O. M. Yaghi, Z. Sun, D. A. Richardson, T. L. Groy, *J. Am. Chem. Soc*. **1994**, *116*, 807; C. L. Bowes, W. U. Huynh, S. J. Kirkby, A. Malek, G. A. Ozin, S. Petrov, M. Twardowski, D. Young, R. L. Bedard, R. Broach, *Chem. Mater*. **1996**, *8*, 2147; C. L. Cahill, J. B. Parise, *Chem. Mater*. **1997**, *9*, 807.
[11] G. M. Sheldrick,. SADABS, absorption corrections for area-detector data, Univ. of Göttingen, Germany, 1997; G. M. Sheldrick, SHELXTL for Windows NT, Bruker AXS Inc., Madison, Wi., USA, 1998.
[12] A. V. Virovets, N. V. Podberezskaya, *Kristallografia* **1992**, *37*, 1017 (in Russian).

Received May 15, 2000
[I00201]