ChemComm

Hydrothermal synthesis and crystal structures of two bimetallic chain-like and cluster complexes $[\{Co(phen)_2\}_2V_6O_{17}]_n$ and $[\{Cu(phen)_2\}_4V_{10}O_{29}]\cdot 6H_2O$†

Xian-Ming Zhang, Ming-Liang Tong and Xiao-Ming Chen*‡

State Key Laboratory of Ultrafast Laser Spectroscopy and School of Chemistry & Chemical Engineering, Zhongshan University, Guangzhou, 510275, P.R. China

Received (in Cambridge, UK) 20th July 2000, Accepted 15th August 2000

Two complexes, $[\{Co(phen)_2\}_2V_6O_{17}]_n$ 1 and $[\{Cu(phen)_2\}_4V_{10}O_{29}]\cdot 6H_2O$ 2, have been hydrothermally synthesized; X-ray crystallography shows that 1 consists of one-dimensional stepped chains built up from covalently linked $\{V_6O_{17}\}_n^{4n-}$ chains and $[Co(phen)_2]^{2+}$ fragments while 2 is composed of a discrete $V_{10}O_{29}^{8-}$ cluster covalently attached to four $[Cu(phen)_2]^{2+}$ fragments.

There has been extensive interest in organic–inorganic hybrid vanadium oxides and polyvanadate clusters owing to their structural diversity and potential application in catalysis and material science.[1–5] An important advance in organic–inorganic vanadium oxides has recently been the study of solid state coordination chemistry, which is characterized by transition metal complexes or fragments covalently bonded to metal oxide framework or polyanion clusters. A variety of vanadium solid state complexes including discrete clusters, infinite chains and layer structures have been prepared by hydrothermal methods.[6–12] However, in terms of discrete organic–inorganic bimetallic clusters formulated as $[(ZnL_2)V_4O_{12}]$ [L = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen)],[6] the vanadium clusters are limited to $V_4O_{12}^{4-}$, and in the metavanadate chain-like compounds formulated as $[(CuL_m)V_2O_6]_n$ (L = NH_3, ethylenediamine, bpy, diethylenetriamine; m = 1, 2) the vanadium oxide chains are limited to $\{V_2O_6\}_n^{2n-}$.[7–9] Herein, we report two interesting solid state vanadium(V) complexes $[\{Co(phen)_2\}_2V_6O_{17}]_n$ **1** and $[\{Cu(phen)_2\}_4V_{10}O_{29}]\cdot 6H_2O$ **2**, where the tetranuclear $V_4O_{12}^{4-}$ and dinuclear $V_2O_7^{4-}$ building units are unprecedentedly linked together by sharing oxygen atoms.

Complex **1** was synthesised as brown blocks in 80% yield based on vanadium by a hydrothermal method. A mixture of V_2O_5, $Co(OAc)_2\cdot 4H_2O$, phen and water in a molar ratio of 1 : 1 : 2 : 1100 was stirred for 20 min in air, before being transferred and sealed in a 23 cm³ Teflon-lined reactor, which was heated to 140 °C and held at this temperature for 72 h. Complex **2** was synthesised as blue blocks in 40% yield under similar conditions to **1** using $Cu(OAc)_2\cdot 2H_2O$ in place of $Co(OAc)_2\cdot 4H_2O$. Both **1** and **2** are insoluble in water and common organic solvents. The IR spectra§ of **1** and **2** exhibit characteristic bands for both V=O and phen. Thermogravimetric analysis shows a weight loss of *ca*. 50% for **1** in the range 300–550 °C corresponding to the loss of phen. A weight loss of *ca*. 4% for **2** in the range 120–150 °C corresponds to removal of the lattice water molecules while a further weight loss of *ca*. 51% occurs in the range 300–550 °C consistent with the loss of phen.

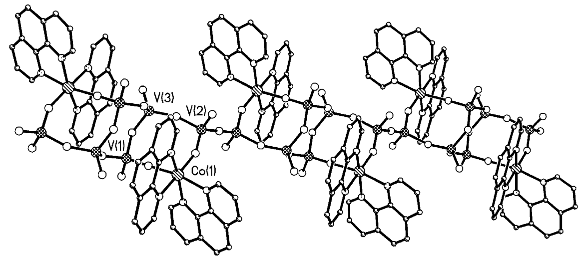

Fig. 1 Perspective view of the stepped chain of **1**.

The crystal structure of **1**¶ shows the presence of an unprecedented one-dimensional stepped chain constructed from $\{V_6O_{17}\}_n^{4n-}$ chains with $[Co(phen)_2]^{2+}$ fragments covalently attached *via* oxygen atoms, as shown in Fig. 1. The anionic chain in **1** is composed of alternate tetranuclear $V_4O_{12}^{4-}$ and dinuclear $V_2O_7^{4-}$ building units, which are linked by sharing oxygen atoms. All vanadium sites show VO_4 tetrahedral geometry, each of which has a terminal vanadyl (V=O) group and shares three corners with CoN_4O_2 octahedra and/or VO_4 tetrahedra. There are three crystallographically independent vanadium atoms in the anionic chain; V(1) and V(2) share oxygen atoms with one CoN_4O_2 octahedron and two VO_4 tetrahedra while V(3) only shares oxygen atoms with three VO_4 tetrahedra. The Co(II) atom, which is in a slightly distorted octahedral geometry, is ligated by two phen ligands, with the $[Co(phen)_2]^{2+}$ fragments further covalently bonded to the anionic chain through atoms O(1) and O(2) and their symmetry equivalents. Such a linking gives rise to three eight-membered rings, CoV_3O_4, V_4O_4 and CoV_3O_4, in chair-like configuration similar to that found in $[Cu(phen)MoO_4]$.[5] Although the empirical formula of **1** is similar to that of $[\{Zn(bpy)_2\}_2V_6O_{17}]$,[6] its architecture is different from the latter in which each VO_4 tetrahedron shares three corners with adjacent VO_4 tetrahedra forming layers rather than chains.

The structure of **2** features a discrete tetradecanuclear heterometallic cluster built up from $V_{10}O_{29}^{8-}$ clusters and four $[Cu(phen)_2]^{2+}$ fragments (Fig. 2). The Cu(II) atoms, which are in a distorted square-pyramidal geometry, are attached to the vanadium cluster *via* O(6) and O(11) and their symmetry equivalents. In contrast to **1**, while the anionic vanadium cluster

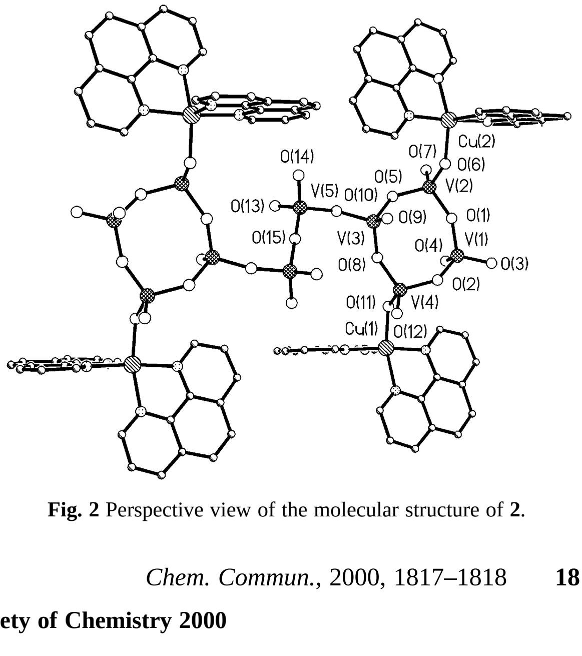

Fig. 2 Perspective view of the molecular structure of **2**.

---

† Electronic supplementary information (ESI) available: Fig. 1S–3S; three-dimensional supramolecular arrays for **1** and **2**. See http://www.rsc.org/suppdata/cc/b0/b005880g/

‡ Correspondence should be directed to School of Chemistry & Chemical Engineering. E-mail: cescxm@zsu.edu.cn

also consists of corner-sharing VO_4 tetrahedra, all VO_4 tetrahedra in **2** have one [V(2)–V(4)] or two [V(1) and V(5)] terminal oxygen atom(s). The $V(1)O_4$ tetrahedron has two terminal oxygen atoms, which may be directly responsible for the formation of the cluster rather than a chain. Similarly to the anion in **1**, the $V_{10}O_{29}^{8-}$ cluster consists of a dinuclear $V_2O_7^{4-}$ and two tetranuclear $V_4O_{12}^{4-}$ fragments linked by sharing oxygen atoms. Although the $V_{10}O_{28}^{6-}$ cluster is common in solution and a chiral $V_{10}O_{22}$ cluster[13] has recently been synthesised, the $V_{10}O_{29}^{8-}$ cluster found in **2** has not been reported before. In addition, the coordination mode of V_4O_{12} fragments in both **1** and **2** is unprecedented, in contrast to all documented and proposed coordination modes of the $V_4O_{12}^{4-}$ cluster, in which each heterometallic atom is attached to two or four oxygen atoms of the $V_4O_{12}^{4-}$ cluster.[6]

It is of note that π–π stacking interaction between interchain or intermolecular phen groups plays a significant role in stabilisation of the structures of **1** and **2**. Adjacent phen groups in **1** or **2** are generally parallel and separated by 3.1–3.5 Å, which indicates strong π–π stacking interactions.[14] Therefore, the heterometallic stepped chains of **1** and discrete tetradecanuclear heterometallic clusters of **2** are further extended into interesting three-dimensional supramolecular arrays *via* π–π stacking interactions of phen groups (see Fig. 1S, 2S and 3S in ESI†). It should also be noted that while **1** and **2** were prepared under the same conditions, their structures differ significantly. This may originate from the nature of heterometallic atoms employed. Co(II) tends to adopt octahedral geometry whereas Cu(II) favours a square-planar or square-pyramidal geometry owing to the strong Jahn–Teller effect. Meanwhile, the steric effect of phen appears to play an important role in the formation of the unique structures of **1** and **2**. The large steric hindrance of phen prevents the formation of heterometallic layered structures.

This work was supported by the National Natural Science Foundation of China (No. 29971033, 29625102).

Notes and references

§ Anal. Calc. for $C_{48}H_{32}N_8O_{17}V_6Co_2$ **1**: C, 40.70; H, 2.28; N, 7.91%. Found: C, 40.58; H, 2.32; N, 7.96. Calc. for $C_{96}H_{76}N_{16}O_{35}V_{10}Cu_4$ **2**: C, 41.52; H, 2.76; N, 8.07. Found: C, 41.38; H, 2.64; N, 8.02%. IR (KBr, cm^{-1}) for **1**: 3356m, 3058w, 1931w, 1607m, 1582m, 1513m, 1421s, 1141m, 1103w, 968s, 891s, 834s, 664s; for **2**: 3431m, 3046w, 1980w, 1607w, 1581m, 1517m, 1427s, 1143m, 968s, 941s, 913m, 787s, 624s.

¶ *Crystal data*: for **1**: triclinic, space group $P\bar{1}$, M_r = 1416.32, a = 10.216(7), b = 11.732(6), c = 11.788(7) Å, α = 82.76(1), β = 72.70(1), γ = 75.57(1)°, V = 1264(1) Å^3, Z = 1, D_c = 1.860 g cm^{-3}. Data collection was performed at 293 K on a Siemens R3m diffractometer (Mo-Kα, λ = 0.71073 Å). Lorentz-polarization and absorption corrections were applied. The structures were solved with direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97), giving a final R_1 value of 0.0671 for 368 parameters and 3279 unique reflections with $I \geqslant 2\sigma(I)$ and wR_2 of 0.1916 for all 4973 reflections.

For **2**: monoclinic, space group $P2_1/n$, M_r = 2777.29, a = 14.726(3), b = 14.612(3), c = 25.310(5) Å, β = 105.81(3)°, V = 5240(2) Å^3, Z = 2, D_c = 1.760 g cm^{-3} Data collection was performed at 293 K on a Bruker CCD diffractometer (Mo-Kα, λ = 0.71073 Å), giving a final R value of 0.0522 for 755 parameters and 8042 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.1547 for all 15179 reflections. All other conditions were the same as for **1**. CCDC 182/1745. See http://www.rsc.org/suppdata/cc/b0/b005880g/ for crystallographic files in .cif format.

1 T. Chirayil, P. Y. Zavalij and M. S. Whittingham, *Chem. Mater.*, 1998, **10**, 2629.
2 Louis C. W. Baker and D. C. Glick, *Chem. Rev.*, 1998, **98**, 3; P. Gouzerh and A. Proust, *Chem. Rev.*, 1998, **98**, 77.
3 G. Centi, F. Trifiro, J. R. Ebner and V. M. Franchetti, *Chem. Rev.*, 1988, **88**, 55.
4 J. M. Tarascon, E. Wang, F. K. Shokoohi, W. R. McKinnon and S. Colson, *J. Electrochem. Soc.*, 1991, **138**, 2859.
5 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268.
6 Y. Zhang, P. J. Zapf, L. M. Meyer, R. C. Haushalter and J. Zubieta, *Inorg. Chem.*, 1997, **36**, 2159.
7 S. Aschwanden, H. W. Schmalle, A. Reller and H. R. Oswald, *Mater. Res. Bull.*, 1993, **28**, 45.
8 J. R. D. DeBord, Y. Zhang, R. C. Aushalter, J. Zubieta and C. J. O'Connor, *J. Solid State Chem.*, 1996, **122**, 251.
9 L.-M. Zheng, J.-S. Zhao, K.-H. Lii, L.-Y. Zhang, Y. Liu and X.-Q. Xin, *J. Chem. Soc., Dalton Trans.*, 1999, 939.
10 Y. Zhang, J. R. D. DeBord, C. J. O'Connor, R. C. Haushalter, A. Clearfield and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 989.
11 L.-R. Zhang, Z. Shi, G.-Y. Yang, X.-M. Chen and S.-H. Feng, *J. Chem. Soc., Dalton Trans.*, 2000, 275.
12 Z. Shi, L.-R. Zhang, G.-S. Zhu, G.-Y. Yang, J. Hua, H. Ding and S.-H. Feng, *Chem. Mater.*, 1999, **11**, 3565.
13 K. Oyaizu and E. Tsuchida, *J. Am. Chem. Soc.*, 1998, **120**, 237.
14 S. B. Ferguson, E. M. Sanford, E. M. Seward and F. Diederich, *J. Am. Chem. Soc.*, 1991, **113**, 5410.