Hydrothermal synthesis and crystal structure of two hetero-transition metal polymers: $[Co(1,10\text{-}phen)_2(V_2O_4)\ (O_3PCH_2CH_2CH_2PO_3)]_n$ and $[\{Co(1,10\text{-}phen)_2\}_2(V_4O_{10})\ (O_3PCH_2CH_2CH_2CH_2PO_3)(2H_2O)]_n$

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Received (in Montpellier, France) 30th September 2002, Accepted 21st November 2002
First published as an Advance Article on the web 12th December 2002

A helical chain of $[Co(1,10\text{-}phen)_2(V_2O_4)(O_3PCH_2CH_2CH_2PO_3)]_n$ (1) and a stepped chain of $[\{Co(1,10\text{-}phen)_2\}_2(V_4O_{10})(O_3PCH_2CH_2CH_2CH_2PO_3)(2H_2O)]_n$ (2) have been synthesized under hydrothermal conditions using $[Co(1,10\text{-}phen)_2]^{2+}$ as the metal-organic subunit and organic diphosphonate ligands of different lengths.

Currently much interest has been focused on oxovanadium-organophosphonate systems due to their potential applications such as sorbents,[1–4] as well as their remarkable structural diversity. Different valences of vanadium, different vanadium coordination polyhedra and the length of the organic spacers can influence the structures of the solids. Many clusters[5–7] and one-, two-, and three-dimensional polymers[8–12] have been synthesized. Recently Zubieta *et al.*[13–15] used $[Cu(1,10\text{-}phen)]^{2+}$ and $[Cu(2,2'\text{-}bpy)]^{2+}$ as metal-organic subunits and synthesized one one-dimensional, six two-dimensional and one three-dimensional complexes. However, the influence of the length of the organic diphosphonate ligand between 1,3-propylene and 1,4-butylene and that of the different transition metal coordination polyhedra on the structure has yet not been studied in oxovanadium–organophosphonate systems. Herein, we used $[Co(1,10\text{-}phen)_2]^{2+}$ as the metal-organic subunit and obtained two novel one-dimensional polymers: a helical chain $[Co(1,10\text{-}phen)_2(V_2O_4)(O_3PCH_2CH_2CH_2PO_3)]_n$, **1**, and the stepped chain $[\{Co(1,10\text{-}phen)_2\}_2(V_4O_{10})(O_3PCH_2CH_2CH_2CH_2PO_3)(2H_2O)]_n$, **2**.

The crystal structure of **1** shows a one-dimensional helical chain constructed from $[Co(1,10\text{-}phen)_2]^{2+}$ fragments and a $[(V_2O_4)(O_3PCH_2CH_2CH_2PO_3)]_n^{2n-}$ anionic chain linked to each other by oxygen atoms [Fig. 1(a)]. The anionic chain consists of twisted $[O_3PCH_2CH_2CH_2PO_3]^{2-}$ and VO_2^+ blocks, connecting through the oxygen atoms of the 1,3-propylenediphosphonate ligand. The Co(II) atom, which is in a slightly distorted octahedral coordination geometry, coordinates to four nitrogen atoms from two equivalent 1,10-phen ligands (Co–N, 2.128 and 2.156 Å) and two equivalent oxygen donors (Co–O, 2.069 Å) from a chelating 1,3-propylenediphosphonate ligand. The $[Co(1,10\text{-}phen)_2]^{2+}$ fragment links to the anionic chain through the two oxygen atoms O(4) and O(4a) from the 1,3-propylenediphosphonate ligand. The tetrahedral V(V) center exhibits coordination to two oxygen atoms from each of two 1,3-propylenediphosphonate ligands (V–O, 1.857 and 1.863 Å) and two terminal oxo groups (V=O, 1.584 and 1.595 Å). This is consistent with the IR spectrum of **1** with a strong band at 960 cm^{-1} attributed to v(V=O). As a result, each 1,3-propylenediphosphonate ligand links four V (V) atoms and one Co (II) atom. Adjacent 1,10-phen groups are generally parallel and separated by about 3.4 Å, which indicates strong π-π stacking interactions between the adjacent chains [Fig. 1(b)].[16–18]

The crystal structure of **2** shows a one-dimensional stepped chain made up of $[Co(1,10\text{-}phen)_2]^{2+}$ fragments and a $[(V_4O_{10})(O_3PCH_2CH_2CH_2CH_2PO_3)]_n^{4n-}$ anionic chain [Fig. 2(a)]. The Co(II) geometry is also in a slightly distorted octahedron, defined by four nitrogen atoms from two 1,10-phen ligands (Co–N, 2.136, 2.124, 2.147 and 2.150 Å), one oxo group (Co–O(4), 2.098 Å) bridging to the V(V) site and one oxygen from the 1,4-butylenediphosphonate ligand (Co–O(1), 2.075 Å). $[Co(1,10\text{-}phen)_2]^{2+}$ connects to the anionic chain *via* O(4) and O(1). The anionic chain is constructed from $[O_3PCH_2CH_2CH_2CH_2PO_3]^{4-}$ and binuclear V_2O_5 building units. In the anionic chain, there are two different tetrahedral coordinations of V (V) atoms. Both V(1) and V(2) coordinate to one oxygen donor from the 1,4-butylenediphosphonate ligand, an oxo group bridging to a V(V) center and a terminal oxo group (V=O). At the same time V(1) also shares one oxygen atom with a $\{CoN_4O_2\}$ octahedron, while V(2) has another terminal oxo group (V=O). This was confirmed by the IR spectrum of **2**, which shows a strong band at 957 cm^{-1} consistent with v(V=O). Consequently, each 1,4-butylenediphosphonate ligand links to four V(V) atoms and two Co(II) atoms. Adjacent 1,10-phen groups are generally parallel and the nearest 1,10-phen groups are separated by about 3.4 Å, which also indicates strong π-π stacking interactions between the adjacent chains [Fig. 2(b) and 2(c)].[16–18]

Complexes **1** and **2** were synthesized under the same conditions, including ratio of the reactants, temperature, reaction time and so on. The only difference is in the lengths of the 1,3-propylenediphosphonate and 1,4-butylenediphosphonate ligands. However, there are some differences in the structures of the two complexes. (1) The two oxygen donors around the Co(II) center are both from a 1,3-propylenediphosphonate ligand in complex **1**, but in complex **2** only one of the two oxygen donors is from the 1,4-butylenediphophonate ligand. (2) Only in complex **2** do we see V–O–V and V–O–Co interactions. (3) In complex **1** the 1,3-propylenediphosphonate ligand is twisted. (4) There are two 8-membered rings $\{V_2O_4P_2\}$ and $\{CoO_2P_2C_3\}$ in complex **1** while complex **2** contains a 6-membered ring $\{CoO_3P_2\}$ and a 12-membered ring $\{V_4O_6P_2\}$. (5) Complex **1** is a helical chain polymer, while complex **2** is a stepped chain polymer. (6) The molar ratios of Co:V:P are 1:2:2 and 1:2:1 in complexes **1** and **2**, respectively.

In conclusion, two one-dimensional inorganic-organic hybrid polymers, **1** and **2**, were successfully synthesized under hydrothermal conditions with $[Co(1,10\text{-}phen)_2]^{2+}$ as

DOI: 10.1039/b209564e

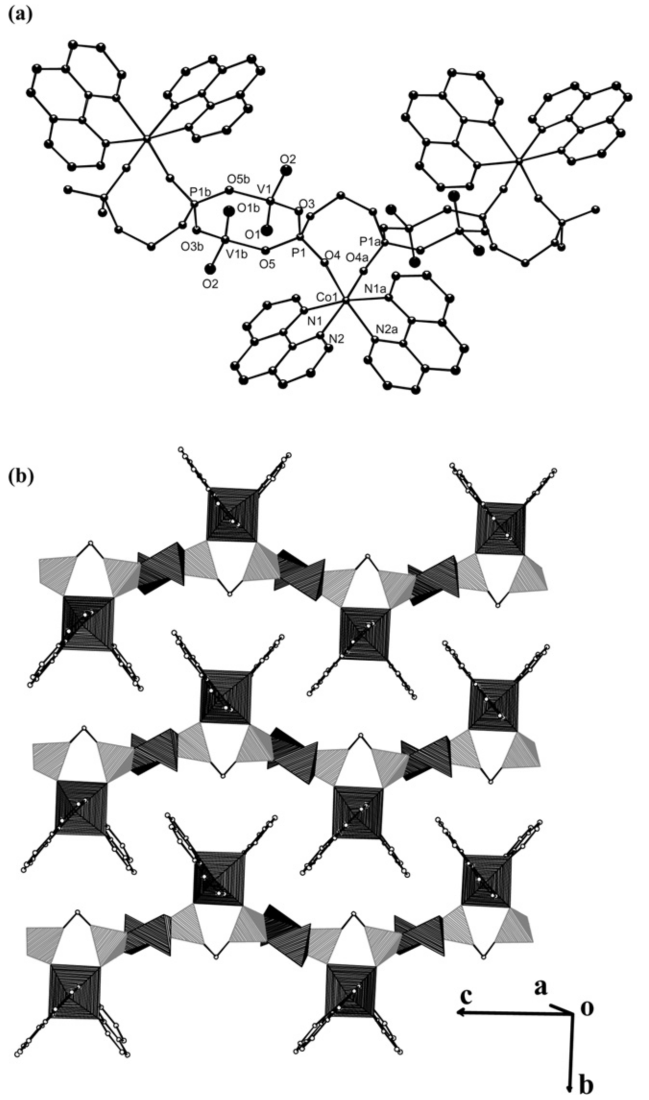

Fig. 1 (a) Perspective view of the helical chain of **1**. The hydrogen atoms are omitted for clarity. Symmetry code: $a = -x, y, 1/2 - z$; $b = -x, -y + 1, -z + 1$. (b) View of the packing of adjacent helical chains, showing the stacking of 1,10-phen with adjacent chains in **1**. Black octahedrons: $\{CoN_4O_2\}$; black tetrahedrons: $\{VO_4\}$; gray tetrahedrons: $\{PCO_3\}$. The hydrogen atoms are omitted for clarity.

the metal-organic subunit. Compounds **1** and **2** exhibit obvious structural differences owing to the different lengths of the 1,3-propylene- and 1,4-butylenediphosphonate ligands employed in their synthesis.

Experimental

1,3-Propylene- and 1,4-butylenediphosphonic acid were prepared according to the reported methods.[19,20] Other chemicals were reagent grade quality and obtained from commercial sources without further purification. Compounds **1** and **2** were synthesized in 25 ml Teflon-lined stainless steel vessels under autogeneous pressure with a filling capacity of ~40%. The reactants were stirred homogeneously before heating. The elemental compositions were determined with a Vario EL III element analyzer and UV-1100 spectrophotometer. Infrared spectra were obtained on a Nicolet Magna 750 FT-IR spectrometer.

Syntheses

Compound 1. A mixture of $Co(CH_3COO)_2{\cdot}4H_2O$ (0.2492 g, 1.000 mmol), $NaVO_3{\cdot}2H_2O$ (0.3144 g, 1.990 mmol), 1,10-phenanthroline·H_2O (0.3938 g, 1.987 mmol), $H_2O_3PCH_2CH_2CH_2PO_3H_2$ (0.4044 g, 1.982 mmol) and H_2O (10.0 ml, 556 mmol) in a molar ratio 1:2:2:2:556 was heated at 120 °C for 72 h. After the mixture was cooled to room temperature, salmon pink crystal of **1** were isolated as parallelepipeds in 70% yield based on cobalt. Anal. calcd for $C_{27}H_{22}N_4O_{10}P_2V_2Co$, **1**: C 41.30, H 2.82, N 7.14, Co 7.50%; found: C 41.30, H 2.13, N 6.73, Co 8.18%. IR (KBr pellet, cm^{-1}): 3500 vs, 3068 m, 2956 w, 2931 w, 2870 w, 1624 m, 1581 m, 1514 s, 1452 w, 1425 s, 1336 m, 1288 w, 1165 s, 1126 s, 1101 m, 1038 s, 960 s, 850 s, 729 s, 642 m, 517 m, 488 m.

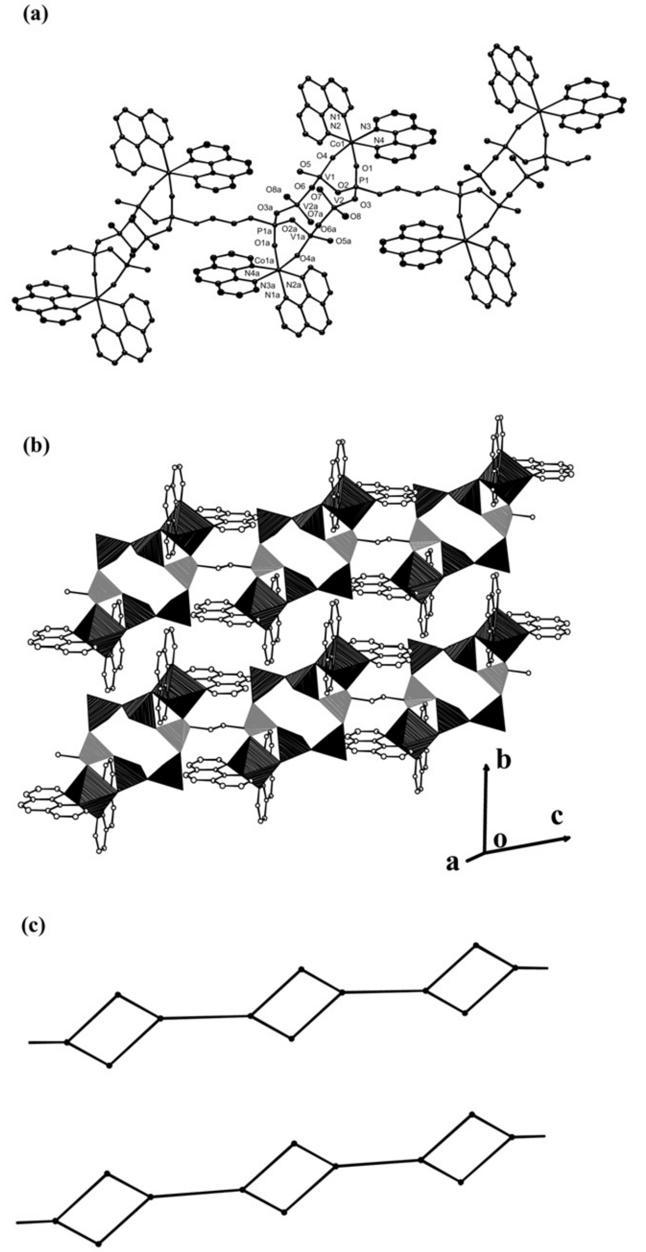

Fig. 2 (a) Perspective view of the stepped chain of **2**. The hydrogen atoms and free water molecules are omitted for clarity. Symmetry code: $a = -x + 1, -y + 1, -z + 1$. (b) View of the packing of adjacent stepped chains of **2**. Black octahedrons: $\{CoN_4O_2\}$; black tetrahedrons: $\{VO_4\}$; gray tetrahedrons: $\{PCO_3\}$. The hydrogen atoms and free water molecules are omitted for clarity. (c) Sketch view of the packing of adjacent stepped chains of **2**.

Compound 2. A mixture of $Co(CH_3COO)_2{\cdot}4H_2O$ (0.2494 g, 1.001 mmol), $NaVO_3{\cdot}2H_2O$ (0.3168 g. 2.006 mmol), 1,10-phenanthroline·H_2O (0.3953 g, 1.994 mmol), $H_2O_3PCH_2CH_2CH_2CH_2PO_3H_2$ (0.4367 g, 2.002 mmol) and H_2O (10.0 ml, 556 mmol) in a molar ratio 1:2:2:2:556 was heated at 120 °C for 72 h. After the mixture was cooled to room temperature, red crystal of **2** were isolated as prisms in 50% yield based on cobalt. Anal. calcd for $C_{52}H_{44}N_8O_{18}P_2V_4Co_2$, **2**: C 43.00, H 3.05, N 7.71, Co 8.81%; found: C 43.44, H 2.46, N 7.56, Co 8.66%. IR (KBr pellet, cm^{-1}): 3500 s, 3057 w, 2949 w, 2912 w, 2872 w, 1624 m, 1578 m, 1516 s, 1462 w, 1425 m, 1344 w, 1288 w, 1144 s, 1105 w, 1032 s, 995 m, 980 s, 957 s, 901 m, 860 s, 829 s, 727 s, 634 m, 555 m, 519 w, 472 w.

X-Ray crystallography

X-ray data on single crystals were collected at a temperature of 293 ± 2 K on a Siemens SMART-CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were reduced and absorption corrected with SMART and SADABS software, respectively. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL-97.[21] All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

CCDC reference numbers 194197 and 194198 for compounds **1** and **2**, respectively. See http://www.rsc.org/suppdata/nj/b2/b209564e/ for crystallographic data in CIF or other electronic format.

Crystal data for 1. $C_{27}H_{22}N_4O_{10}P_2V_2Co$, $M = 785.24$, monoclinic, $C2/c$, $a = 16.553(2)$, $b = 10.5323(15)$, $c = 17.341(3)$ Å, $\beta = 104.430(3)°$, $U = 2927.9(7)$ Å^3, $Z = 4$, μ(Mo-Kα) = 1.360 mm^{-1}. A total of 4896 reflections were measured in the range of $4.62 \leqslant 2\theta \leqslant 50.18°$, with 2582 independent reflections ($R_{int} = 0.0368$). Final $R_1 = 0.0570$ for 1773 observed reflections [$I > 2\sigma(I)$] and $wR_2 = 0.1306$.

Crystal data for 2. $C_{52}H_{44}N_8O_{18}P_2V_4Co_2$, $M = 1452.51$, triclinic, $P{-}1$, $a = 10.2132(3)$, $b = 11.7055(5)$, $c = 12.3666(5)$ Å, $\alpha = 75.594(2)°$, $\beta = 82.445(2)°$, $\gamma = 86.071(2)°$, $U = 1418.53(9)$ Å^3, $Z = 1$, μ(Mo-Kα) = 1.340 mm^{-1}. A total of 7439 reflections were measured in the range of $3.42 \leqslant 2\theta \leqslant 50.06°$, with 4961 independent reflections ($R_{int} = 0.0299$). 0.0299). Final $R_1 = 0.0567$ for 3742 observed reflections [$I > 2\sigma(I)$] and $wR_2 = 0.1029$.

Acknowledgements

This research was supported by grants from the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the National Ministry of Science and Technology of China (001CB1089), Chinese Academy of Sciences (CAS), the National Science Foundation of China (20273073), the Science Foundation of CAS and Fujian Province for research funding support (2002F014).

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