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Hydrothermal synthesis and crystal structure of a hybrid material based on $[Co_4(phen)_8(H_2O)_2(HPO_3)_2]^{4+}$ and a highly reduced polyoxoanion

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An unusual composite hybrid material $[Co_4(phen)_8(H_2O)_2(HPO_3)_2](H_3O)_3[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]$ **1** (phen = 1,10-phenanthroline) has been hydrothermally synthesized from a mixture of NH_4VO_3, $Na_2MoO_4\cdot 2H_2O$, $CoCl_2\cdot 6H_2O$, phen, H_3PO_3 and water. It was characterized by elemental analysis, IR, UV-vis, XPS, EPR, TG and single crystal X-ray diffraction. The title compound is constructed from the organic–inorganic hybrid $[Co_4(phen)_8(H_2O)_2(HPO_3)_2]^{4+}$ and highly reduced bi-capped pseudo-Keggin $[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]^{7-}$ polyoxoanions The structure exhibits an extended 2D network through hydrogen bonds among cations, anions and H_2O, combining polyoxometalates with metal phosphonates for the first time.

Introduction

Polyoxometalates[1] (POMs) have been attracting extensive interest in solid state materials chemistry due to the richness of their structures and special properties in catalysis, photochemistry, electrochromism and magnetism.[2,3] Several successful strategies have been developed to design materials based on POMs. Müller's group have reported giant mixed-valence polyoxomolybdates from "big wheel" Mo_{154} anions[4] to capped cyclic Mo_{248}[5] and "basket" Mo_{116}[6] architectures. Pope's group have reported a new simple way to yield infinite one-dimensional POMs with lanthanide (Ln) or actinide cations as assembling groups.[7,8] Zubieta and co-workers have reported a number of organic–inorganic hybrid materials based on oxometalates with 1D and 2D frameworks.[9] Furthermore, the integration of POMs into hybrid solid state materials has been reported, such as ion-exchange into vinylpyridine–styrene copolymers,[10] intercalation into layered double hydroxides[11,12] and incorporation into organic–inorganic hybrid charge-transfer salts,[13] however, few examples of complete crystal structure determinations have been reported. Recently, several crystal structures based on metal coordination polymers and POMs have been realized, including the covalent tethering of $Mo_6O_{19}^{2-}$ derivatives onto a styrene polymer,[14] polyoxomolybdate clusters into a copper(II)-organoamine network[15,16] and the incorporation of a POM ion as a non-coordinating anion into a 3D copper(I) 4,4′-bipyridine network.[17] The incorporation of POMs into conventional polymeric systems therefore may provide additional opportunities for their technological development.

Our group has been devoting a lot of reserach time to the syntheses of POMs with various structures.[18–22] As an expansion of the strategies mentioned above to develop POMs, we have been attempting to incorporate POMs into porous transition metal phosphates[23] and to explore the synergistic reaction between them. Here, we report such an unusual composite crystal $[Co_4(phen)_8(H_2O)_2(HPO_3)_2](H_3O)_3[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]$ **1**, in which a cobalt phosphonate serves as the counter cation with organoamine ligand directly coordinated to the scaffolding and the anion is a highly reduced bi-capped pseudo-Keggin cluster. Its structure shows an extended 2D network through the linking of extensive hydrogen bonds. To our knowledge, it is the first example of such a type of structure which combines the unique features of not only inorganic and organic structures but also transition metal phosphonates and POMs.

Experimental

Materials and methods

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. P, Mo, V, and Co were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer using KBr pellets. Diffuse reflectance UV-vis spectrum ($BaSO_4$ pellet) was obtained with a Varian Cary 500 UV-vis NIR spectroscopy. EPR spectrum was recorded on a Japanese JES-FE3AX spectrometer at 77 K. XPS analysis was performed on a VG ESCALAB MK II spectrometer with a Mg-Kα (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}.

Synthesis

The title compound **1** was hydrothermally synthesized under autogenous pressure. A mixture of NH_4VO_3 (0.4024 g, 3.43 mmol), $Na_2MoO_4\cdot 2H_2O$ (0.6100 g, 2.52 mmol), $CoCl_2\cdot 6H_2O$

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Table 1 Crystal data for structure refinement for compound **1**

Empirical formula	$C_{96}H_{79}Co_4Mo_8N_{16}O_{53}P_3V_6$
Formula weight	3706.54
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.430(4)
b/Å	23.352(5)
c/Å	18.785(3)
β/°	94.99(2)
V/Å^3	5869(2)
Z	2
D_c/Mg m^{-3}	2.097
F(000)	3636
μ/mm^{-1}	1.965
Reflections collected/unique	12267/9868 [R(int) = 0.0300]
Goodness-of-fit on F^2	1.076
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0566$, $wR2 = 0.1428$
R indices (all data)	$R1 = 0.0858$, $wR2 = 0.1538$

(0.2988 g, 1.26 mmol), phen (0.4010 g, 2.03 mmol), and water (10 ml) was neutralized to pH 4.0 with 8 M H_3PO_3 under continuous stirring and then sealed in a 20 ml Teflon-lined autoclave, which was heated to 160 °C for six days. After slow cooling to room temperature, black block crystals of **1** were separated as a major phase (70% yield based on V) together with a small amount of an unidentified brown powder. Anal. calc. for **1**: C, 31.11; H, 2.15; N, 6.05; P, 2.51; Mo, 20.71; V, 8.25; Co, 6.36%. Found: C, 31.32; H, 2.21; N, 5.96; P, 2.28; Mo, 21.01; V, 8.10; Co, 6.53%.

X-Ray crystallography

The crystal structure determination for compound **1** was performed on a Siemens P4 four-circle diffractometer with Mo-Kα radiaiton (λ = 0.71073 Å) at 293 K in the range of $1.52 < \theta < 25.01°$ using the ω-scan technique. Empirical absorption correction (ψ-scans) was applied. A total of 12267 (9868 unique, R_{int} = 0.0300) reflections were measured. The structure was solved by direct methods using the program SHELXS-97[24] and refined by full-matrix least-squares methods on F^2 using the SHELXL-97[25] program package. All of the non-hydrogen atoms were refined anisotropically except for OW3 atoms. Positions of the hydrogen atoms attached to phosphorus were located from difference maps and isotropically refined and those attached to carbon atoms were fixed in calculated positions. The hydrogen atoms attached to oxygen atoms were not located accurately. Crystal data are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

CCDC reference number 181115.

See http://www.rsc.org/suppdata/dt/b2/b203737h/ for crystallographic data in CIF or other electronic format.

Results and discussion

The isolation of compound **1** depends on the use of hydrothermal techniques and we found that the choice of starting materials and pH are vital for the success of this reaction. If $CoCl_2{\cdot}6H_2O$ was replaced by $NiCl_2{\cdot}6H_2O$ or $MnCl_2{\cdot}4H_2O$ in a similar hydrothermal reaction for compound **1**, we could not obtain the expected single crystal but only blue powders or a slurry. If the pH of the reaction was lower or higher than 4, polycrystals were obtained.

A single crystal X-ray analysis revealed that **1** consists of an unusual cobalt phosphonate cation $[Co_4(phen)_8(H_2O)_2(HPO_3)_2]^{4+}$, a bi-capped pseudo-Keggin polyoxoanion $[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]^{7-}$ and three protonated water molecules. The structure of the polyoxoanion (shown in Fig. 1a, selected bond lengths and angles in Table 2), is essentially based on the well-known Keggin sructure with two additional five-coordinated terminal $\{VO\}^{2+}$ units and contains a disordered central P^{5+} similar to that in $[PMo_8V_8O_{44}]^{5-}$.[26] All vanadium atoms show a distorted $\{VO_5\}$ square pyramidal environment with

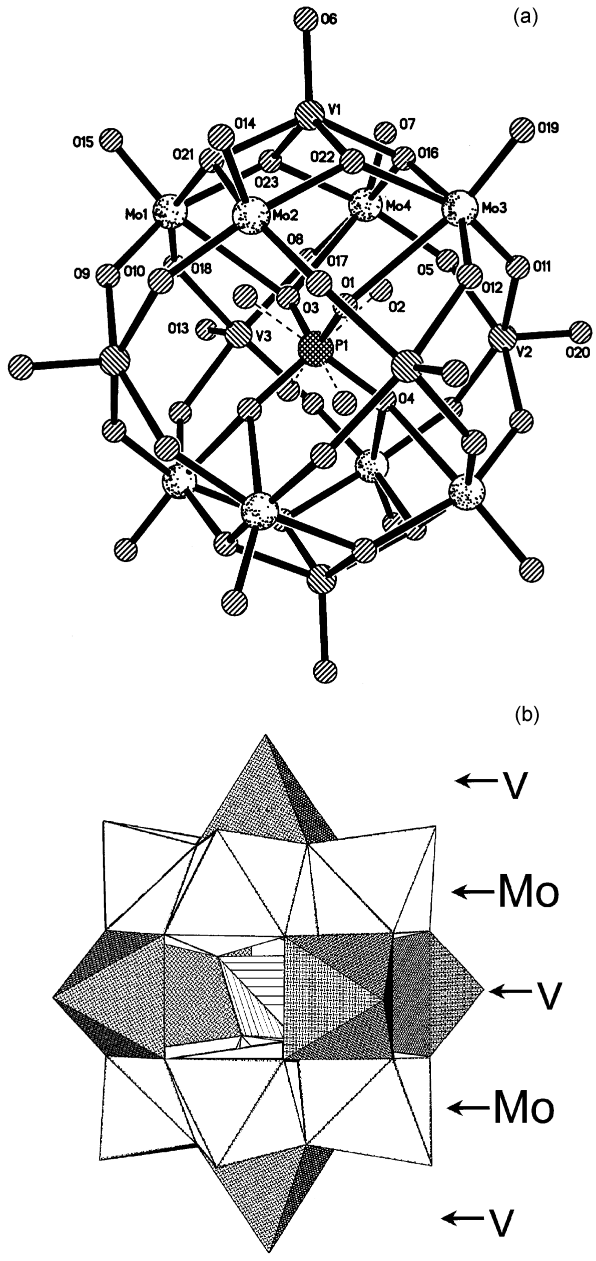

Fig. 1 (a) View of the polyoxoanion, $[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]^{7-}$, showing the coordination environments around Mo, V and the disordered P atom. (b) Polyhedral representation of the polyoxoanion, showing the alternating vanadium and molybdenum oxide layers.

V–O distances in the range 1.603(6)~1.950(6) Å and bond angles 80.6(2)~156.6(4)°. All molybdenum atoms have a distorted $\{MoO_6\}$ octahedral environment with Mo–O distances 1.668(5)~2.505(10) Å and bond angles 63.6(3)~159.5(3)°. The disordered PO_4 tetrahedron has P–O distances of 1.466(10)~1.584(9) Å and O–P–O angles 105.6(5)~113.8(5)°. Four $\{MoO_6\}$ octahedra form a $\{Mo_4O_{18}\}$ ring *via* the corner-and/or edge-sharing mode. Two $\{Mo_4O_{18}\}$ rings are connected with four $\{VO_5\}$ pyramids through the edge-sharing mode. Thus, the polyoxoanion exhibits an unusual phosphorus-centered regular arrangement of vanadium and molybdenum oxide layers, as shown in Fig. 1b. In addition, the polyoxoanion reveals a high negative charge due to the introduction of the strong reductive reagent H_3PO_3. The valence sum calculations[27] give the values of 6.03~6.16 and 4.33~4.38 for Mo and V, respectively, confirming all Mo atoms are in the 6+ oxidation state while all the V atoms are 4+, which leads the polyoxoanion to be formulated as $[PMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]^{7-}$.

It is noteworthy that in the structure of **1**, it is the $[Co_4(phen)_8(H_2O)_2(HPO_3)_2]^{4+}$ moiety that serves as the cation,

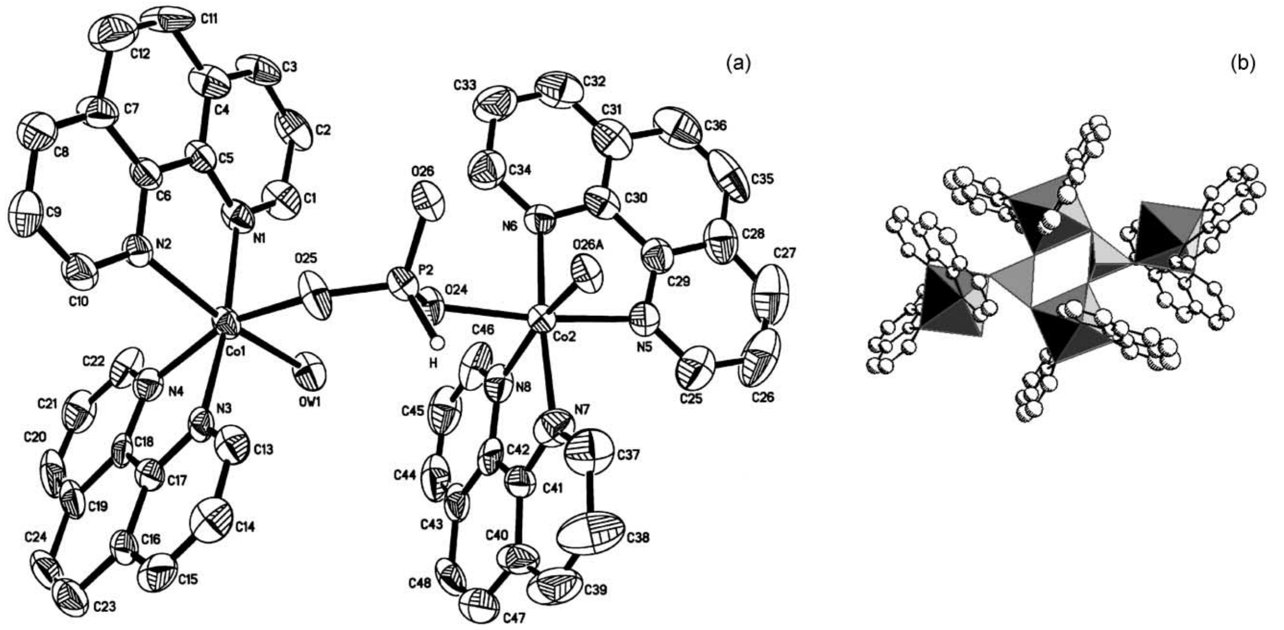

Fig. 2 (a) The asymmetric unit of the cation, $\{[Co(phen)_2]_2[Co(phen)_2(H_2O)]_2(HPO_3)_2\}^{4+}$, showing two types of Co atoms. (b) The polyhedral representation of the cation, exhibiting the four-membered ring and the connection of Co octahedra and P pseudo-pyramids.

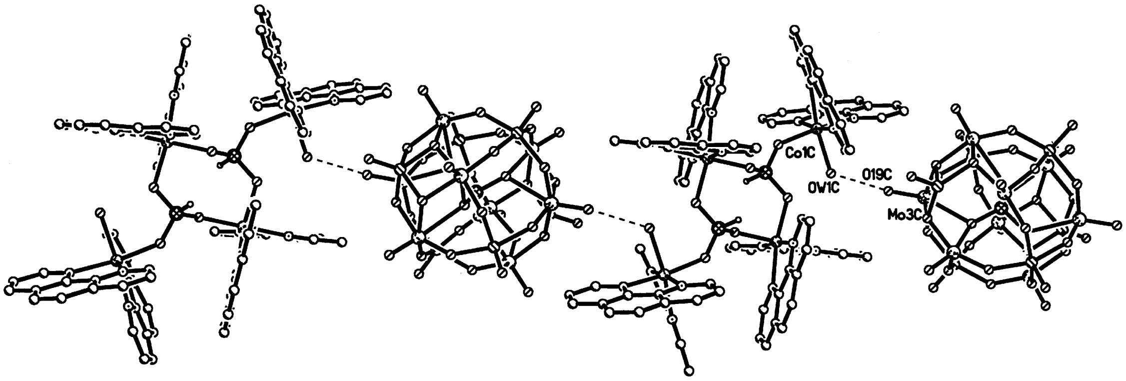

Fig. 3 Hydrogen-bonding interaction between cations and polyoxoanions.

which, as far as we are aware, has never been met before in solid state materials chemistry. The cation itself may be considered as a type of organic–inorganic hybrid material with the organoamine ligand directly coordinated to the scaffolding. Such a connection is rarely encountered in metal-phosphonates,[28] though several organic–inorganic hybrid metal-phosphonates with 2D and 3D open frameworks have been reported.[29,30] The asymmetric unit of the cation is shown in Fig. 2a. The Co–N bond corresponds to a direct link between cobalt and the phen template. Two types of Co(II) species, indicated as Co(1) and Co(2), respectively, which are not crystallographically identical have been revealed. Their common feature is that they are both covalently bonded to two phen molecules with Co–N distances 2.108(8)~2.189(7) Å to yield a $[Co_4(phen)_8(H_2O)_2(HPO_3)_2]$ cluster, which is often encountered in organic–inorganic hybrids.[9,31,32] The main difference between them is that Co(1) coordinates with only one oxygen atom from the P–O group in $\{HPO_3\}$ and with a terminal ligand water molecule to finish its octahedral environment [*d*Co(1)–OW1 = 2.184(6) Å, longer than other Co–O distances], while Co(2) makes two Co–O–P links to nearby P atoms [*d*Co(2)–O(24) = 2.091(6) Å and *d*Co(2)–O(26) = 2.009(6) Å]. P(2) makes three bonds to Co atoms with P–O distances 1.511(6)~1.531(6) Å, with the expected[28,33] terminal P–H bond as its fourth vertex. The average Co–O–P bond angle of the three bridging O atoms is 131.94°, which is about 10° smaller than in that $[H_2N(CH_2)_2NH_2]_{0.5}\cdot ZnHPO_3$[28] with an open framework. Two $\{CoN_4O_2\}$ octahedra and two $\{HPO_3\}$ pseudo-pyramids form a four-membered ring *via* the corner-sharing mode with two additional Co atoms and eight organodiamine phen groups around the periphery of the ring to generate a discrete cluster (shown in Fig. 2b), consequently formulated as $[Co_4(phen)_8(H_2O)_2(HPO_3)_2]^{4+}$. This kind of linking between P and Co was once found in the oxovanadium(IV)-phosphonate phase, $[HN(Me)(CH_2CH_2)N(Me)H][(VO)_4(OH)_2(HPO_3)_4]$,[29] which had a 2D framework. The low dimensionality of compound **1** may be ascribed to the occurrence of a bidentate ligand directly coordinated to Co atoms so as to impede the expansion of the framework. The retained negative charge in the structure of **1** was balanced by the protonation of three lattice water molecules.

It is also striking that the structure of compound **1** exhibits a hydrogen-bonding interaction between the ligand water molecules coordinated to cations and the terminal oxo groups of polyoxoanions [OW1 ··· O(19) 2.828 Å] (shown in Fig. 3). Thus the polyoxoanions and cations are both stabilized by the extensive hydrogen bonds and are alternately arranged to give a chain. Also, hydrogen-bonding contacts are observed between polyoxoanions through the lattice water [OW2 ··· O(6) 2.904 and OW2 ··· O(21) 2.912 Å], as shown in Fig. 4. Thus, each chain is linked to two other chains by hydrogen bonds to yield a layer parallel to the *ac* plane. The angle between the two types of hydrogen bonds is about 51.17°.

The IR spectrum of **1** exhibited complex bands at 1086, 967, 841 and 777 cm^{-1}, ascribed to ν(P–O$_a$), ν(M=O$_d$), ν(M–O$_b$–M) and ν(M–O$_c$–M), respectively. The features at 1581, 1504, 1414

Table 2 Selected bond lengths (Å) and bond angles (°) for compound **1**[a]

Mo(1)–O(15)	1.676(6)	Mo(1)–O(18)	1.790(6)
Mo(1)–O(9)	1.809(6)	Mo(1)–O(23)	2.042(5)
Mo(1)–O(21)	2.091(6)	Mo(1)–O(4)#1	2.419(10)
Mo(3)–O(19)	1.674(6)	Mo(3)–O(12)	1.804(7)
Mo(3)–O(11)	1.806(7)	Mo(3)–O(16)	2.053(7)
Mo(3)–O(22)	2.065(6)	Mo(3)–O(2)	2.440(10)
Mo(3)–O(1)	2.505(10)	V(3)–O(17)#1	1.909(7)
V(3)–O(8)	1.917(6)	V(3)–O(12)#1	1.941(6)
V(3)–O(18)	1.950(6)	V(3)–O(13)	1.603(6)
Co(1)–N(4)	2.145(7)	Co(1)–N(2)	2.152(7)
Co(1)–N(3)	2.173(7)	Co(1)–OW1	2.184(6)
Co(1)–N(1)	2.189(7)	Co(1)–O(25)	2.007(6)
Co(2)–O(24)	2.091(6)	Co(2)–O(26)#2	2.009(6)
Co(2)–N(8)	2.113(8)	Co(2)–N(7)	2.108(8)
Co(2)–N(5)	2.148(8)	Co(2)–N(6)	2.115(7)
P(1)–O(3)	1.466(10)	P(1)–O(1)	1.521(9)
P(1)–O(4)	1.584(9)	P(1)–O(2)#1	1.584(9)
P(2)–O(26)	1.513(7)	P(2)–O(25)	1.511(6)
P(2)–O(24)	1.531(6)		
O(15)–Mo(1)–O(18)	103.1(3)	O(18)–Mo(1)–O(23)	90.2(2)
O(22)–Mo(3)–O(1)	63.6(3)	O(16)–Mo(3)–O(22)	74.5(2)
O(16)–Mo(4)–O(3)	88.8(3)	O(7)–Mo(4)–O(3)	159.5(3)
O(6)–V(1)–O(22)	115.3(3)	O(22)–V(1)–O(23)	132.3(3)
O(22)–V(1)–O(21)	80.6(2)	O(20)–V(2)–O(9)#1	102.4(3)
O(9)#1–V(2)–O(5)	156.6(4)	O(9)#1–V(2)–O(11)	87.1(3)
O(3)–P(1)–O(1)	113.8(5)	O(3)–P(1)–O(4)	109.5(5)
O(1)–P(1)–O(2)#1	108.0(5)	O(1)–P(1)–O(4)	108.3(5)
O(3)–P(1)–O(2)#1	111.3(5)	O(2)#1–P(1)–O(4)	105.6(5)
O(25)–P(2)–O(26)	111.8(4)	O(25)–P(2)–O(24)	112.4(3)
O(26)–P(2)–O(24)	112.8(4)	P(2)–O(25)–Co(1)	138.9(4)
P(2)–O(24)–Co(2)	123.4(3)	P(2)–O(26)–Co(2)#2	133.4(4)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, -y, -z + 1$; #2: $-x, -y + 1, -z + 1$.

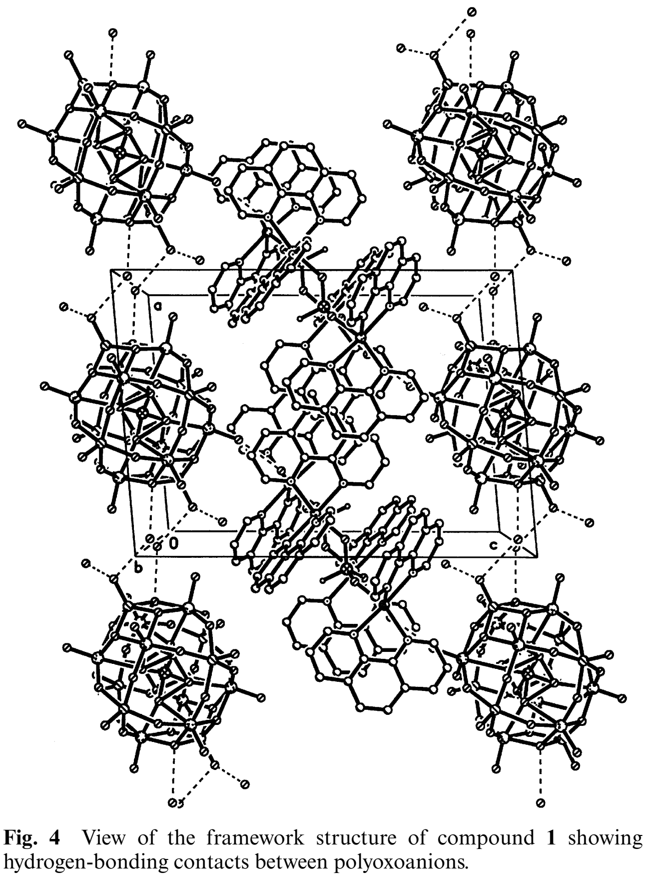

Fig. 4 View of the framework structure of compound **1** showing hydrogen-bonding contacts between polyoxoanions.

and 1214 cm^{-1} can be regarded as characteristic of phen. In the UV-vis spectrum, the bands at 218~397 nm correspond to the LMCT transition of terminal or bridging oxygen atoms to metal atoms, while the broad band at 573 nm is an important signal of the formation of reduced polyoxoanions, attributed to the intervalence charge transfer (IVCT).[34]

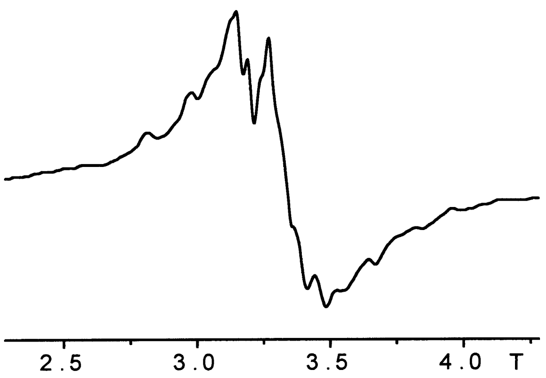

Fig. 5 EPR spectrum for compound **1**, showing the signal of V^{4+}.

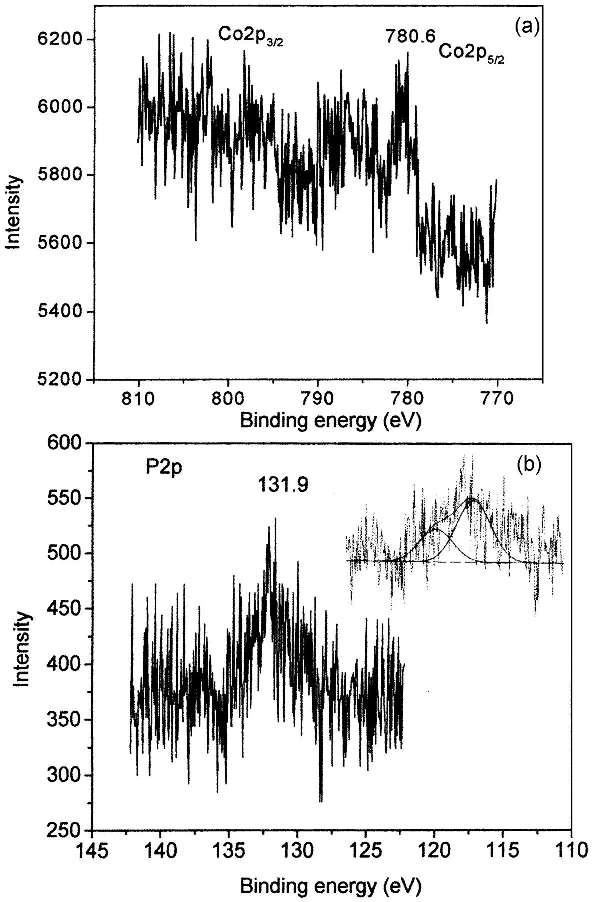

Fig. 6 (a) XPS spectra for Co^{2+} in compound **1**. (b) XPS spectra for P in compound **1**, showing the existence of mixed-valence P.

The EPR spectrum of **1** (Fig. 5) at low temperature shows the V^{4+} signal with $g_{\perp} = 1.9980$, $A_{\perp} = 1.8754$, $g_{\parallel} = 1.9346$, $A_{\parallel} = 1.6709$, in accordance with the valence sum calculations. In the XPS spectra for compound **1**, Fig. 6a gives one peak at 780.6 eV, attributed to Co^{2+},[35] and Fig. 6b shows two overlapped peaks at 131.6 eV and 133.5 eV with a peak area ratio of 2 : 1, ascribed to P^{3+} and P^{5+}, respectively.[36,37] The results further confirm the structure analysis.

The TG curve gives a total weight loss of 41.85% in the range of 50–720 °C, which agrees well with the calculated value of 41.40%. The weight loss of 3.00% at 50–250 °C corresponds to the loss of lattice water and ligand water molecules (calc. 2.51%). The weight loss of 38.85% at 350–620 °C arises from the decomposition of organic amine (calc. 38.89%).

In conclusion, we have successfully combined an organic–inorganic hybrid transition metal phosphonate with a highly reduced capped POM through hydrogen-bonding interactions to obtain a new type of composite solid-state material. Compound **1** can also be considered as one example of the hybrids of phosphates and POMs, which may possess new and unique properties in contrast to discrete phosphates and POMs and provide a new strategy for the design of solid state materials. This work also shows that hydrothermal synthesis is a powerful method to obtain novel structural materials.

Acknowledgements

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