Synthesis and Structure of an Unprecedented Layered Vanadate Complex Containing Double-Helical Chains: $[\{Co^{III}(phen)_2\}_2V_8O_{23}]$

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A novel two-dimensional organic–inorganic hybrid vanadate complex $[\{Co^{III}(phen)_2\}_2V_8O_{23}]$ has been hydrothermally synthesized and characterized by elemental analyses, IR spectroscopy, XPS spectroscopy, TG analysis and single-crystal X-ray diffraction. The single-crystal X-ray diffraction analysis reveals that compound **1** contains an unprecedented neutral 2D framework constructed of 4,10,12-net sheets. To the best of our knowledge, compound **1** represents the first example of 2D layered vanadium oxide complex constructed of 4,10,12-net sheets. Furthermore, the title compound consists of left-handed and right-handed helical chains, which are further interconnected to form the double-helical chains. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

A current focus on the chemistry of polyoxovanadates is the rational design and synthesis of organic−inorganic hybrid vanadium oxides in order to explore their potential applications in catalysis, medicine, biology, electron conductivity, magnetism and photochemistry.[1−4] Recently, the introduction of hydrothermal techniques and the use of organic−templating agents have led to the production of various organic−inorganic hybrid vanadium oxides with discrete clusters, one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) structures.[5−8] Typically, the organic substituents have been presented as charge-compensating cations and structural filling agents, such as organoammonium units. More recently, an important advance in this field is that the organic components directly coordinate to the inorganic vanadium oxide scaffoldings or to secondary metal centers.[3,4] The introduction of transition metal−ligand units will not only enrich the frameworks of vanadium oxides, but also improve their electronic and magnetic properties.[3−5] Based on this strategy, a large variety of organic−inorganic hybrid materials belonging to the $\{M_xL_yVO\}$ system (M = transition metal, L = organic ligand) have been isolated.[2−7]

Among the large amount of reported work, the design and synthesis of organic−inorganic materials with helical structures are of particular interest and great challenge.[9−12] It is well-known that vanadium exhibits a variety of coordination geometries, which can be used for the synthesis of double-helical structures.[12] We report the hydrothermal synthesis and crystal structure of an unprecedented layered solid-state vanadium oxide complex, $[\{Co^{III}(phen)_2\}_2V_8O_{23}]$ (**1**; phen = 1,10-phenanthroline), which consists of left-handed and right-handed helical chains. Furthermore, **1** represents the first example of a 2D layered vanadium oxide complex constructed of 4,10,12-net sheets.

Results and Discussion

The asymmetric unit of **1** (Figure 1) shows four crystallographically independent V atoms and one crystallographically independent Co atom. All vanadium sites exhibit distorted tetrahedral coordination geometries [V−O 1.589(5)−1.852(4) Å]. Each of the V(1), V(2) and V(3) atoms has a terminal vanadyl group (V=O), while V(4) has two terminal vanadyl groups. Moreover, V(2) and V(3) share oxygen atoms with one CoN_4O_2 octahedron and two VO_4 tetrahedra, while V(1) and V(4) only share oxygen atoms with VO_4 tetrahedra. The Co^{III} center adopts an octahedral geometry, being coordinated by four nitrogen donors [Co−N 1.929(4)−1.953(4) Å] of phen groups, and two oxygen atoms [Co−O 1.886(3)−1.898(4) Å] from the VO_4 units, which adopt *cis* orientation.

Single-crystal X-ray diffraction analysis reveals that compound **1** consists of an unprecedented neutral 2D frame-

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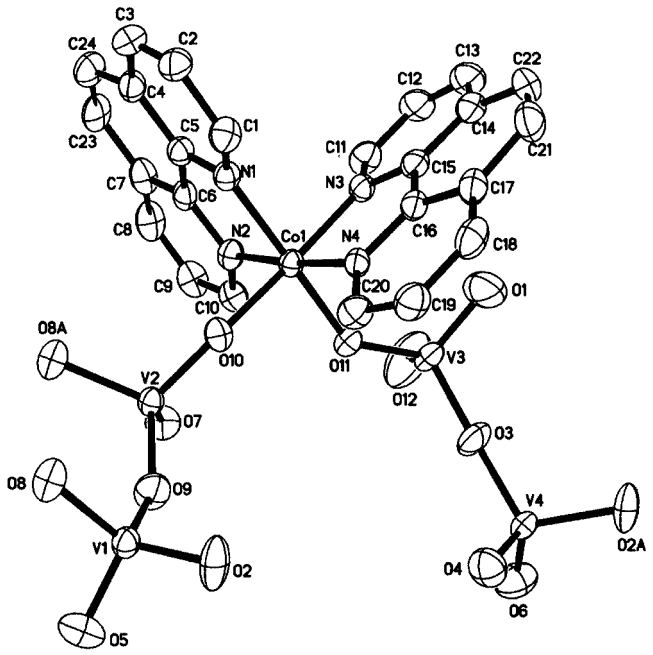

Figure 1. ORTEP drawing of compound **1** with thermal ellipsoids at 50 % probability; H atoms are omitted for clarity

work with $[Co^{III}(phen)_2]^{3+}$ coordination complex cations covalently linked to the vanadium oxide (V_8O_{23}) chains. Each V_8O_{23} chain is composed of alternating V_4O_{12} tetramer rings and V_4O_{13} units, which are linked by corner-sharing oxygen atoms. The V_4O_{12} tetramer rings and V_4O_{13} units of neighboring V_8O_{23} chains are further connected by $[Co^{III}(phen)_2]^{3+}$ fragments to form an extended 2D network with a unique 4,10,12-net structure (Figure 2 and Figure S1, see Supporting Information). To the best of our knowledge, compound **1** represents the first example of a 2D layered vanadium oxide complex that is constructed of 4,10,12-net sheets. The most interesting structural feature of compound **1** is that the CoN_4O_2 octahedra and VO_4 tetrahedra are connected to each other by corner-sharing oxygen atoms to form the right- and left-handed helical chains, which are further interconnected through oxygen atoms to produce the double-helical chains (Figure 3).

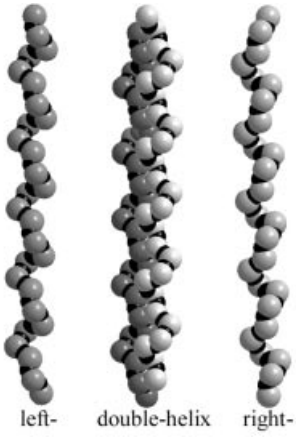

Figure 3. Space-filling view of the left-handed, right-handed, and double helices

It is striking that the adjacent layers are stably packed together, exhibiting an interesting three-dimensional supramolecular architecture through two types of supramolecular interactions. One interaction is the significant hydrogen bonding interaction between the hydrogen atoms of the phen groups and the unshared oxygen atoms of the inor-

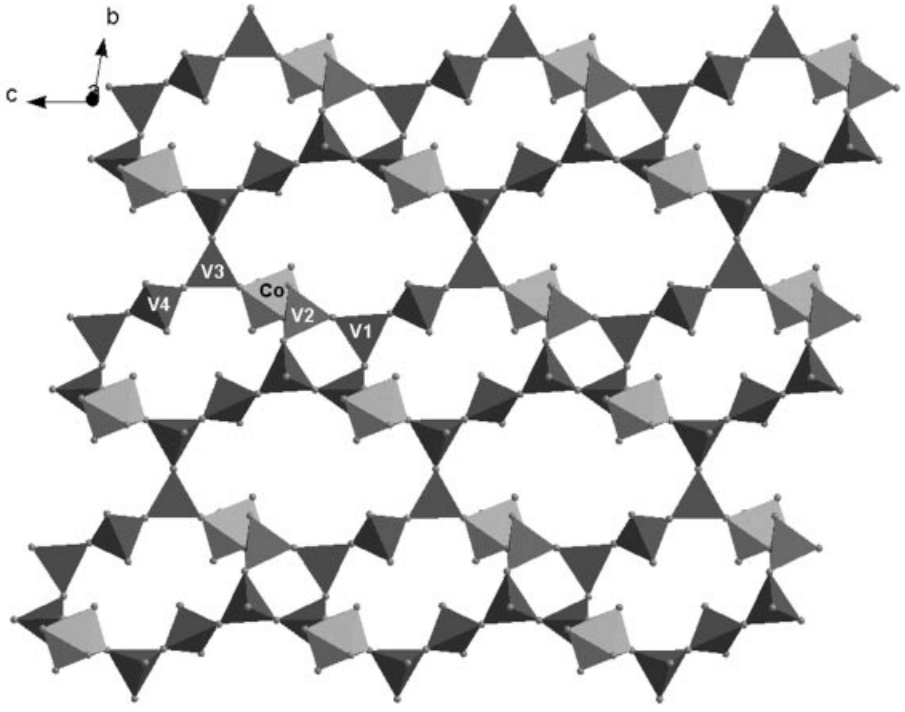

Figure 2. Polyhedral representation of compound **1** packed along the *a* axis; all C and H atoms are omitted for clarity

ganic layers (Figure S3, see Supporting Information).The typical hydrogen bonds are C(1)−H(1)···O(5) 2.305 Å, C(3)−H(3)···O(6) 2.415 Å, and C(21)−H(21)···O(4) 2.562 Å (Table S1, see supporting information). The other interaction is the aromatic π−π stacking interactions of the phen groups between adjacent layers; the close-contact distance between adjacent phen rings is 3.40−3.43 Å (Figure S2, see Supporting Information).

The bond valence sum calculations[14a] indicate that all V metal centers are in the +5 oxidation state and the Co metal center is in the +3 oxidation state within compound **1**. No signal was found in the EPR spectrum, which confirms that all cobalt atoms in **1** are in the +3 oxidation state and all vanadium atoms are in the +5 oxidation state. The X-ray photoelectron spectrum (XPS) of compound **1** in the energy regions of V_{2p} shows one peak at 516.7 eV, attributable to V^{5+} (Figure S4, see Supporting Information).[14b] It is noteworthy that compound **1** is the first vanadate complex containing cobalt in the +3 oxidation state.

The TG curve of compound **1** (Figure S5, see Supporting Information) is divided into two stages. The first mass loss is equal to 6.12 % from 335 to 440 °C and the second mass loss is equal to 37.69 % from 445−630 °C. These two continuous mass loss regions are ascribed to loss of the phen groups. The total mass loss (43.81 %) is in agreement with the calculated value (44.66 %). The sample does not lose mass at temperatures higher than 630 °C.

The variable-temperature magnetic susceptibility of compound **1** was measured from 2 to 300 K at 5000 Oe and are displayed in Figure 4, plotted as the thermal variation of χ_M and $\chi_M T$. At 300 K, the $\chi_M T$ value is 3.527 emu·K·mol^{-1}, which is slightly higher than that of an isolated spin-only Co^{3+} ion (3.00 emu·K·mol^{-1}, S = 2, g = 2.0) with diamagnetic V^{5+} ions (S = 0). It gives g = 2.18 if we assume the Co^{3+} ions are uncoupled. As T is lowered, $\chi_M T$ decreases continuously to a value of 0.173 emu·K·mol^{-1} at 2 K. This behavior of the $\chi_M T$ curve indicates that antiferromagnetic interactions exist in **1**. The effective magnetic moment at 300 K, 5.35 μ_B, is in the range of experimentally observed values for Co^{3+} ions. The magnetism of a Co^{3+} ion in molecular compounds is fairly complex because of the combined effects of spin−orbit coupling and the distortion of the octahedral crystal field. The consequence is that $\chi_M T$ deviates from the Curie law for an isolated Co^{3+} ion as it decreases with temperature.[15]

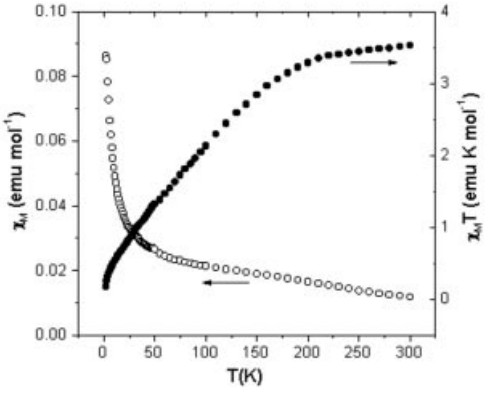

Figure 4. Thermal variation of χ_M and $\chi_M T$ for compound **1**

Conclusion

We have prepared the first vanadate complex with 4,10,12-net structure, in which the phen ligands coordinated to the cobalt−vanadate backbone. The title compound consists of left-handed and right-handed helical chains, which are further interconnected to form double-helical chains. The successful isolation of **1** confirms the observation that the transition-metal-complex moieties may profoundly influence the structure of the vanadium−oxide frameworks.

Experimental Section

Materials and General Methods: All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed with a Perkin−Elmer 2400 CHN Elemental Analyzer. Co and V were determined by a PLASMASPEC(I) ICP atomic emission spectrometer. EPR spectrum was recorded with a Japanese JES-FE3AX spectrometer at 293 K. XPS analysis was performed with a VG ESCALABMKII spectrometer using an Mg-K_α (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis. IR spectrum was recorded in the range 400−4000 cm^{-1} with an Alpha Centaurt FT/IR Spectrophotometer using KBr pellets. TG analysis was performed with a Perkin−Elmer TGA7 instrument in a stream of N_2 with a heating rate of 10 °C·min^{-1}. X-ray powder diffraction (XRPD) patterns were recorded with a Siemens D5005 diffractometer with Cu-K_α (λ = 1.5418 Å) radiation. Variable-temperature magnetic susceptibility was measured (SQUID, Quantum Design) in the temperature range of 2−300 K at 5000 Oe.

Synthesis: In a typical synthesis procedure for **1**, a mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.25 mmol), V_2O_5 (0.65 mmol), H_2O_2 (30 %, 4 mL), phen (0.5 mmol) and H_2O (6 mL) was stirred in air for 30 min. The mixture was then sealed in an 18-mL Teflon-lined autoclave, which was heated to 170 °C for 120 h. After slow cooling to room temperature, the resulting purple block crystals **1** were filtered off, washed with distilled water, and dried at ambient temperature (yield: ca. 0.16 g, 80 % based on cobalt). Powder X-ray diffraction patterns of the bulk product are in good agreement with the calculated pattern base on the results from single-crystal X-ray diffraction (Figure S7, see Supporting Information). The use of NH_4VO_3 as an alternative vanadium source also leads to the same product (yield: ca. 0.13 g, 65 % based on cobalt). In the reaction, the role of H_2O_2 as oxidant is critical in the formation of compound **1**.[13] Elemental analyses results of the purple crystals are consistent with the stoichiometry of **1**. $C_{48}H_{32}Co_2N_8O_{23}V_8$ (1614.2): calcd. C 35.7, H 2.0, Co 7.3, N 6.9, V 25.2; found C 35.5, H 1.9, Co 7.5, N 7.0, V 25.0. FT/IR: $\tilde{\nu}$ = 3056 (w) cm^{-1}, 1605 (w), 1582 (w), 1518 (m), 1491 (w), 1460 (w), 1426 (m), 1343 (w), 1228 (w), 1148 (w), 1111 (w), 1038 (w), 982 (s), 961 (s), 926 (s), 866 (m), 853 (m), 793 (s), 750 (s), 703 (s), 526 (m), 445 (w).

X-ray Crystallography: The structure of compound **1** was determined by single-crystal X-ray diffraction. A purple single crystal of **1** with dimensions 0.581 × 0.498 × 0.418 mm was mounted onto a glass fiber. Data were collected with a Rigaku R-AXIS RAPID

IP diffractometer using monochromated Mo-K_α (λ = 0.71073 Å) radiation at 293 K in the range of $1.59° < \theta < 27.48°$. Empirical absorption correction (ψ scan) was applied. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 software.[16] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps. A total of 8823 (5797 unique, R_{int} = 0.0526) reflections were measured. Structure solution and refinement based on 5797 independent reflections with $I > 2\sigma(I)$ and 403 parameters gave $R_1(wR_2) = 0.0560$ (0.1516) $\{R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}\}$. CCDC-215475 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **1**

Empirical formula	$C_{48}H_{32}Co_2N_8O_{23}V_8$
M_r (gmol^{-1})	1614.20
λ (Å)	0.71073
Space group	$P\bar{1}$
a (Å)	8.940 (2)
b (Å)	11.950(2)
c (Å)	13.060(3)
α (°)	97.05(3)
β (°)	96.29(3)
γ (°)	103.01(3)
V (Å^3)	1335.5(5)
Z	1
D_c (gcm^{-3})	2.007
μ (mm^{-1})	2.029
Final R indices [$I > 2\sigma(I)$]	R_1[a] = 0.0560, wR_2[b] = 0.1516
R indices (all data)	R_1[a] = 0.0736, wR_2[b] = 0.1657

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Acknowledgments

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