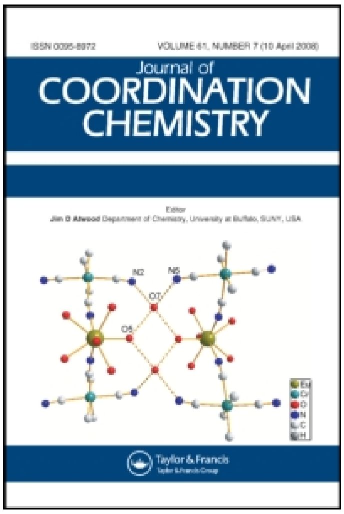

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A novel inorganic-organic hybrid material: hydrothermal synthesis and properties of $[V_6O_{12}(CH_3O)_4(phen)_4\cdot 4H_2O]$ (phen = 1,10-phenanthroline)

C. Dai[a]; W. Mi[a]; F. Yang[a]; B. Chen[a]; H. Ding[a]; Y. Shan[a]
[a] Department of Chemistry, East China Normal University, Shanghai, PR China

To cite this Article Dai, C. , Mi, W. , Yang, F. , Chen, B. , Ding, H. and Shan, Y.(2006) 'A novel inorganic-organic hybrid material: hydrothermal synthesis and properties of $[V_6O_{12}(CH_3O)_4(phen)_4\cdot 4H_2O]$ (phen = 1,10-phenanthroline)', Journal of Coordination Chemistry, 59: 3, 317 — 324

To link to this Article: DOI: 10.1080/00958970500270836

URL: http://dx.doi.org/10.1080/00958970500270836

Journal of Coordination Chemistry
Vol. 59, No. 3, 15 February 2006, 317–324

A novel inorganic–organic hybrid material: hydrothermal synthesis and properties of $[V_6O_{12}(CH_3O)_4(phen)_4 \cdot 4H_2O]$ (phen = 1,10-phenanthroline)

C. DAI, W. MI, F. YANG, B. CHEN, H. DING and Y. SHAN*

Department of Chemistry, East China Normal University,
Shanghai, 200062, PR China

(*Received 11 October 2004; in final form 3 March 2005*)

An oxo-vanadium cluster $[V_6O_{12}(CH_3O)_4(phen)_4 \cdot 4H_2O]$ (phen = 1,10-phenanthroline) was synthesized hydrothermally and characterized by IR, XPS, TG-DTA and single crystal X-ray diffraction analysis. It crystallizes in the triclinic space group $P\bar{1}$, with cell parameters $a = 9.709(1)$, $b = 11.701(1)$, $c = 13.365(2)$ Å, $\alpha = 74.430(2)^\circ$, $\beta = 77.073(2)^\circ$, $\gamma = 87.982(2)^\circ$, $V = 1425.0(3)$ Å^3, $Z = 2$. The crystal is built up as an organic–inorganic hybrid compound with an unusual oxo-vanadium skeleton and water molecules. Water molecules make up a tetramer linking neighboring oxo-vanadium clusters to form one-dimensional chains, and then further build up three-dimensional supramolecular arrays through the π–π stacking interactions of phen.

Keywords: Vanadium oxides; Phenanthroline; Hydrothermal Synthesis; Inorganic–organic hybrid

1. Introduction

Oxovanadate compounds have received attention in solid-state materials chemistry for their various structural features and potential practical interest in catalysis, biology, magnetism and photochemistry [1–4]. More recently, many researchers have focused their attention on the preparation of inorganic–organic hybrid materials constructed by inorganic vanadium oxides with various organic ligands or other molecular fragments with metal ions. A number of oxovanadate compounds with unusual structures have been synthesized, such as the 1-D structure: $[V_4O_{10}(Phen)]$ [5], $[VO_2(phen)_2] \cdot 6H_2O$ [6], $[(VO)_2(HAsO_4)_2(phen)_2]$ [7]; 2-D structure: $[V_4O_7(HAsO_4)_2(phen)_2]$ [8], $[Cu(phen)V_4O_{10}]_8$ [9], $[Ni(phen)_2V_4O_{11}]$ [10]; and 3-D net structure: $[Co(phen)_3][V_{10}O_{26}] \cdot H_2O$ [11]. However, in contrast to the abundant polyoxovanadates,

---

*Corresponding author. Fax: +86-21-62233503. Email: ykshan@chem.ecnu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500270836

compounds with two kinds of organic ligands coordinated directly to the oxo-vanadium skeleton are rare. In this article, we report a new inorganic–organic hybrid material with two organic compounds as ligands linking directly to the oxo-vanadium backbone. To the best of our knowledge, it is the first cluster compound with the methoxyl group as bridge-sharing ligand coordinated to two vanadium atoms in the oxo-vanadium skeleton.

2. Experimental section

2.1. *Hydrothermal synthesis*

All the chemicals are purchased and used without further purification. A mixture of V_2O_5 (0.100 g) and phen (0.108 g) was poured into a thick-wall Pyrex tube (6 mm ID). Then a mixture of water and methanol with the volume ratio of 1 : 3 was added. After sealing it was kept at 110°C under autogenous pressure for 7 days. Black quadrate crystals were isolated in ca. 40% yield (based on phen) by mechanical separation from a yellow-brown amorphous solid. This compound is insoluble in water and common organic solvents; it is stable in air.

2.2. *X-ray crystallography*

A single crystal of $[V_6O_{12}(CH_3O)_4(phen)_4 \cdot 4H_2O]$ ($0.2 \times 0.2 \times 0.1\,cm^3$) was used for data collection on a Bruker Smart CCD diffractometer using graphite-monochromated Mo/Kα radiation ($\lambda = 0.071073$ nm) and the ω-scan technique. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXTL-97 software. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon were located in calculated positions and those attached to oxygen atoms were located from difference Fourier maps. Structure solution and refinement based on 2188 independent reflections with $I > 2\delta(I)$ and 407 parameters gave $R_1 = 0.0681$. A summary of crystal data and structure refinement for the compound is given in table 1. Some selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *The crystal structure of the compound*

Single crystal X-ray analysis reveals that the asymmetric unit of $[V_6O_{12}(CH_3O)_4(phen)_4 \cdot 4H_2O]$ (figure 1) includes three crystallographically independent V atoms, five O atoms, two methoxy groups and two phenanthrolines. The V(1) displays a trigonal bipyramidal coordination geometry (VO_5) with two unshared oxygens and three bridging oxygens, two of which are oxygens from methoxy groups linking V(2) and V(3A) atoms, respectively. The other oxygen atom is coordinated to three V atoms (V(1), V(2) and V(3A)) simultaneously. The V(2) site exhibits (VN_2O_4) octahedral geometry with two nitrogens from the same phen ligand, one terminal oxygen, one oxygen from methoxy group connecting with V(1) atom and two bridging oxygens linking V(3) and V(3A) atoms. The coordination environment

Table 1. Crystal data and structure refinement for $[V_6O_{12}(CH_3O)_4(phen)_4 \cdot 4H_2O]$.

Formula	$V_6C_{52}H_{52}N_8O_{20}$
M	1414.66
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.709(1)
b (Å)	11.701(1)
c (Å)	13.365(2)
α (°)	74.430(2)
β (°)	77.073(2)
γ (°)	87.982(2)
U (Å^3)	1425.0(3)
Z	2
Index ranges	$-12 < h < 12$, $-14 < k < 14$, $-16 < l < 14$
Reflections collected/unique	7272/5161
Reflections used ($I > 2\delta(I)$)	2188
Final R indices ($I > 2\delta(I)$)	$R_1 = 0.0681/wR_2 = 0.1271$
R indices (all data)	$R_1 = 0.1784/wR_2 = 0.1642$

Table 2. Selected bond lengths (Å) and angels (°) for $[V_6O_{12}(CH_3O)_4(phen)_4 \cdot 4H_2O]$.

Bonds			
V1–O1	1.625(4)	V2–O6	1.802(5)
V1–O2	1.641(5)	V2–O8	1.889(4)
V1–O3	1.977(4)	V3–N3	2.160(5)
V1–O4	1.973(4)	V3–N4	2.340(6)
V1–O8	1.986(5)	V3–O4	2.024(5)
V2–N1	2.170(5)	V3–O6	1.889(5)
V2–N2	2.332(5)	V3–O7	1.589(4)
V2–O3	2.064(5)	V3–O8	1.921(4)
V2–O5	1.593(4)		
Angles			
V1–O3–V2	100.64(19)	O6–V2–N2	81.36(19)
V1–O4–V3	102.0(2)	O8–V2–N2	88.37(19)
V2–O6–V3	150.3(2)	O3–V2–N2	81.74(18)
V2–O8–V3	147.8(3)	N1–V2–N2	72.6(2)
V2–O8–V1	106.7(2)	O7–V3–O6	100.0(2)
V3–O8–V1	105.3(2)	O7–V3–O8	107.0(2)
O4–V1–O3	148.2(2)	O6–V3–O8	95.60(19)
O1–V1–O8	116.0(2)	O7–V3–O4	98.8(2)
O2–V1–O8	135.8(2)	O6–V3–O4	160.85(19)
O4–V1–O8	75.27(18)	O8–V3–O4	75.54(18)
O3–V1–O8	76.26(18)	O7–V3–N3	92.2(2)
O6–V2–O8	96.70(19)	O6–V3–N3	92.24(19)
O5–V2–O3	95.5(2)	O8–V3–N3	157.6(2)
O6–V2–O3	161.89(19)	O4–V3–N3	90.4(2)
O8–V2–O3	76.36(18)	O7–V3–N4	164.5(2)
O5–V2–N1	90.0(2)	O6–V3–N4	80.42(19)
O6–V2–N1	97.3(2)	O8–V3–N4	88.33(18)
O8–V2–N1	154.3(2)	O4–V3–N4	82.4(2)
O3–V2–N1	83.7(2)	N3–V3–N4	72.3(2)
O5–V2–N2	162.5(2)		

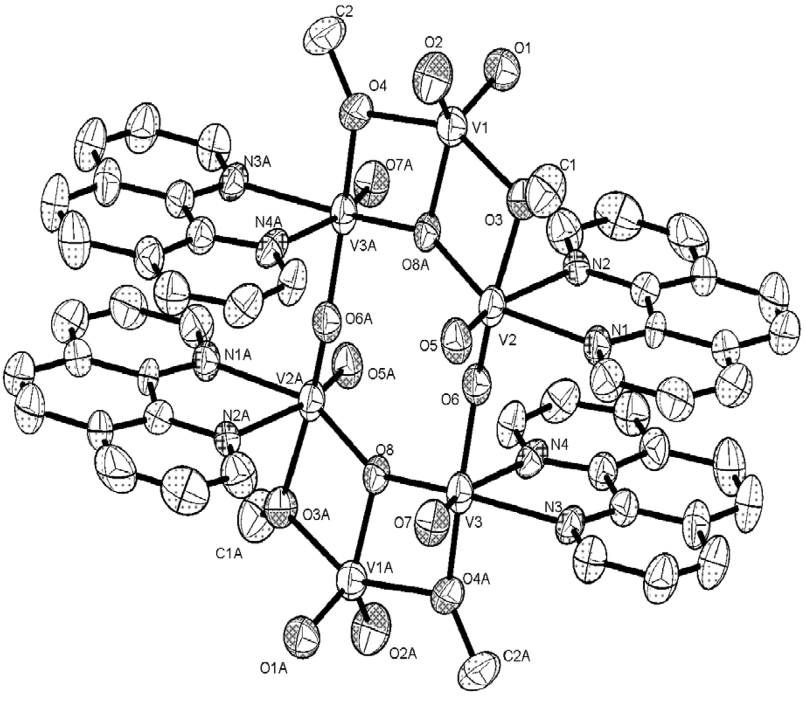

Figure 1. View of the crystal structure (the hydrogen atoms are omitted for clarity).

of V(3) is topologically similar to V(2), and each of them is approximatively a mirror-symmetric isomer.

The asymmetric units build up a whole cluster structure by inversion (figure 1). In the structure, four (VN_2O_4) octahedrons are linked by sharing a common corner to form an eight-member oxo-vanadium ring (V_4O_4). This ring and two trigonal bipyramids (VO_5) are zygomorphously linked together by sharing the common edge to construct the unusual oxo-vanadium skeleton of the cluster compound (see figure 1). Each trigonal bipyramid is linked with two (VN_2O_4) octahedra by two neighboring edges to form four four-member and one eight-member rings in the oxo-vanadium skeleton. The connectivity among the trigonal bipyramids and octahedra results in an interesting phenomenon in that there are two terminal oxygen atoms in the trigonal bipyramid and one terminal oxygen atom in the octahedron. The main skeleton is close to a rectangle.

A tetramer of water molecules observed in the crystals plays an important role in the formation of the crystal (figure 2). In the tetramer the water molecules construct a rectangle by hydrogen bonding at distances of 2.8 Å and 3.2 Å ($O \cdots O$), respectively. As linker, it connects the adjacent clusters via strong H-bond interactions between water molecules and the terminal oxygen atoms of oxo-vanadium trigonal bipyramids in the rectangle skeleton at $O \cdots O$ distances of 2.8 Å to form a one-dimensional infinite chain belt (see figures 2 and 3). In one chain belt, each terminal oxygen of the trigonal bipyramids participated in formation of the hydrogen bond, so a pair of hydrogen bond chains were observed as shown in figure 2. Each water molecule forms three hydrogen bonds, two as donors and one as acceptor for protons. This structure

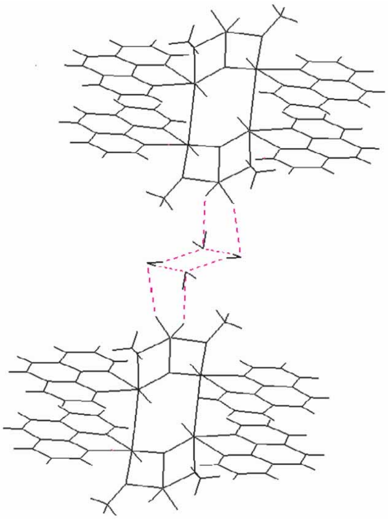

Figure 2. The one-dimension chain via 5-4-5-net H-bond interaction.

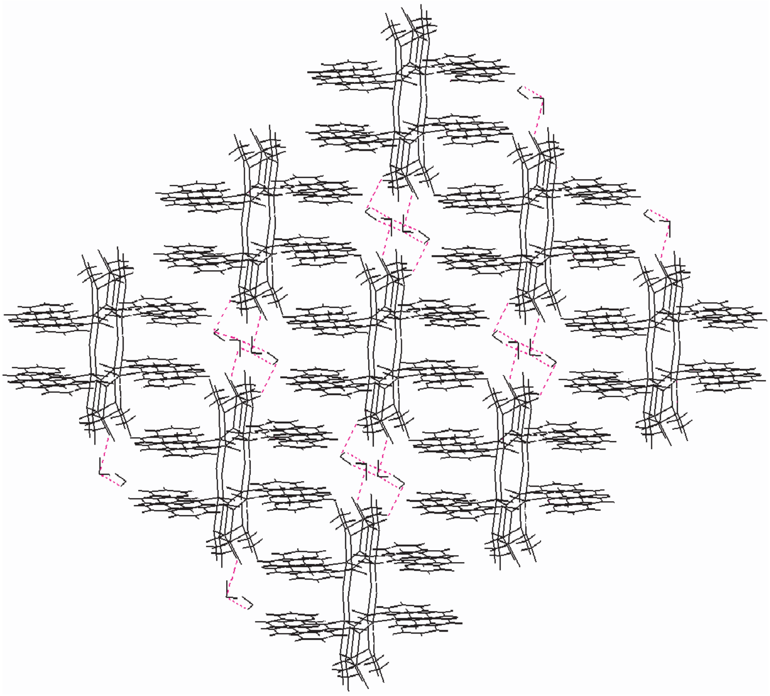

Figure 3. The packing array of compound viewed along the a-axis direction.

is unusual and contributes to the stability of the oxo-vanadium skeleton and the crystals. The one-dimension infinite chains are linked together by π–π stacking interactions of the phen groups to form the three-dimensional supramolecular crystals (see figure 3).

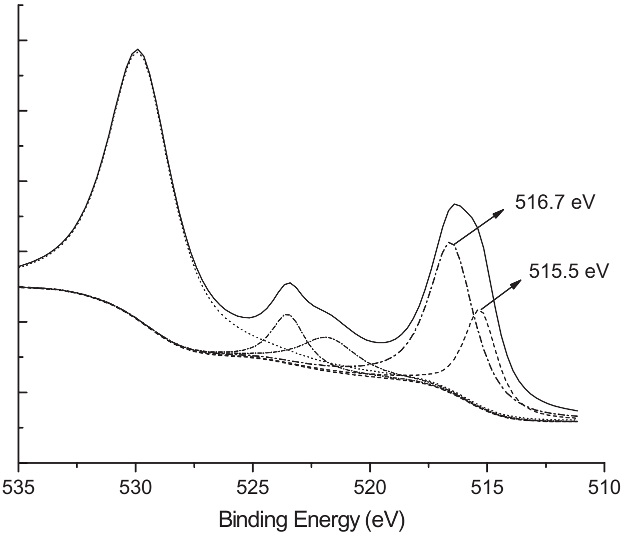

Figure 4. The X-ray photoelectron spectra (XPS) of the compound.

The shortest distance between planes of the phen groups on the different infinite chains is about 3.37 Å, which indicates strong π–π stacking interactions. The same effect was also found in [V_4O_{10}(phen)$_2$] [5] and [$(CuCl)_2$(phen)]$_8$ [9].

The V–O distance is in the reasonable range from 1.589(4) to 2.064(5) Å. The V(2)–O(3) distance (2.06 Å) is the longest, which may be due to low valence of V(2) and the strong steric effect between the methoxy and phen groups.

3.2. *Bond valence analysis through X-ray photoelectron spectra*

Bond valence sum calculations [12] give the values of 5.0, 4.6, and 4.3 for V(1), V(2) and V(3), indicating that V(2) and V(3) are mixed-valence vanadium with +4.5 oxidation state [13]. Presumably one electron is delocalized between the V(2) and V(3) sites via an oxygen bridge. This conclusion is further supported by X-ray photoelectron spectra (XPS). The result shown in figure 4 indicates the existence of two kinds of vanadium in +4 and +5 oxidation state corresponding to the peaks at 515.5 and 516.7 eV, respectively. In comparison, the binding energy of the vanadium in this crystals is smaller than the reported vanadium binding energy values 516.0 eV (V_2O_5) and 517.2 eV (VO_2) [14], indicating an electron-rich environment around vanadium and the dislocation of an electron in the oxo-vanadium skeleton. Furthermore, the ratio of the area for the two peaks is about 2.1 in good agreement with the bond valence sum calculation.

3.3. *Thermal analysis*

The TG thermal analysis (figure 5) is carried out at a heating rate of 10°C/min in nitrogen. The TG curve is divided into three steps of weight loss. The first weight loss is 5.35% corresponding to the release of all the crystal water molecules. It agrees well with the calculated value 5.08%. The weight loss in the second step is about

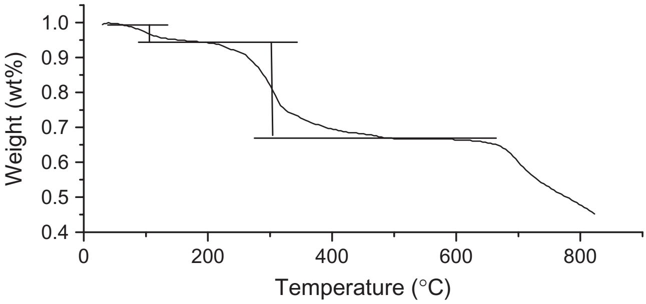

Figure 5. The TG thermal analysis of compound.

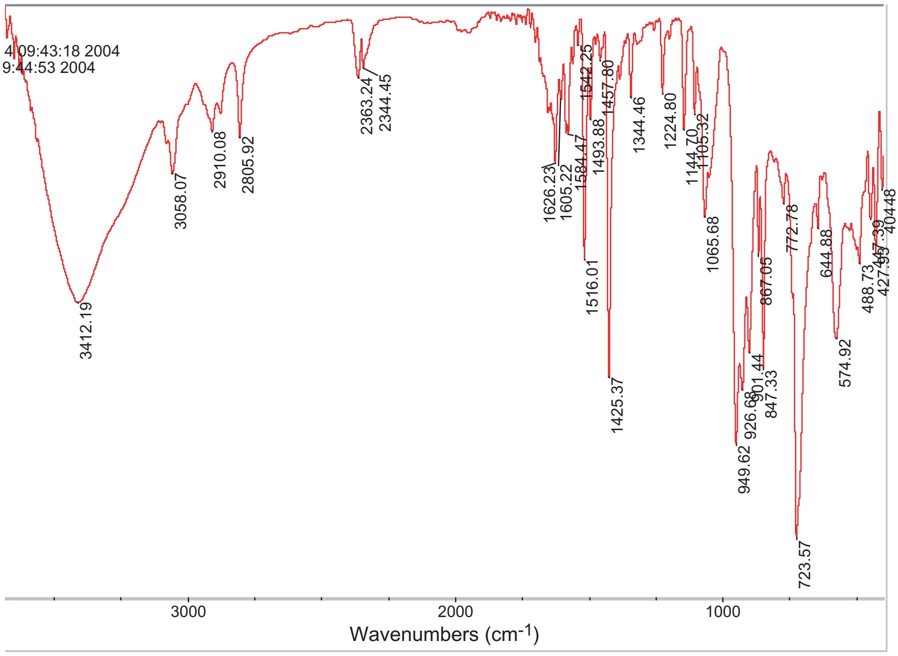

Figure 6. The IR spectra of the compound.

28% in the temperature range from 180 to 490°C, which is less than the theoretical value (51%) for loss of 1,10-phenanthroline. It may arise from the part decomposition of phen groups and accompany the carbonization on heating. Higher than 690°C, continued weight loss was observed on the TG curve. This phenomenon may have been attributed to decomposing of the organic fragments and the vaporization of the vanadium oxides on further heating.

3.4. *Infrared spectra of compound*

The IR spectrum (figure 6) exhibits a complex pattern, The bands at 867, 847, 773, 723 and 574 $\mathrm{cm^{-1}}$ are attributed to $\nu(\mathrm{V=O})$ or $\nu(\mathrm{V–O–V})$ vibrations. The band at 949 $\mathrm{cm^{-1}}$ indicates the existence of a (C–O) bond. Bands in the 1626–1065 $\mathrm{cm^{-1}}$ regions are due to phen rings. The broad band in $3412\,\mathrm{cm}^{-1}$ can be attributed to O–H stretching. These results are consistent with X-ray single crystal analysis.

4. Conclusions

We have synthesized hydrothermally a novel organic–inorganic hybrid compound with an unusual oxo-vanadium skeleton. In the crystal, a tetramer of water molecules is observed which link neighboring oxo-vanadium clusters to form one-dimensional chains belts, and then further build up three-dimensional supramolecular arrays crystals through the π–π stacking interactions of the phen group.

Acknowledgements

We thank the National Natural Science Foundation (No. 20173017, No. 20273021) for financial support.

References

[1] P.J. Hagrman, R.C. Finn, J. Zubieta. *Solid State Sci.*, **3**, 745 (2001).
[2] T. Chirayil, P.Y. Zavalij, M.S. Whittingham. *Chem. Mater.*, **10**, 2629 (1998).
[3] L.C.W. Baker, D.C. Glick. *Chem. Rev.*, **98**, 3 (1998).
[4] P. Gouzerh, A. Proust. *Chem. Rev.*, **98**, 77 (1998).
[5] Y. Li, E. Wang, S. Wang, Y. Lu, C. Hu, N. Hu, H. Jia. *J. Molecular Structure*, **606**, 175 (2002).
[6] Y. Qi, Y. Yang, M. Cao, C. Hu, E. Wang, N. Hu, H. Jia. *J. Molecular Structure*, **648**, 191 (2003).
[7] D. Xiao, Y. Lu, E. Wang, Y. Li, S. Wang, Y. Hou, G. Dea. *Inorg. Chem. Communications*, **7**, 128 (2004).
[8] D. Xiao, Y. Lu, E. Wang, Y. Li, S. Wang, Y. Hou, G. De. *J. Solid State Chem.*, **175**, 146 (2003).
[9] X.-B. Cui, Z.-E. Lin, G.-Y. Yang. *J. Solid State Sci.*, **5**, 311 (2003).
[10] C.-M. Liu, Y.-L. Hou, J. Zhang, S. Gao. *Inorg. Chem.*, **41**, 141 (2002).
[11] Y. Lu, E. Wang, J. Chen, Y. Qi, C. Hu, L. Xu, J. Peng. *J. Solid State Chem.*, **177**, 946 (2004).
[12] D. Brown, D. Altermatt. *Acta Cryst. B*, **41**, 244 (1985).
[13] Y. Hou, Y. Wei, D. Xiao, E. Shen, E. Wang, Y. Li, L. Xu, C. Hu. *Inorg. Chimica Acta*, **357**, 2477 (2004).
[14] M. Demeter, M. Neumann, W. Reichelt. *Surf. Sci.*, **41**, 454 (2000).