Asian Journal of Chemistry Vol. 21, No. 6 (2009), 4919-4926

Hydrothermal Synthesis, Crystal Structure and Optical Property of A 2-D Organic-Inorganic Compound $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$ (bpy = 4,4'-Bipyridine)

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A hydrothermal reaction of NH_4VO_3, WO_3, $NiCl_2$ and 4,4'-bipyridine yields a novel organic-inorganic hybrid compound, $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$ (bpy = 4,4'-bipyridine) ($C_{30}H_{26}N_6NiO_{19}V_2W_4$, M_r = 1670.56), which was characterized by elemental analysis, IR, single-crystal X-ray diffraction analysis and UV-Vis-NIR diffuse reflectance spectrum. It crystallizes in monoclinic, space group C2/c with a = 19.977(12) Å, b = 11.4602(13) Å, c = 16.0794(18) Å, β = 96.473(2)º, V = 3657.7(7) Å^3, Z = 4, D_c = 3.304 Mg/m^3, μ = 3.034 mm^{-1} and F(000) = 3080. The final R = 0.0525 and wR = 0.1552 for 3234 observed reflections with $I>2\sigma(I)$. In the crystal, each Ni(II) is six-coordinated by two oxygen atoms from two $[V_2W_4O_{19}]^{4-}$ and two nitrogen atoms from two bidentate bpy ligands and two nitrogen atoms from two protonated and terminal bpy ligands. The title compound is found to have an optical energy gap of 2.3 eV from UV-Vis-NIR diffuse reflectance spectrum.

Key Words: Polyoxometalate, 4,4'-Bipyridine, Protonated, Divanadium hexatungstate, Crystal structure.

INTRODUCTION

Polyoxometalates (POMs) are a rapidly growing class compound, due to their so-called ‘value-adding properties’ like diverse chemistry and favourable structural and electronic properties[1-3]. As species of extremely versatile inorganic building blocks, POMs are found to participate the construction of the organic-inorganic hybrid materials with novel structures and unusual properties[4-6]. Up to now, all reported hybrid compounds of POMs can be chemically formulated as $M_xL_u(X_mO_n)$, where M is cationic metal center, L is multidentate organic ligand and (X_mO_n) anionic POMs. In the reported $M_xL_y(X_mO_n)$ hybrid compounds, most of the (X_mO_n) anionic clusters are (Mo_mO_n) and (V_mO_n) and the (W_mO_n) and $(V_lW_mO_n)$ clusters are rare[7]. In this article, we report a novel organic-inorganic compound constructed by Ni(II), $(V_2W_4O_{19})^{4-}$, bidentate bpy ligands and protonated bpy, where positional disorder with respect to the vanadium atoms is observed.

EXPERIMENTAL

All commercially available chemicals are reagent grade and used as received without further purification. Elemental analysis for the title compound was performed by Elementar Vario EL-III. Infrared (IR) spectra, in the region (4000-400 cm^{-1}), were recorded on Perkin-Elmer spectrum 100 Fourier transform infrared spectrophotometer. UV-Vis-NIR diffuse reflectance spectra of the solid sample were measured by UV-3100 recording spectrophotometer, Barium sulfate ($BaSO_4$) was used as the standard with 100 % reflectance[8]. The Semi-quantitative element analysis was performed on electronic probe microanalyzer (JXA-8100+INCA EDS).

Synthesis: Yellow block-like $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$ was obtained from hydrothermal reaction of the mixture of $NiCl_2·6H_2O$ (0.0476 g, 0.20 mmol), WO_3 (0.0928 g, 0.40 mmol), NH_4VO_3 (0.0468 g, 0.4 mmol), 4,4'-bipyridine (0.0769 g, 0.4 mmol) and distilled water (13 mL, 0.722 mol) in a mole ratio of 1:2:2:3610 in 25 mL polytetrafluoroethylene-lined stainless steel reaction container at 150 ºC for 72 h. Anal. Calcd. (%) for $C_{30}H_{26}N_6NiO_{19}V_2W_4$: N 5.03, C 21.55, H 1.56. Found: N 5.11, C 23.09, H 1.59. IR (KBr, ν_{max})/cm^{-1}: 3450 (w), 3086 (w), 3060 (m), 1641 (w), 1601 (m), 1549 (w), 1515 (w), 1485 (m), 1414 (m), 1330 (w), 1290 (w), 1221 (w), 1200 (w), 1100 (w), 1077 (w), 1010 (m), 952 (s), 930 (s), 877 (m), 788 (s), 630 (m), 577 (s), 525 (m), 440 (s). The Semi-quantitative element analysis revealed that the ratio of Co:V:W is *ca.* 1:2:4.

Crystal structure determination: A yellow single crystal (0.34 mm × 0.32 mm × 0.31 mm) was carefully selected under microscope and was mounted inside a glass fiber capillary for intensity data collection on a Rigaku R-axis Rapid IP diffractometer with a graphite monochromated MoKα radiation (λ=0.71073 Å). The intensity data were collected in the range of $2.05^o \leq \theta \leq 25.01^o$ by ω Oscillation scan technique at 293(±2) K. The total reflections of 16,444 were collected, of which 3234 reflections with R_{int} = 0.0482 were unique and 3161 were observed ($I>2\sigma(I)$). Absorption corrections were applied by correlation of symmetry-equivalent reflections using the ABSCOR program[7]. The structure has been solved by direct methods (SHELXS-97)[9] and refined by full-matrix-least squares techniques on F^2 with anisotropic thermal parameters for all of the non-hydrogen atoms (SHELXL-97)[9]. Hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. These hydrogen atoms were allowed to ride on their respective parent atoms. The final R = 0.0525, wR = 0.1552 ($w = 1/[\sigma^2(F_0^2) + (0.0816(F_o^2 + 2F_c^2)/3)^2 + 0.09 (F_0^2 + 2F_c^2)/3]$, $(\Delta\rho)_{max}$ = 1.557 e.Å-3, $(\Delta\rho)_{min}$ = -2.698 e.$Å^{-3}$, (Δ/σ) = 0.001 and S = 1.262. All structural calculations were carried out using the SHELX-97 program package[9]. Table-1 shows crystallographic crystal data and processing parameters of the complex. Selected bond lengths and bond angles are listed in Tables 2 and 3.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR COMPLEX $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$

Empirical formula	$C_{30}H_{26}N_6NiO_{19}V_2W_4$	
Formula weight	1670.56	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.977(2) Å	α = 90°.
	b = 11.4602(13) Å	β = 6.473(2)°.
	c = 16.0794(18) Å	γ = 90°.
Volume	3657.7(7) $Å^3$	
Z	4	
Density (calculated)	3.034 Mg/m^3	
Absorption coefficient	13.611 mm^{-1}	
F(000)	3080	
Crystal size	0.34 × 0.32 × 0.31 mm^3	
Theta range for data collection	2.05 to 25.01°.	
Index ranges	$-23 \leq h \leq 23$, $-13 \leq k \leq 13$, $-19 \leq l \leq 19$	
Reflections collected	9842	
Independent reflections	3234 [R(int) = 0.0482]	
Completeness to theta = 25.01°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.1014 and 0.0904	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3234 / 0 / 287	
Goodness-of-fit on F^2	1.262	
Final R indices [I>2σ(I)]	R1 = 0.0525, wR2 = 0.1552	
R indices (all data)	R1 = 0.0547, wR2 = 0.1566	
Largest diff. peak and hole	1.557 and -2.698 e.$Å^{-3}$	

TABLE-2
SELECTED BOND LENGTHS (Å) OF $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$

Bond	Dist.	Bond	Dist.	Bond	Dist.
W(1)- O(8)	1.7090(9)	W(3)-O(10)	1.6480(9)	O(1)-W(2)^a	2.2921(7)
W(1)-O(7)	1.8790(9)	W(3)-O(3)	1.8930(9)	O(1)-V(3)^a	2.2931(7)
W(1)-O(4)	1.8970(9)	W(3)-O(6)^a	1.9210(9)	O(1)-W(3)^a	2.2931(7)
W(1)-O(5)	1.9300(9)	W(3)-O(4)	1.9250(9)	O(1)-W(1)^a	2.2986(6)
W(1)-O(2)	1.9430(9)	W(3)-O(5)^a	1.9360(9)	O(1)-V(1)^a	2.2986(6)
W(1)-O(1)	2.2986(6)	W(3)-O(1)	2.2931(7)	O(5)-V(3)^a	1.9360(9)
W(2)-O(9)	1.6470(10)	Ni(1)-O(8)	2.0780(9)	O(5)-W(3)^a	1.9360(9)
W(2)-O(6)	1.8790(9)	Ni(1)-N(1)	2.1180(10)	O(6)-V(3)^a	1.9210(9)
W(2)-O(3)	1.9100(9)	Ni(1)-N(3)	2.1650(15)	O(6)-W(3)^a	1.9210(9)
W(2)-O(2)	1.9250(9)	Ni(1)-N(4)^c	2.1810(15)	O(7)-V(2)^a	1.9260(9)
W(2)- O(7)^a	1.9260(9)	O(1)-V(2)^a	2.2921(7)	O(7)-W(2)^a	1.9260(9)
W(2)-O(1)	2.2921(7)	W(3)-O(10)	1.6480(9)	–	–

Symmetry transformation: (a): -x+1/2, -y+3/2, -z; (c): x, y+1, z.

TABLE-3
SELECTED BOND ANGLES (°) OF $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$

Angle	(°)	Angle	(°)	Angle	(°)
O(8)^{b}-Ni(1)-O(8)	176.0(5)	N(1)-Ni(1)-N(1)^{b}	179.7(6)	O(8)^{b}-Ni(1)-N(4)^{c}	92.0(2)
O(8)^{b}-Ni(1)-N(1)	90.6(4)	O(8)^{b}-Ni(1)-N(3)	88.0(2)	O(8)-Ni(1)-N(4)^{c}	92.0(2)
O(8)-Ni(1)-N(1)	89.4(4)	O(8)-Ni(1)-N(3)	88.0(2)	N(1)-Ni(1)-N(4)^{c}	89.9(3)
O(8)^{b} -Ni(1)-N(1)^{b}	89.4(4)	N(1)-Ni(1)-N(3)	90.1(3)	N(1)^{b}-Ni(1)-N(4)^{c}	89.9(3)
O(8)-Ni(1)-N(1)^{b}	90.6(4)	N(1)^{b}-Ni(1)-N(3)	90.1(3)	N(3)-Ni(1)-N(4)^{c}	180.000(3)

Symmetry transformations used to generate equivalent atoms: (b): -x+1, y, -z+1/2; (c): x, y+1, z.

RESULTS AND DISCUSSION

The complex $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$ crystallizes in monoclinic system with space group symmetry of C2/c. Positional disorder with respect to the vanadium atoms is present in the structure, which is common for the substituted heteropoly anions[10,11]. The X-ray data can be explained assuming random orientation of vanadium atoms in the tungstate framework. The stoichiometry of substituted heteropoly anions in the crystal structures can only be inferred from the relative site occupancies and this kind of analysis is intrinsically associated with large errors. The structure of $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$ was refined to relatively W:V occupancies of 2:1, which indicates two vanadium atoms could be present in the crystal, in well agreement with the stoichiometry of $[V_2W_4O_{19}]^{4-}$. In detail, the position occupancy factor ratio of W1/V1, W2/V2, W3/V3 are 0.85/0.15, 0.57/0.43 and 0.58/0.42, respectively.

In the crystal structure, the Ni(II) centre is octahedrally coordinated by two oxygen atoms, O8 and O8$^{\#2}$, at the axial direction, respectively from two divanadium hexatungstates $[V_2W_4O_{19}]^{4-}$ and 4 pyridyl nitrogen atoms, N1, N1^{b}, N3, N4^{c}, in equatorial plane, respectively from four 4,4'-bipyridine ligands, as shown in Fig. 1. The Ni-centered coordination octahedron is slightly distorted, with bonds length 2.078(9) Å for Ni-O and 2.118(10)-20181(15) Å for Ni-N bonds and the related bond angles approximate to 90° and 180°.

As illustrated in Fig. 2, of the four 4,4'-bipyridine ligands coordinating to Ni(II) centres, two at *para* positions are terminal and the nitrogen atom in the another end of pyridyl ring was protonated to balance the charge of the compound. While the other two act as N,N'-bidentate bridging ligands to link Ni centres of the adjancent two 1-D $[Ni(V_2W_4O_{19})]^{2-}$ anion chains, to build a 2-D organic-inorganic covalent layer $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$, as drawn in Fig. 3. The layers are packed by intermolecular forces to build up the whole crystal structure for the title compound.

The inorganic building blocks of divanadium hexatungstate $[V_2W_4O_{19}]^{4-}$ are coordinated to two Ni centres *via* its two centrically symmetric O8 atoms respectively (Fig. 4). And $[V_2W_4O_{19}]^{4-}$ basically keeps 'super-octahedral' Lindqvist-structure just like $[W_6O_{19}]^{2-}$, which is also reported earlier[11].

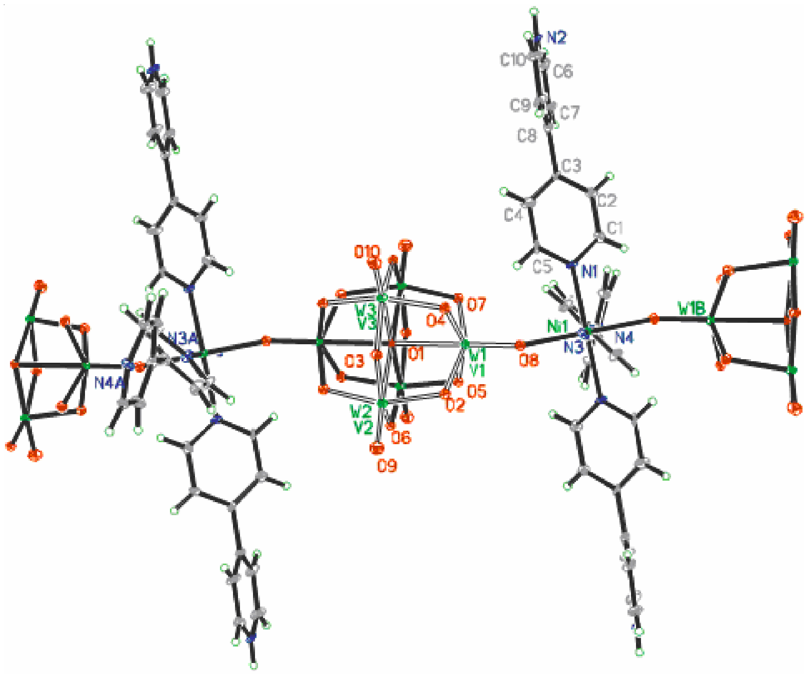

Fig. 1. Ortep view of the $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$ structure with atomic labelling of one asymmetric unit. The position occupancy factor ratio of W1/V1, W2/V2, W3/V3 are 0.85/0.15, 0.57/0.43 and 0.58/0.42, respectively

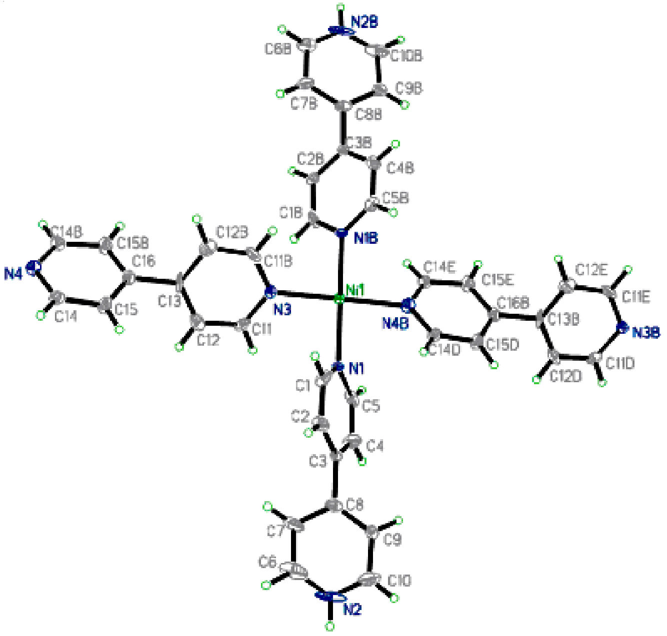

Fig. 2. The equatorial plane of Ni octahedron defined by four bpy ligands, in which two act as bidentate ligands, another two were protonated as terminal ligands

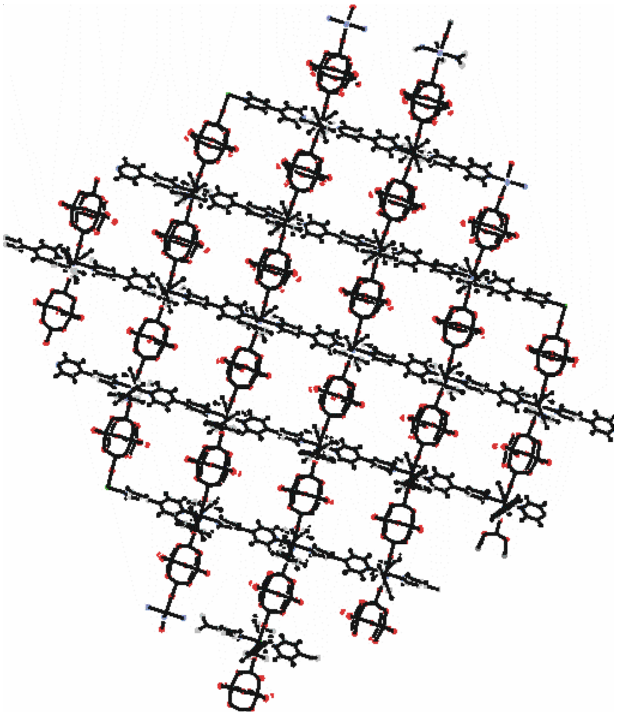

Fig. 3. Structure of the ${}^{2}_{\infty}[Ni(V_2W_4O_{19})(bpy)(Hbpy)_2]$ layer of the title compound

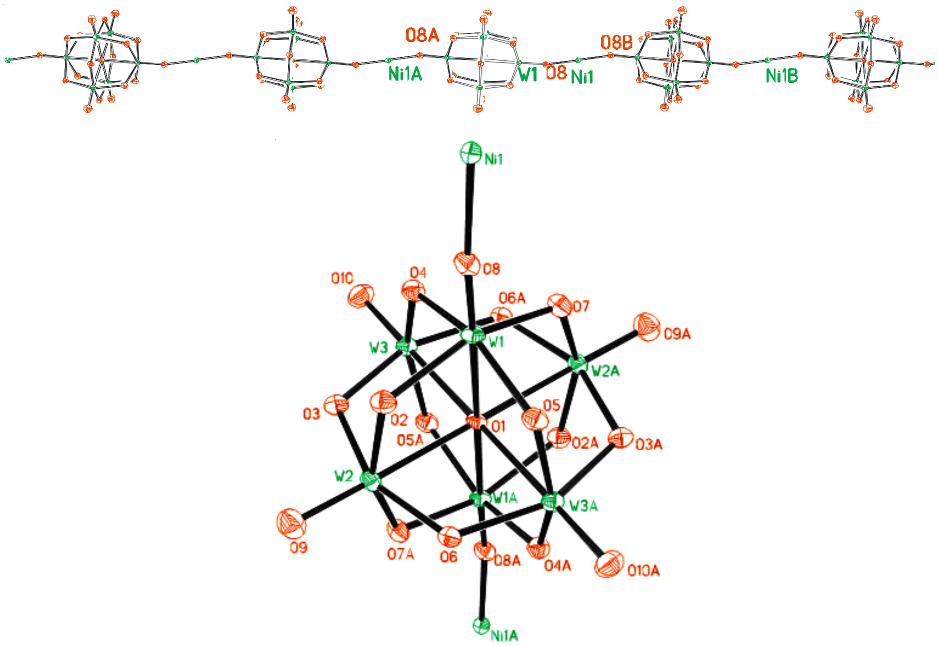

Fig. 4. The 1-D $[Ni(V_2W_4O_{19})]^{2-}$ anion chains (above) and divanadium hexatungstate unit (bottom)

The compound $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$ is a novel organic-inorganic hybrid compound, in which both the divanadium hexatungstate $[V_2W_4O_{19}]^{4-}$ and 4,4'-bipyridine act as bidenate ligand to coordinate with the Ni(II) centres to build the extended 2-D covalent framework. Up to now, $[V_2W_4O_{19}]^{4-}$ unit is often chemically modified on the surface[11], quiet different from acting as building blocks together with 4,4'-bipyridine ligands in the construction of the 2-D network of the compound $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$ described in this paper.

Optical energy gap: In order to explore the conductivity of present compound, the measurement of diffuse reflectivity for a powder sample was used to obtain its band gap E_g; which agrees rather well with that obtained by absorption measurement from a single crystal[12]. The band gap E_g was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a plot of Kubelka-Munk function F against energy E[13]. Kubelka-Munk function, $F = (1-R)^2/2R$, was converted from the recorded diffuse reflectance data, where R is the reflectance of an infinitely thick layer at a given wavelength[14]. The F *versus* E plot of compound $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$ is shown in Fig. 5, where a steep absorption edge is displayed and the E_g can be assessed at 2.3 eV.

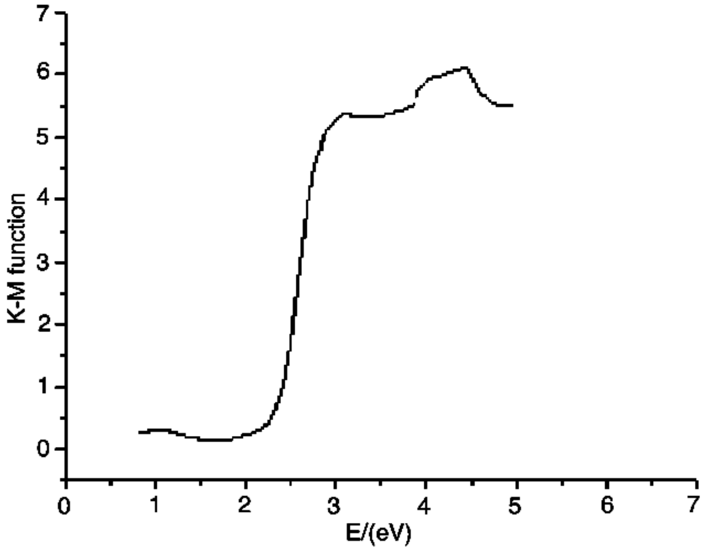

Fig. 5. Plot of K-M function versus energy E (eV) of compound $Ni(V_2W_4O_{19})(bpy)(Hbpy)_2$

ACKNOWLEDGEMENT

This work is financially supported by Funding Project for Academic Human Resources Development in Institutions of Higher Learning under the jurisdicton of Beijing Municipality (Grant No. BJE10016200611) and the Rsearch Fund of Beijing University of Civil Engineering and Architecture (Grant No. 100700502).

REFERENCES

1. M.I. Khan, *J. Solid State Chem.*, **152**, 105 (2000).
2. M.I. Khan, E. Yohannes and R. Doedens, *J. Angew. Chem. Int. Ed.*, **38**, 1292 (1999).
3. M.I. Khan, E. Yohannes and D. Powell, *Inorg. Chem.*, **38**, 212 (1999).
4. L.J. Zhang, Y.G. Wei, C.C. Wang, P. Wang and H.Y. Guo, *J. Solid State Chem.*, **177**, 3433 (2004).
5. C.C. Wang and C. Yin, *Z. Kristallogr. NCS*, **233**, 13 (2008)
6. M.I. Khan, S. Deb and R. Doedens, *J. Inorg. Chem. Commun.*, **9**, 25 (2006).
7. T. Higashi, ABSCOR-Empirical Absorption Correction Based on Fourier Series Approximation, Rigaku Corporation, Tokyo, Japan (1995).
8. J. Li, Z. Chen, X. Wang and M. Proserpio, *J. Alloys Compds.*, **28**, 262 (1997).
9. G.M. Sheldrick, SHELXS97 and SHELXL97, University of GÖttingen, Germany (1997).
10. Q.H. Luo, R. Howell and M. Dankova, *Inorg. Chem.*, **40**, 1894 (2001).
11. W. Huang, L. Todaro and L.C. Francesconi, *J. Am. Chem. Soc.*, **125**, 8512 (2003).
12. T.J. McCarthy, S.P. Ngeyi, J.H. Liao, DeGroot, T. Hogan, C.R. Kannewurf and M.G. Kanatzidis, *Chem. Mater.*, **5**, 331 (1993).
13. J.I. Pankove, Optical Processes in Semiconductors; Prentice-Hall, Inc.: Englewood Cliffs, NJ, pp. 34-86 (1997).
14. G. Kortum, Reflectance Spectroscopy, Springer: New York, 104 (1966).

(*Received*: 6 December 2008; *Accepted*: 13 April 2009) AJC-7411