A series of inorganic aggregates composed of $[MnV_{13}O_{38}]^{7-}$ polyoxoanions and transition metal cations

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ARTICLE INFO

ABSTRACT

In this paper, three new extended solid frameworks based on polyoxoanion $[MnV_{13}O_{38}]^{7-}$: $K_{0.5}Na_{2.5}Co_2[MnV_{13}O_{38}] \cdot 22H_2O$ (**1**), $K_{1.5}Na_{1.5}Mn_2[MnV_{13}O_{38}]$ $22H_2O$ (**2**) and $K_{0.5}Na_{2.5}Ni_2[MnV_{13}O_{38}]$ $22H_2O$ (**3**) have been synthesized and characterized by elemental analysis, IR spectrum, UV–Vis spectrum, thermal gravimetric analysis, magnetism, electrochemical analyses and single crystal X-ray diffraction. The structure analyses reveal that the polyoxoanions in compounds **1–3** are isostructural, which can be described as two transition metal-supported $\{M_2(H_2O)_{10}(MnV_{13}O_{38})\}$ ($M=Co^{2+}$, Mn^{2+} and Ni^{2+}) units connected by a K^+. And then the polyoxoanions are stacked by the electrostatic interactions with other K^+ and Na^+ cation to form a 2D layer. The variable-temperature magnetic susceptibility of compound **1** has been studied as the example, which shows an antiferromagnetic interaction.

1. Introduction

Interest in metal oxides has mushroomed recently because of their numerous applications in catalysis [1–3]. However, the mechanisms of their catalytic reactions are less understood due mainly to the complex nature of poorly characterized surfaces which are inaccessible to many physicochemical techniques [4,5]. Polyoxometalates (POMs), as an important family of metal-oxide clusters with plenty of structural topologies and a variety of physical and chemical properties, which are soluble, well-defined, and exhibiting similar structures of metal oxide surfaces, have been considered to be one of the best models and candidates to generate well characterized metal oxide surfaces [6–11]. To date, exploitation of polyoxometalates as building blocks to construct the extended solid-state frameworks has become an intriguing field in the solid-state polyoxometalate chemistry. A large number of inorganic–organic hybrid materials with POMs-based extended frameworks have been obtained under hydrothermal conditions [12–15]. However, It still remains rarely to be explored that linking suitable metal oxide building blocks together by simple metal cations to generate true metal oxide surfaces and framework materials [16–23], which is very advantageous to expand application of POM-based materials in catalysis and chemically bulk-modified electrode. In addition, the commonly used polyoxometalate building

blocks are still limited to the well-known Keggin- [24,25], Wells-Dawson- [26], Anderson- [22], Silverton- [27], and Waugh-type [28–30] polyoxoanions. In contrast, the well studied works on heteropolymolybdates and heteropolytungstates, the heteropolyvanadates is largely unexplored.

Among the various of heteropolyvanadates, the unusual tridecavanadomanganate (IV) anion $[MnV_{13}O_{38}]^{7-}$ seized our attention because of its high charge density, which can make the oxygen atoms of surface activate so as to facilitate combine with simple metal cations. The polyoxoanion $[MnV_{13}O_{38}]^{7-}$ was first synthesized by Pope and co-workers [31] and structurally characterized by Sasaki's group [32]. And recent studies have shown the inhibition of tumors and bacteria activities, and the catalytic properties of $[MnV_{13}O_{38}]^{7-}$ [33–36]. However, as we know, the examples utilizing of this anion for the design and synthesis of new POMs-based extended structures are reported scarcely [37,38]. Herein, we report three extended solid frameworks based on $[MnV_{13}O_{38}]^{7-}$: $K_{0.5}Na_{2.5}Co_2[MnV_{13}O_{38}] \cdot 22H_2O$ (**1**), $K_{1.5}Na_{1.5}Mn_2[MnV_{13}O_{38}]$ $22H_2O$ (**2**) and $K_{0.5}Na_{2.5}Ni_2[MnV_{13}O_{38}]$ $22H_2O$ (**3**).

2. Experimental section

2.1. General procedures

All regents were commercially purchased and used without further purification. $K_7[MnV_{13}O_{38}] \cdot 18H_2O$ was prepared according

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to the literature method [31] and characterized by IR spectrum. Elemental analyses (Co, Ni, Mn, V, Na, K) were determined by a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer using KBr pellets. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. The magnetic susceptibility measurements for **1** were carried out on polycrystalline samples using a SQUID magnetometer Quantum Design, in the temperature range of 2–300 K with an applied field of 0.1 T. Electrochemical measurements were carried out on a CHI 600A electrochemical workstation at room temperature (25–30 °C) under nitrogen atmosphere.

2.2. Synthesis of compounds

Synthesis of **1**: $K_7[MnV_{13}O_{38}] \cdot 18H_2O$ (1.021 g) was dissolved in water (30 mL). A solution of $CoCl_2 \cdot 6H_2O$ (1.1900 g, 5 mmol) in water (5 mL) was added with stirring. The pH value of the mixture was carefully adjusted with a dilute H_2SO_4 solution (1 M) to approximately 3.00–0.5000 g NaCl was added. And then, the mixture was heated to 80 °C for 3 h. After cooling to room temperature, the filtrate was kept at room temperature, and slow evaporation for two weeks resulted in the red crystals (Yield 85% based on $K_7[MnV_{13}O_{38}] \cdot 18H_2O$). Anal. Calcd for $K_{0.5}Na_{2.5}H_{44}Co_2MnV_{13}O_{60}$ (%): K 1.02, Na 3.00, Co 6.15, Mn 2.87, V 34.56; Found: K 0.95, Na 3.14, Co 6.03, Mn 2.76, V 34.65. IR (KBr pellet): 3442 (m), 3167 (m), 1612 (m), 1403 (m), 967 (s), 889 (m), 817 (m), 668 (s), 584 (s).

Synthesis of **2**: The preparation of **2** was similarly to that of **1**, except that $MnCl_2 \cdot 4H_2O$ (0.9911 g, 5 mmol) was used in place of $CoCl_2 \cdot 6H_2O$. Orange block crystals were obtained from the solution after two weeks (yield 60%, based on $K_7[MnV_{13}O_{38}] \cdot 18H_2O$). Anal. Calcd for $K_{1.5}Na_{1.5}H_{44}Mn_3V_{13}O_{60}$ (%): K 3.05, Na 1.79, Mn 8.56, V 34.41; Found: K 2.99, Na 1.84, Mn 8.44, V 34.38. IR (KBr pellet): 3419 (m), 3174 (m), 1616 (m), 1407 (m), 972 (s), 900 (m), 811 (m), 673 (s), 584 (s).

Synthesis of **3**: The preparation of **3** was similarly to that of **1**, except that $NiCl_2 \cdot 6H_2O$ (1.1892 g, 5 mmol) was used in place of $CoCl_2 \cdot 6H_2O$. Orange block crystals were obtained from the solution after two weeks (yield 75%, based on $K_7[MnV_{13}O_{38}] \cdot 18H_2O$). Anal. Calcd for $K_{0.5}Na_{2.5}H_{44}Ni_2MnV_{13}O_{60}$ (%): K 1.02, Na 3.00, Ni 6.13, Mn 2.87, V 34.56; Found: K 0.97, Na 2.95, Ni 6.25, Mn 2.73, V 34.69. IR (KBr pellet): 3441 (m), 3196 (m), 1620 (m), 1405 (m), 980 (s), 896 (m), 800 (m), 662 (s), 578 (s).

2.3. X-ray crystallography

Single-crystal X-ray data for compounds **1–3** were collected on a Rigaku R-AXIS RAPID IP diffractometer equipped with a normal focus 18 kW sealed tube X-ray source (Mo–Ka radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 200 mA. Data processing was accomplished with the RAXWISH processing program. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL 97 software [39,40]. All the non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data and structure refinement for compounds **1–3** are given in Table 1. Further details of the crystal structures can be obtained from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif with CCDC- 891877 (**1**), 891878 (**2**) and 891879 (**3**), respectively.

3. Result and discussion

3.1. Crystal structure of compounds

Single crystal X-ray diffraction analyses reveal that the polyoxoanions in compounds **1–3** are isostructural. Therefore, **1** is described as an example below. The polyoxoanion of compound **1** consists of two $\{Co_2(H_2O)_{10}(MnV_{13}O_{38})\}$ units connected by a K^+ ion. As shown in Fig. 1, the polyoxoanion $[MnV_{13}O_{38}]^{7-}$ has a similar sherwoodite structure which lacks one of the "equatorial" VO_6 octahedra. It is constructed by thirteen VO_6 octahedra always sharing edges, with the manganese atom occupying octahedral cavity in the center of the anion. The V–O and Mn–O bond lengths are 1.58(2)–2.40(1) Å and 1.84(0)–1.92(2) Å, respectively. The O–V–O and O–Mn–O angles are in the range of 68.7(2)–177.7(2)° and 87.3(2)–178.1(2)°, respectively. These bond lengths and bond

Table 1
Crystal data and structure refinement for **1–3**.

	Compound **1**	Compound **2**	Compound **3**
Empirical formula	$K_{0.5}Na_{2.5}H_{44}Co_2MnV_{13}O_{60}$	$K_{1.5}Na_{1.5}H_{44}Mn_3V_{13}O_{60}$	$K_{0.5}Na_{2.5}H_{44}Ni_2MnV_{13}O_{60}$
Formula mass	1916.40	1924.53	1915.96
Temperature [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a [Å]	11.832(2)	11.871(2)	11.871(2)
b [Å]	11.973(2)	12.102(2)	11.972(2)
c [Å]	20.593(4)	20.648(4)	20.475(4)
α [°]	89.23(3)	89.37(3)	89.45(3)
β [°]	81.65(3)	81.50(3)	81.65(3)
γ [°]	62.95(3)	62.72(3)	62.78(3)
V [Å^3]	2566.0(8)	2602.0(8)	2554.9(8)
Z	2	2	2
Dcalcd. [g cm^{-3}]	2.480	2.456	2.491
μ [mm^{-1}]	3.307	3.181	3.409
F000	1878.0	1886	1882
Data/restraints/parameters	8975/0/722	11726/0/709	8698/0/641
Goodness-of-fit on F^2	0.991	1.070	1.014
R_1[a] [$I > 2\sigma(I)$]	0.0547	0.0639	0.0813
wR_2[b]	0.1611	0.1827	0.2398
Largest diff. peak and hole [e Å^{-3}]	2.125 and −0.974	2.670 and −2.912	1.659 and −0.956

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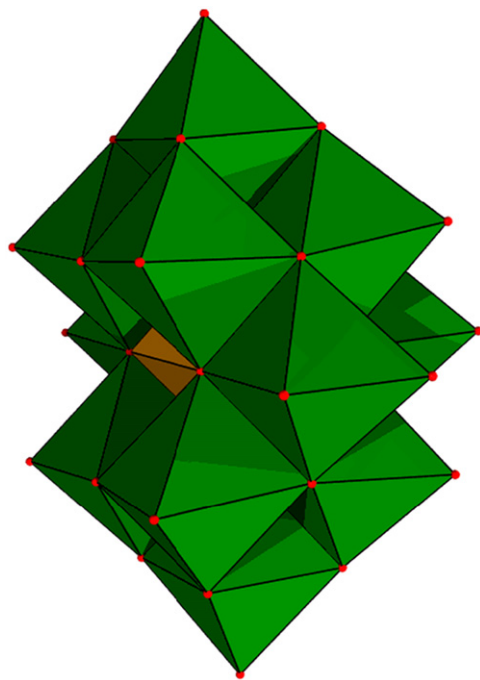[b] $wR_2 = \Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]^{1/2}$.

Fig. 1. Polyhedral drawing of polyoxoanion $[MnV_{13}O_{38}]^{7-}$.

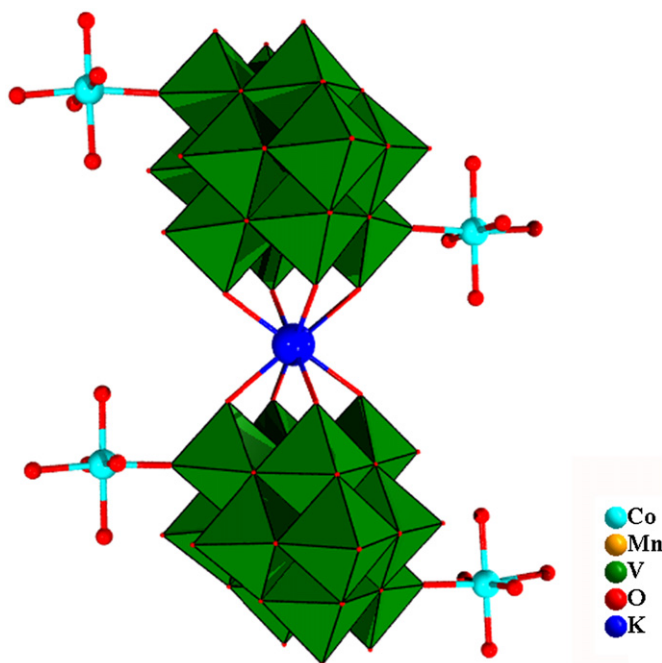**Fig. 2.** The combined polyhedral and ball-and-stick presentation of polyoxoanion **1**.

As shown in the Fig. 2, two divalent cobalt-aqua complex $[Co(H_2O)_5]^{2+}$ (Co–O:2.03(5)–2.04(8) Å, Co–Ow:2.06(0)–2.13(6) Å) are supported by the polyoxoanion $[MnV_{13}O_{38}]^{7-}$ via V–O_t–Co coordinate covalently bond, resulting the $\{Co_2(H_2O)_{10}(MnV_{13}O_{38})\}$ unit. And then two $\{Co_2(H_2O)_{10}(MnV_{13}O_{38})\}$ units are connected together by a K^+ ion to form the polyoxoanion of **1** (K–O, 2.612–2.840 Å).

And then, in compound **1** the polyoxoanions $\{K[Co_2(H_2O)_5 MnV_{13}O_{38}]_2\}^{4-}$ are further stacked by the electrostatic interactions with Na^+ ions to form a 2D layer, as shown in Fig. 3. The structure of compounds **2** and **3** are almost the same with **1**, except the difference of counterions (Fig. S1). The bond lengths of K–O and Na–O are in the range of 2.66(8)–3.17(5) Å.

3.2. Magnetic property

The variable-temperature magnetic susceptibility of compound **1** was measured from 2 to 300 K at 1000 Oe and was displayed in Fig. 4, plotted as the thermal variation of $\chi_M T$ and $\chi_{\bar{M}}^{-1}$. At 300 K, the $\chi_M T$ product is 7.80 cm^3 K mol^{-1}. As temperature is lowered, the $\chi_M T$ value decreases continuously to a value of 2.82 cm^3 K mol^{-1} at 2 K. Such a behavior of $\chi_M T$ curve indicates a mainly antiferromagnetic interaction in **1**. The $\chi_{\bar{M}}^{-1}$ vs T curve is well fitted by the Curie–Weiss law above 30 K with the Curie constant of 8.05 cm^3 K mol^{-1} (3.09 cm^3 K mol^{-1} for each Co^{2+} ion) and Weiss temperature of −9.40 K, respectively. The Curie constant is larger than that of one isolated spin-only Mn(IV) (1.875 cm^3 K mol^{-1}, S=3/2, g=2.0) and two isolated spin-only Co^{2+} ions (1.875 cm^3 K mol^{-1}, S=3/2, g=2.0), indicating that an important orbital contribution is involved [41]. The negative Weiss constant further indicates that the antiferromagnetic interaction might exist in compound **1**.

3.3. Electrochemical properties

The electrochemical behaviors of parent compound $K_7[MnV_{13}O_{38}] \cdot 18H_2O$ and compounds **1–3** have been studied by cyclic voltammetry in 0.5 mol/L (CH$_3$COOK/CH$_3$COOH) pH=5 buffer containing 1×10^{-3} mol/L samples under an nitrogen atmosphere at the scan rate of 100 mV s^{-1} (see Fig. 5). In the potential range +1200 to −1200 mV, $K_7[MnV_{13}O_{38}] \cdot 18H_2O$ exhibits one irreversible redox pair at $E_{1/2} = 135$ mV ($E_{1/2} = (E_{pa} + E_{pc})/2$). The similar electrochemical behaviors are also observed in the voltammogram pattern of compounds **1–3** at $E_{1/2} = 262$ mV, 247 mV and 123 mV, respectively, which can be ascribed to the redox processes of V^V. As shown in Fig. 5a and b, except for the waves cooresponding to vanadium reduction, the CV of **1** exhibits a cathodic peak at $E_{pc} = 878$ mV
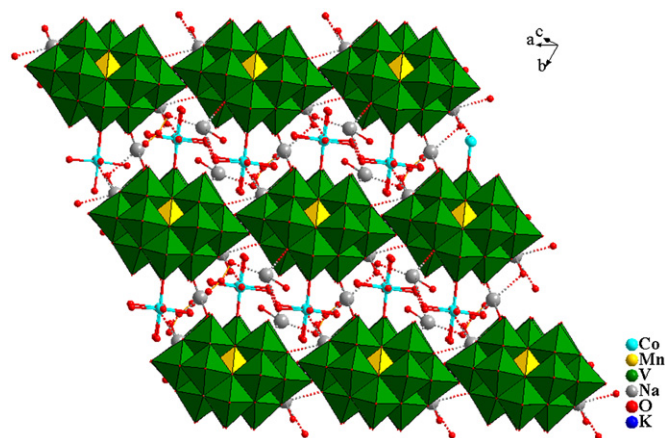

Fig. 3. The polyoxoanions $\{K[Co_2(H_2O)_5MnV_{13}O_{38}]_2\}^{4-}$ are stacked by the electrostatic interactions with Na^+ ions to form a 2D layer in compound **1**.

angles observed for the $[MnV_{13}O_{38}]^{7-}$ unit in compounds **1–3** is quite similar to that found in previously reported structure of heptapotassium tridecavanadomanganate (IV) octadecahydrate [32]. It is noteworthy that previous reported $[MnV_{13}O_{38}]^{7-}$ structures are disordered for random orientation of the anions [32,33]. The three VO$_6$ octahedra on the equatorial plan are statistically disordered at four sites around the apparent 4-fold axis. However in compounds **1–3,** the $[MnV_{13}O_{38}]^{7-}$ clusters are non-disordered.
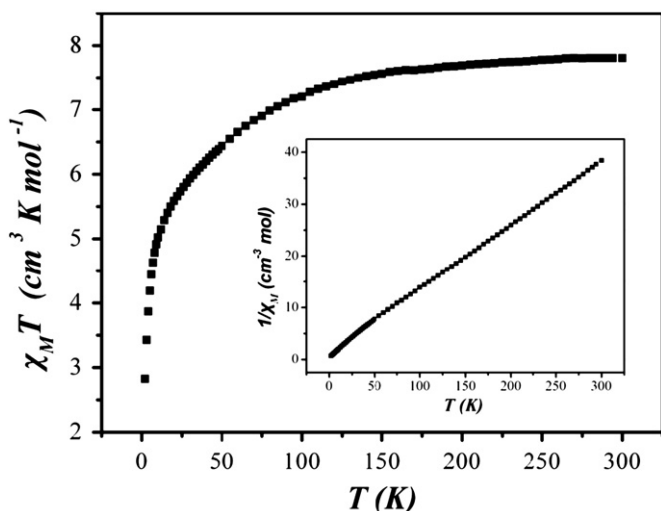
Fig. 4. The temperature dependence of reciprocal magnetic susceptibility χ_M^{-1} and the product $\chi_M T$ of a polycrystalline sample of **1** at 0.1 T.
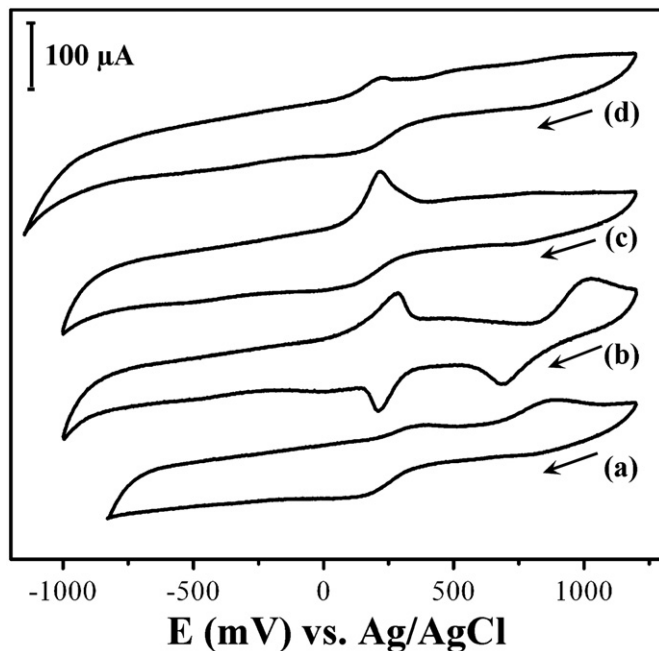

Fig. 5. Cyclic voltammetry at a glassy carbon working electrode of 1×10^{-3} mol/L compound solutions (0.5 mol/L CH_3COOK/CH_3COOH buffer, pH=5, scan rate of 100 mV/s: (a) **1**; (b) **2**; (c) **3**; (d) $K_7[MnV_{13}O_{38}] \cdot 18H_2O$.

attributed to the redox processes of the Co^{2+} centers [42]. And the CV of 2 shows one quasi-reversible one-electron redox pair at $E_{1/2}=857$ mV should correspond to the redox process of Mn(III)/Mn(II) [43].

4. Conclusion

In summary, we successfully obtained three new extended solid frameworks based on $[MnV_{13}O_{38}]^{7-}$ polyoxoanion by the reaction of the mixture of $K_7[MnV_{13}O_{38}] \cdot 18H_2O$ with transition metal ions (Co^{2+}, Mn^{2+} and Ni^{2+}) in aqueous solution. Single crystal analyses reveal that the polyoxoanions of **1–3** are iso-structural, which consists of two bi-supported $\{M_2(H_2O)_{10}$

$(MnV_{13}O_{38})\}$ units connected by a K^+. The future research will focus on attempting to study the detailed catalytic properties of these compounds.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2012.12.005.

References

[1] J.L.G. Fierro, Metal Oxides Chemistry and Applications, CRC, New York, 2006.
[2] J.P. Jolivet, Metal Oxide Chemistry and Synthesis, Wiley, Weinheim, 2000.
[3] H.H. Kung, Transition Metal Oxides, Elsevier, New York, 1989.
[4] I.M. Campbell, Catalysis at Surfaces, Chapman and Hadd, London, 1988.
[5] J.M. Thomas, W.J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH, Weinheim, 1997.
[6] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer, Berlin, 1983.
[7] M.T. Pope, A. Müller, Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity, Kluwer, Dordrecht, 1993.
[8] T. Yamase, M.T. Pope, Polyoxometalate Chemistry for Nano-Composite Design, Kluwer, Dordrecht, 2002.
[9] C.L. Hill, Chem. Rev. 98 (1998) 1–389.
[10] M.T. Pope, A. Müller, Angew. Chem. Int. Ed. 30 (1991) 34–48.
[11] D.L. Long, E. Burkholder, L. Cronin, Chem. Soc. Rev. 36 (2007) 105–121.
[12] Y.Z. Gao, Y.Q. Xu, Z.G. Han, C.H. Li, F.Y. Cui, Y.N. Chi, C.W. Hu, J. Solid State Chem. 183 (2010) 1000–1006.
[13] D.B. Dang, Y. Bai, C. He, J. Wang, C.Y. Duan, J.Y. Niu, Inorg. Chem. 49 (2010) 1280–1282.
[14] F.J. Ma, S.X. Liu, C.Y. Sun, D.D. Liang, G.J. Ren, F. Wei, Y.G. Chen, Z.M. Su, J. Am. Chem. Soc. 133 (2011) 4178–4181.
[15] X.F. Kuang, X.Y. Wu, R.M. Yu, J.P. Donahue, J.S. Huang, C.Z. Lu, Nat. Chem. 2 (2010) 461–465.
[16] M. Ishaque Khan, E. Yohannes, D. Powell, Chem. Commun. (1999) 23–24.
[17] M. Ishaque Khan, E. Yohannes, R.J. Doedens, Inorg. Chem. 42 (2003) 3125–3129.
[18] M.Ishaque Khan, J. Solid State Chem. 152 (2000) 105–112.
[19] M. Ishaque Khan, E. Yohannes, R.J. Doedens, Angew. Chem. Int. Ed. 38 (1999) 1292–1294.
[20] M. Ishaque Khan, E. Yohannes, D. Powell, Inorg. Chem. 38 (1999) 212–213.
[21] C.D. Wu, C.Z. Lu, H.H. Zhuang, J.S. Huang, J. Am. Chem. Soc. 124 (2002) 3836–3837.
[22] B. Gao, S.X. Liu, L.H. Xie, M. Yu, C.D. Zhang, C.Y. Sun, H.Y. Cheng, J. Solid State Chem. 179 (2006) 1681–1689.
[23] C.Y. Sun, S.X. Liu, L.H. Xie, C.L. Wang, B. Gao, C.D. Zhang, Z.M. Su, J. Solid State Chem. 179 (2006) 2093–2100.
[24] M. Sadakane, M.H. Dickman, M.T. Pope, Angew. Chem. Int. Ed. 39 (2000) 2914–2916.
[25] P. Mialane, L. Lisnard, A. Mallard, J. Marrot, E. Antic-Fidancev, P. Aschehoug, D. Vivien, F. Sécheresse, Inorg. Chem. 42 (2003) 2102–2108.
[26] J.Y. Niu, D.J. Guo, J.P. Wang, J.W. Zhao, Cryst. Growth Des. 4 (2004) 241–247.
[27] H.Q. Tan, W.L. Chen, Y.G. Li, D. Liu, L.M. Chen, E.B. Wang, J. Solid State Chem. 182 (2009) 465–470.
[28] H.Q. Tan, Y.G. Li, Z.M. Zhang, C. Qin, X.L. Wang, E.B. Wang, Z.M. Su, J. Am. Chem. Soc. 129 (2007) 10066–10067.
[29] H.Q. Tan, Y.G. Li, W.L. Chen, D. Liu, Z.M Su, Y. Lu, E.B. Wang, Chem. Eur. J. 15 (2009) 10940–10947.
[30] H.Q. Tan, Y.G. Li, W.L. Chen, A.X. Yan, D. Liu, E.B. Wang, Cryst. Growth Des. 12 (2012) 1111–1117.
[31] C.M. Flynn, M.T. Pope, J. Am. Chem. Soc. 92 (1970) 85–90.
[32] K. Nagai, H. Ichida, Y. Sasaki, Chem. Lett. (1986) 1267–1270.
[33] S.X. Liu, Y.Y. Liu, E.B. Wang, Huaxue Xuebao 54 (1996) 673–678.
[34] N. Fukuda, T. Yamase, Biol. Pharm. Bull. 20 (1997) 927–930.
[35] T. Yoshitaka, N. Chitose, S. Taro, J. Mol. Catal. 42 (1987) 57–66.
[36] Y. Tatsuno, C. Nakamura, T. Saito, Stud. Org. Chem. 33 (1988) 321–324.
[37] D.H. Li, S.X. Liu, C.Y. Sun, L.H. Xie, E.B. Wang, N.H. Hu, H.Q. Jia, Inorg. Chem. Commun. 8 (2005) 433–436.

[38] S.X. Liu, D.H. Li, L.H. Xie, H.Y. Chen, X.Y. Zhao, Z.M. Su, Inorg. Chem. 45 (2006) 8036–8040.

[39] G.M. Sheldrick, SHELXS97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.

[40] G.M. Sheldrick, Acta Crystallogr., Sect. A:Found. Crystallogr. 64 (2008) 112–122.

[41] X.H. Bu, M.L. Tong, Y.B. Xie, J.R. Li, H.C. Chang, S. KitagawaJ. Ribas, Inorg. Chem. 44 (2005) 9837–9846.

[42] B.S. Bassil, U. Kortz, A.S. Tigan, J.M. Clemente-Juan, B. Keita, P.D Oliveira, L. Nadjo, Inorg. Chem. 44 (2005) 9360–9368.

[43] B. Li, Y. Yan, F.Y. Li, L. Xu, L.H. Bi, L.X. Wu, Inorg. Chim. Acta 362 (2009) 2796–2801.