

New inorganic discrete 8-membered wheel clusters: Organically directed titanium sulfate supermolecules

Yunlong Fu *, Zhiwei Xu, Fanfan Zhang

School of Chemistry and Materials Science, Shanxi Normal University, Linfen 041004, PR China

Received 12 January 2007; received in revised form 11 March 2007; accepted 11 March 2007

Available online 19 March 2007

Abstract

Two organically directed titanium sulfates $(\text{C}_4\text{N}_3\text{H}_{16})_5(\text{H}_3\text{O})[\text{TiO}(\text{SO}_4)_2]_8 \cdot 15\text{H}_2\text{O}$ (**I**) and $(\text{C}_4\text{N}_2\text{H}_{12})_8[\text{TiO}(\text{SO}_4)_2]_8 \cdot 23\text{H}_2\text{O}$ (**II**), have been synthesized and characterized. **I** crystallizes in the orthorhombic space group Pnma, crystal data: $a = 16.5834 \text{ \AA}$, $b = 19.9129 \text{ \AA}$, $c = 29.1383 \text{ \AA}$, $V = 9622.15 \text{ \AA}^3$, and $Z = 4$; **II** crystallizes in the monoclinic space group C2/c, crystal data: $a = 23.1596(17) \text{ \AA}$, $b = 28.786(2) \text{ \AA}$, $c = 20.7720(15) \text{ \AA}$, $\beta = 121.0930(10)^\circ$, $V = 11858.6(15) \text{ \AA}^3$, and $Z = 4$. Two compounds are featured as uncommon discrete $[\text{TiO}(\text{SO}_4)_2]_8$ wheel clusters encapsulating different amines. The amines with linear and cyclic structures are located in different positions, respectively, involving host–guest interaction.

© 2008 Published by Elsevier B.V.

Keywords: Wheel cluster; Ti8; Sulfates; Organic amine

1. Introduction

Design and synthesis of wheel clusters have attracted intense interest because of their architectural beauty and their fascinating physical properties [1]. So far, most known wheel clusters have been assembled by using organic ligands in the periphery [2] or inside surface of the wheel [1], leading to discrete or continuous structures, respectively. Relatively, study of discrete inorganic metal wheel-cluster is undeveloped [3], although various rings have been observed in silicate and phosphate frameworks [4]. In the past few years, many organically directed metal sulfates have been reported and reviewed by Rao et al. [4]. Due to the low electric density of SO_4^{2-} compared to SiO_4^{4-} and PO_4^{3-} groups, the TM (transition metal) sulfates tend to form low dimensional framework [4]. This tendency provides a way to obtain discrete sulfated clusters. However, the discrete wheel-cluster sulfate is very rare, especially tetravalent metal(IV) sulfates.

On the other hand, a very wide range of transition metals (Sc, Zr, V, Fe, Co, Ni, Zn, Cd, Mo, etc.) and rare earth elements have been incorporated into the sulfate frameworks. However, Ti-based sulfates are unknown to date. Of particular interest is that incorporation of Ti elements may lead to crystal materials with interesting redox properties and photocatalytic activity [5–8]. In terms of crystal design, linear Ti–O–Ti connectivity has widely been observed in the known Ti-based compounds, but ring-like Ti–O–Ti connectivity was rarely reported [9,10].

Recently, we are interested in the synthesis of organically directed metal sulfates, and have introduced tetravalent Zr(IV) ions into metal sulfate system under room temperature and have separated three isolated ZrSO_4 monomers [11]. Using tetrabutyl titanate as Ti source to react with sulfuric acid in the presence of organic amine, we have separated two new titanium sulfates, $(\text{C}_4\text{N}_2\text{H}_{12})_8[\text{TiO}(\text{SO}_4)_2]_8 \cdot 23\text{H}_2\text{O}$ (**I**) and $(\text{C}_4\text{N}_3\text{H}_{16})_5(\text{H}_3\text{O})[\text{TiO}(\text{SO}_4)_2]_8 \cdot 15\text{H}_2\text{O}$ (**II**). They both exhibit uncommon anionic $[\text{TiO}(\text{SO}_4)_2]_8^{16-}$ wheel cluster encapsulating different organic amines.

* Corresponding author. Tel./fax: +86 357 2053716.

E-mail address: yunlongfu@dns.sxnu.edu.cn (Y. Fu).

2. Experimental

2.1. Synthesis and initial characterizations

All manipulations were carried out under the room temperature using analytical grade chemicals. Two compounds were prepared by the reaction of piperazine/diethylenetriamine, tetrabutyl titanate, sulfuric acid and distilled water with a molar ratio of 1:1:15:555. After evaporating for a few days, colorless blocked crystals were harvested (yield 50% to Ti). The compounds were characterized by IR spectroscopy and single crystal X-ray diffraction, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and CHN analysis.

X-ray powder diffraction data were recorded at room temperature on a D8X diffractometer equipped with monochromatized Cu K α 1 ($\lambda = 1.541 \text{ \AA}$) radiation. Data were collected in the range of $4^\circ \leq 2\theta \leq 40^\circ$. The powder X-ray diffraction patterns were in good agreement with the simulated patterns generated from the single-crystal XRD data, respectively, indicating the pure phases. Two compounds were given satisfactory elemental analysis on the PE2400 CHN element analyzer, conforming stoichiometry of organic amine. For **I**, Anal. Calcd, C 8.37%, N 7.33%, H 3.97%, Found, C 8.40%, N 7.23%, H 3.79%; For **II**, Anal. Calcd, C 12.13%, N 7.08%, H 4.48%, Found, C 11.93%, N 6.9%, H 4.4165%. The infrared (IR) spectra were recorded within the 400–4000 cm^{-1} region on a Nicolet 5DX spectrometer using KBr pellets. For **I**: 3436(s), 3174(m), 2930(s), 2855(w), 1633(s), 1535(s), 1404(m), 1207(s), 1130(vs), 989(s), 665(m), 602(m), 508(m); for **II**: 3445(vs), 3118(vs), 1624(s), 1512(s), 1240(s), 1135(s), 991(s), 696(w), 595(w), 482(w). The characteristic peaks conformed the presence of lattice waters, organic amines and sulfate groups.

2.2. X-ray crystallography study

Suitable single crystals were carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate adhesive. Single-crystal data were collected on a Bruker SMART-CCD diffractometer [graphite-monochromated Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$ ($T = 298 \text{ K}$)]. Absorption corrections based on symmetry-equivalent reflections were applied using SADABS [12]. The structures were solved by direct methods using SHELXS-97 [13] and difference Fourier synthesis. The direct methods solution readily revealed the heavy atom position (Ti and S) and enabled us to locate the other non-hydrogen positions (O, C, and N) from the Fourier difference maps. The hydrogen atoms of amines were generated theoretically and those of the lattice water molecules were not found at last. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for all hydrogen atoms. In **II**, besides of the fully protonated amines, charge balancing requirements necessitated a protonated

Table 1

Crystal data and refinement parameters of **I** and **II**

Structural parameters	I	II
Empirical formula	(C ₄ N ₂ H ₁₂) ₈ [TiO(SO ₄) ₂] ₈ ·23H ₂ O	(C ₄ N ₃ H ₁₆) ₅ (H ₃ O) ⁺ [TiO(SO ₄) ₂] ₈ ·15H ₂ O
fw	3167.684	2868.3204
Temperature (K)	298(2)	298(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c	Pnma
<i>a</i> (Å)	23.1596(17)	19.9129(12)
<i>b</i> (Å)	28.786(2)	29.1383(18)
<i>c</i> (Å)	20.7720(15)	16.5834(10)
α (deg)	90	90
β (deg)	121.0930(10)	90
γ (deg)	90	90
<i>V</i> (Å ³)	11858.6(15)	9622.2(10)
<i>Z</i>	4	4
θ range, deg	1.41–26.00	1.60–25.00
Reflections	26469/11506	47210/8550
collected/unique		
<i>R</i> (int)	0.0455	0.1299

$$^a \text{R1} = \sum |F_o| - |F_c| / \sum |F_o|; \text{wR2} = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}.$$

water. Details of the final refinements are given in Table 1. Selected bond distances and angles, and hydrogen-bonding interactions for two compounds are given in the Supporting information. Crystallographic data for structural analysis have been deposited with Cambridge Data center, CCDC reference number: 271330 for **I** and 271331 for **II**.

3. Results and discussion

Single crystal X-ray diffraction showed that **I** and **II** have the similar anionic [TiO(SO₄)₂]₈¹⁶⁻ rings encapsulating different amines. The asymmetric unit of (C₄N₂H₁₂)₈[TiO(SO₄)₂]₈·23H₂O contains four crystallographically distinct Ti atoms and eight S atoms. Each of Ti(IV) centers is coordinated to six O atoms in a distorted octahedral geometry (Table 2). Eight TiO₆ octahedra share corners in their all-*cis* positions to form a Ti₈O₈ ring-like structure. The titanium atoms are nearly situated at the vertices of a regular planar octagon and μ -O atoms are positioned alternatively above and below the plane of the ring in a staggered manner. A pair of sulfate groups bridge adjacent Ti sites and such repeated motifs give an anionic [TiO(SO₄)₂]₈¹⁶⁻ wheel clusters (Fig. 1). These bridging sulfate groups can be subdivided into two distinct groups by their orientations. One type of SO₄ group stretches outward from the rim of the wheel and the others are perpendicular to the Ti₈ plane. These Ti₈ clusters are stacked parallel to each other along the *a* axis and *c* axis (Fig. 2). Such array is repeatedly stacked along the *b* axis following AA sequence. It is worthy to note that some piperaziniums reside above and below the center of the Ti₈ rings involving host–guest interaction, the rest of piperaziniums are located in common positions like lattice water molecules

Table 2
Selected bond distances (Å) and angle (°) for **I** and **II**

Compound I					
Ti(1)–O(3)	1.814(2)	Ti(2)–O(35)	1.989(5)	Ti(3)–O(17)	2.067(4)
Ti(1)–O(12)	1.829(4)	Ti(2)–O(21)	2.015(4)	Ti(3)–O(9)	2.069(4)
Ti(1)–O(5)	1.971(4)	Ti(2)–O(26)	2.033(4)	Ti(4)–O(4)	1.818(4)
Ti(1)–O(6)	2.014(4)	Ti(2)–O(27)	2.064(4)	Ti(4)–O(2)	1.834(4)
Ti(1)–O(10)	2.042(4)	Ti(3)–O(1)	1.817(2)	Ti(4)–O(24)	1.993(4)
Ti(1)–O(13)	2.076(4)	Ti(3)–O(4)	1.817(4)	Ti(4)–O(18)	1.996(5)
Ti(2)–O(12)	1.807(4)	Ti(3)–O(11)	1.995(4)	Ti(4)–O(15)	2.047(4)
Ti(2)–O(2)	1.833(4)	Ti(3)–O(16)	2.003(4)	Ti(4)–O(22)	2.068(4)
O5–Ti1–O6	171.08(17)	O12–Ti2–O26	164.56(18)	O4–Ti3–O9	169.33(16)
O3–Ti1–O10	168.47(12)	O2–Ti2–O27	167.17(15)	O24–Ti4–O18	173.53(16)
O12–Ti1–O13	170.87(16)	O11–Ti3–O16	175.82(17)	O2–Ti4–O15	166.11(16)
O35–Ti2–O21	175.06(17)	O1–Ti3–O17	166.53(13)	O4–Ti4–O22	168.87(18)
Compound II					
Ti(1)–O(3)	1.824(4)	Ti(3)–O(13)	1.977(4)	Ti(4)–O(21)	2.034(4)
Ti(1)–O(7)	1.997(4)	Ti(3)–O(12)	2.009(4)	Ti(4)–O(36)#1	2.067(4)
Ti(1)–O(16)	2.071(4)	Ti(3)–O(11)	2.041(4)	Ti(5)–O(1)	1.804(4)
Ti(2)–O(5)	1.822(4)	Ti(3)–O(4)	2.073(4)	Ti(5)–O(5)	1.837(4)
Ti(2)–O(15)	1.992(4)	Ti(4)–O(3)	1.816(4)	Ti(5)–O(17)	2.006(4)
Ti(2)–O(14)	2.053(4)	Ti(4)–O(2)	1.817(4)	Ti(5)–O(8)	2.007(4)
Ti(3)–O(2)	1.812(4)	Ti(4)–O(6)	2.001(4)	Ti(5)–O(10)	2.044(4)
Ti(3)–O(1)	1.847(4)	Ti(4)–O(18)	2.002(4)	Ti(5)–O(19)	2.068(4)
O(7)#1–Ti(1)–O(7)	171.5(3)	O(5)–Ti(2)–O(14)	169.33(17)	O(3)–Ti(4)–O(21)	167.87(17)
O(3)–Ti(1)–O(16)	165.38(17)	O(1)–Ti(3)–O(11)	166.71(16)	O(2)–Ti(4)–O(36)#1	167.09(18)
O(3)#1–Ti(1)–O(16)#1	165.38(17)	O(13)–Ti(3)–O(12)	172.54(19)	O(17)–Ti(5)–O(8)	170.96(18)
O(15)#1–Ti(2)–O(15)	171.2(3)	O(2)–Ti(3)–O(4)	169.18(17)	O(5)–Ti(5)–O(10)	167.74(17)
O(5)#1–Ti(2)–O(14)#1	169.33(17)	O(6)–Ti(4)–O(18)	174.13(19)	O(1)–Ti(5)–O(19)	171.02(17)

#1 = $-x, y, -z+1/2$.

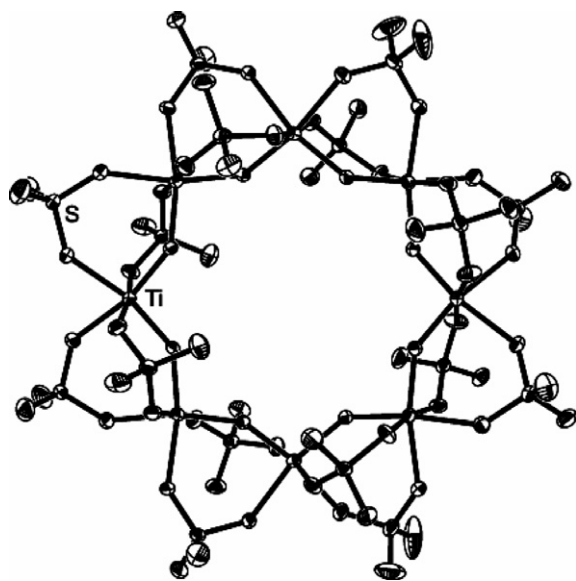


Fig. 1. The ORTEP with 30% probability of Ti8 rings which is constructed from tancoite-type unit $[\text{TiO}(\text{SO}_4)_2]^{2-}$ with all-*cis* connectivity.

(Fig. 3a). Such host–guest interaction is comparable to a similar neutral wheel clusters $[\text{TiO}(\text{O}_2\text{CC}_6\text{F}_5)_2]_8$ [9] encapsulating two toluene molecules that one above and one below the ring in the molecular cavity. The diprotonated piperazine molecules and lattice water interact with Ti8

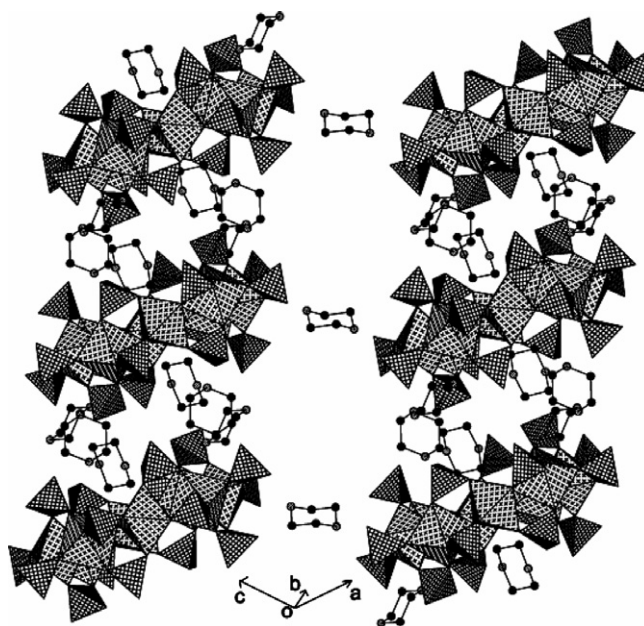


Fig. 2. Parallel packing modes of wheel clusters both along a axis and c axis in **I**, piperaziniums are located between the cluster. (The lattice water are not drawn for clarity).

wheel clusters *via* hydrogen bonds to stabilize the 3D assembly.

$(\text{C}_4\text{N}_3\text{H}_{16})_5 (\text{H}_3\text{O})[\text{TiO}(\text{SO}_4)_2]_8 \cdot 15\text{H}_2\text{O}$ (**II**) possesses the same anionic $[\text{TiO}(\text{SO}_4)_2]_8^{16-}$ rings. These rings are

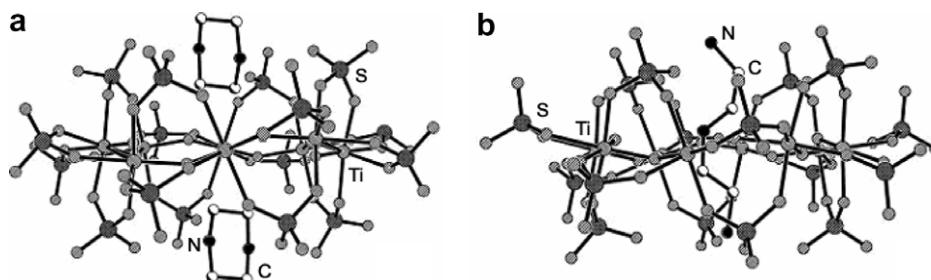


Fig. 3. Viewing different encapsulation behaviors for different amines: (a) piperazinium reside above and below the Ti8 ring; (b) diethylenetriamines cross through the Ti8 ring.

arranged parallel to each other along the *c* axis, but unparallel along the *a*-axis with an angle of *ca.* 64.72° between neighbored Ti8 plane (Fig. 4). Such array is further stacked along the *b* axis following AB sequences. Similarly, besides the diethylenetriamines which are located in common positions like lattice water molecules, the other types of diethylenetriamines cross through the center of Ti8 rings (Fig. 3b), and such an encapsulation behavior is similar to a linear NH(Et)₂ molecule crossing through the center of [Fe₈F₈(Me₃CCO₂)₁₆] [14] ring. In addition, there are lots of lattice water molecules in **II** as well as in **I**, leading to a great deal of hydrogen bonds to stabilize 3D assembly [10,15].

Besides octanuclear analogues mentioned above, similar host–guest interaction has also been observed in a neutral [NH₄][EtOEt][Co₈(MeCO₂)₈(OMe)₁₆][PF₆] [15] wheel cluster encapsulating a small cationic ammonium in the center of the 8-membered rings. It is notable that small ammonium can be trapped in the center of 8-membered ring, while some linear amines cross through the center of ring and some cyclic molecule/amine reside above and below the ring. Therefore, size effect should be a main factor for

host–guest interaction in these neutral wheel clusters. Besides of size effect, however, static effect and N–H···O hydrogen-bonding interaction are other two important factors here. (Detailed hydrogen-bonding information is in the Supporting information).

For the known TM sulfates, many low dimensional structures have been observed commonly when organic amines were introduced into the reaction system. This can also be resulted from the low negative charge of SO₄^{2−} compared with SiO₄^{4−} and PO₄^{3−} group. In view of crystal engineering, this octanuclear wheel cluster [TiO(SO₄)₂]₈^{16−} has a SBU [TiO(SO₄)₂]^{2−} denoted as tancoite-type unit [ML(TO₄)₂] (M is a octahedral, L is a ligand, T is tetrahedral) [16]. Such unit [ML(TO₄)₂] has widely been observed in sulfate [4], arsenate [17] and phosphate [18]. For example, the [TiO(PO₄)₂] unit has assembled into linear tancoite-type TiPO₄ [19] and chiral TiPO [20], *via* the different linking modes of μ-O atoms with all-*trans* and *trans*–*cis*–*cis* fashions, respectively. However, other type of topologies constructed from [ML(TO₄)₂] units is unknown. Herein, all-*cis* fashion of the μ₂-O atoms of [TiO(SO₄)₂]₈^{16−} leads to a new ring-like [TiO(SO₄)₂]₈^{16−} topology.

3.1. Thermal analysis

Thermogravimetric analyses (TGA) of the title compounds were performed on a ZRP-2P thermal analyzer. Single-phased sample was heated with a heating rate of 10 °C/min from room temperature (30 °C) to 600 °C at N₂ atmosphere. Two TGA curves show similar shapes but different weight losses in each temperature range (Fig. 5). For **I**, the weight loss of H₂O molecules is from 50 to 230 °C [obsd = 13.5%, calcd = 13.08%], and the weight losses for SO₃ and amine are from 326 to 570 °C [obsd = 65.50%, calcd = 66.73%]. For **II**, a gradual weight loss from 50 to 170 °C corresponds to the loss of H₂O [obsd = 8.9%, calcd = 10%], and a major loss from 268 to 511.65 °C corresponds to SO₃ and the amine [obsd = 67.16%, calcd = 67.72%]. The residues of two compounds after calcination at 600 °C were TiO₂, indicated by XRD pattern (ICSD #24780) [9]. The curves of TGA show that the total weight loss is close to the calculated value, conforming the right formula.

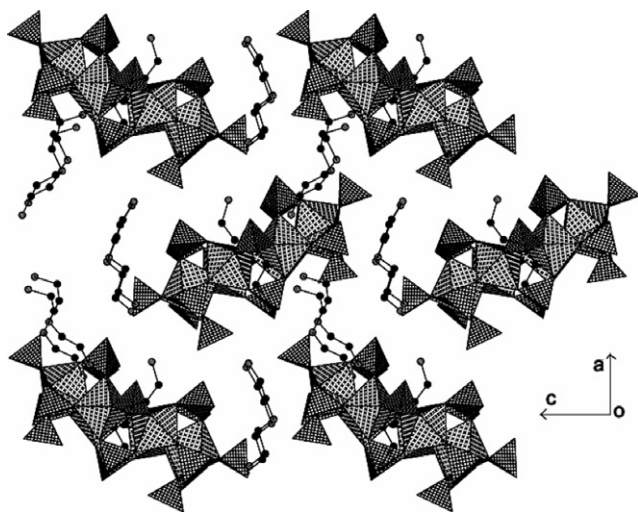


Fig. 4. Packing array of wheel clusters and amines in *ac* plane for **II**: parallel along the *c* axis and unparallel along the *a* axis and linear amines cross through the wheel and reside around it. (water molecules are not drawn for clarity).

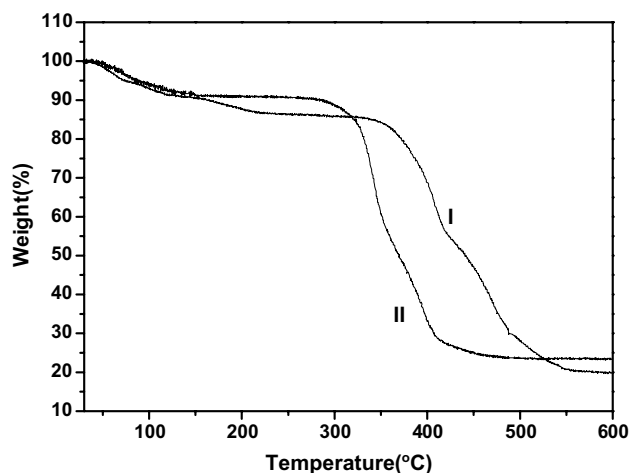


Fig. 5. TGA curves for I and II.

4. Conclusion

Uncommon inorganic octameric oxo titanium wheel clusters encapsulate different amines has been separated under room temperature. Such host–guest interaction has also been compared with analogue octamers to reveal a size effect as a main factor. $[\text{TiO}(\text{SO}_4)_2]_8^{16-}$ is a rare anionic octanuclear wheel cluster, especially in inorganic compounds. The hydrogen bonding interaction involving amines and waters play an important part in the formation of 3D supermolecule.

Acknowledgement

We acknowledge Natural Scientific Funds Committee of Shanxi Province for funding the project (20041031).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2007.03.021](https://doi.org/10.1016/j.molstruc.2007.03.021).

References

- [1] J.W. Cheng, J. Zhang, S.T. Zheng, M.B. Zhang, G.Y. Yang, *Angew. Chem. Int. Ed.* 44 (2005) 1.
- [2] (a) A.J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K.A. Abboud, G. Christou, *Angew. Chem.* 116 (2004) 2169; *Angew. Chem. Int. Ed.* 43 (2004) 2117, and references therein; (b) M. Murugesu, J. Raftery, W. Wernsdorfer, G. Christou, E.K. Brechin, *Inorg. Chem.* 43 (2004) 4203, and references therein; (c) A.L. Dearden, S. Parsons, R.E.P. Winpenny, *Angew. Chem.* 113 (2001) 155; *Angew. Chem. Int. Ed.* 40 (2001) 151, and references therein; (d) C. Cadiou, M. Murrie, C. Paulsen, V. Villar, W. Wernsdorfer, R.E.P. Winpenny, *Chem. Commun.* (2001) 2666; (e) S.P. Watton, R. Fuhrmann, L.E. Pence, A. Caneschi, A. Cornia, G.L. Abbati, S.J. Lippard, *Angew. Chem.* 109 (1997) 2917; *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2774, and references therein; (f) O.L. Sydora, P.T. Wolecanski, E.B. Lobkovsky, *Angew. Chem.* 115 (2003) 2789; *Angew. Chem. Int. Ed.* 42 (2003) 2685, and references therein; (g) L.F. Jones, A. Batsanov, E.K. Brechin, D. Collison, M. Helliwell, T. Mallah, E.J.L. McInnes, S. Piligkos, *Angew. Chem.* 114 (2002) 4494; *Angew. Chem. Int. Ed.* 41 (2002) 4318, and references therein; (h) E.J.L. McInnes, C. Anson, A.K. Powell, A.J. Thomson, S. Poussereau, R. Sessoli, *Chem. Commun.* (2001) 89, and references therein; (i) E.K. Brechin, O. Cador, A. Caneschi, C. Cadiou, S.G. Harris, S. Parsons, M. Vonci, R.E.P. Winpenny, *Chem. Commun.* (2002) 1860, and references therein; (j) C.H. Chang, K.C. Hwang, C.S. Liu, Y. Chi, A.J. Carty, L. Scoles, S.M. Peng, G.H. Lee, J. Reedijk, *Angew. Chem.* 113 (2001) 4787; *Angew. Chem. Int. Ed.* 40 (2001) 4651; (k) G.A. Ardizzoia, M.A. Angaroni, G.L. Monica, F. Cariati, S. Cenini, M. Moret, N. Masciocchi, *Inorg. Chem.* 30 (1991) 4347; (l) M. Eshel, A. Bino, I. Felner, D.C. Johnston, M. Luban, L. Miller, *Inorg. Chem.* 39 (2000) 1376; (m) A.S. Batsanov, G.A. Timko, Y.T. Struchkov, N.V. Gérébélou, K.M. Indrichan, *Koord. Khim.* 17 (1991) 662.
- [3] (a) A. Müller, E. Krichemeyer, H. Bögge, M. Schmidtman, C. Beugholt, P. Kögerler, C. Lu, *Angew. Chem.* 110 (1998) 1278; (b) *Angew. Chem. Int. Ed.* 37 (1998) 1220; (c) A. Müller, E. Krichemeyer, H. Bögge, M. Schmidtman, F. Peters, C. Carsten, J. Meyer, *Angew. Chem.* 109 (1997) 500; (d) A. Name, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 484; (e) A. Müller, S.K. Das, H. Bögge, C. Beugholt, M. Schmidtman, *Chem. Commun.* (1999) 1035; (f) A. Müller, E. Krichemeyer, H. Bögge, M. Schmidtman, C. Beugholt, S.K. Das, F. Peters, *Chem. Eur. J.* 5 (1999) 1496, and references therein.
- [4] (a) C.N.R. Rao, J.N. Behera, M. Dan, *Chem. Soc. Rev.* 35 (2006) 375; (b) J.N. Behera, C.N.R. Rao, *Chem. – Asian J.* 5 (2006) 742.
- [5] A.M. Chippindale, M.R. Grimshaw, A.V. Powell, A.R. Cowley, *Inorg. Chem.* 44 (2005) 4121.
- [6] J. Rocha, M.W. Anderson, *Eur. J. Inorg. Chem.* 5 (2000) 801.
- [7] E.K. Brechin, O. Cador, A. Caneschi, C. Cadiou, S.G. Harris, S. Parsons, M. Vonci, R.E.P. Winpenny, *Chem. Commun.* (2002) 1860, and references therein.
- [8] M.L.F. Phillips, W.T.A. Harrison, G.D. Stucky, E.M. McCarron, J.C. Calabrese, T.E. Giers, *Chem. Mater.* 4 (1992) 222.
- [9] H. Barrow, D.A. Brown, N.W. Alcock, H.J. Clase, M.G.H. Wallbridge, *Chem. Commun.* 12 (1995) 1231.
- [10] G. Kickelbick, U. Schubert, *Eur. J. Inorg. Chem.* 2 (1998) 159.
- [11] (a) Z.W. Xu, Y.L. Fu, S.Q. Teng, S.W. Ng, *Acta Cryst. E62* (2006) m3420–m3422; (b) Z.W. Xu, Y.L. Fu, S.Q. Teng, S.W. Ng, *Acta Cryst. E63* (2007) m140–m142; (c) Y.L. Fu, Z.W. Xu, J.L. Ren, S.W. Ng, *Acta Cryst. E61* (2005) m1520–m1522.
- [12] G.M. Sheldrick, SADABS, Program for Area Detector Adsorption Correction, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
- [13] G.M. Sheldrick, SHELXL97. University of Göttingen, Germany, 1997.
- [14] N.V. Gereleu, Yu. T. Stuchkov, O.S. Manole, G.A. Timko, A.S. Batsanov, *Dokl. Akad. Nauk SSSR* 331 (1993) 184.
- [15] J.K. Beattie, T.W. Hambley, J.A. Klepetko, A.F. Masters, P. Turner, *Chem. Commun.* (1998) 45.
- [16] F.C. Hawthorne, *Tschermaks Mineral. Petrogr. Mitt.* 31 (1983) 121.
- [17] A. Yaakoubi, T. Jouini, *Acta Cryst. C54* (1998) 1200.
- [18] R.I. Walton, F. Millange, A.L. Bail, T. Loiseau, C. Serre, D. O'Hare, G. Férey, *Chem. Commun.* (2000) 203.
- [19] (a) B.A. Maximov, N.E. Klokova, I.A. Verin, V.A. Timofeeva, *Kristallografiya* 35 (1990) 847; (b) N.E. Klokova, B.A. Maksimov, R.A. Tamazyanyan, *Kristallografiya* 38 (1993) 56.
- [20] Y.H. Guo, Z. Shi, J.H. Yu, J.D. Wang, Y.L. Liu, N. Bai, W.Q. Pang, *Chem. Mater.* 13 (2001) 203.