Synthesis of a novel chromium-phosphate built up with unprecedented $[CR_9P_{12}O_{58}H_{12}]^{17-}$ clusters under hydrothermal conditions

Wei Liu[a], Ding-Bang Xiong[b], Xin-Xin Yang[b], Jing-Tai Zhao[b,*]

[a]*Institute of Material Science and Engineering, The Ocean University of China, Qingdao 266100, PR China*
[b]*The State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics,*
Chinese Academy of Science, Shanghai 200050, PR China

Abstract

A new chromium-phosphate has been prepared under hydrothermal conditions for the first time. It crystallizes in the Monoclinic system, space group $C2/c$, $a = 17.002(3)$ Å, $b = 26.333(5)$ Å, $c = 16.017(4)$ Å, $\beta = 96.63\ (3)°$, $V = 7123.07(2)$ Å^3 and $Z = 4$. The crystal structure displays a centrosymmetric complex aggregate $[Cr_9P_{12}O_{58}H_{12}]^{17-}$, constructed from the unprecedented enneanucleus chromic core Cr_9O_{10} with peripheral ligations provided by 12 phosphate groups. The sodium ions and water as guests fill in the cavities among the clusters to satisfy the charge balance and keep the structural stability. The magnetic measurement indicates the existence of antiferromagnetic interactions.
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Keywords: Phosphate; Chromium; Crystal structure; Magnetic property

1. Introduction

Because of a unique multitude of properties based on their highly alterable sizes, shapes, charge densities and reversible redox potentials, high nuclearity complexes are of significant attention in many research fields including catalysis, medicine, materials science, photochemistry and magnetochemistry [1–3]. During the past decades, self-assembly processes involving Mo, W and V were successfully extended into the silicate, phosphate and arsenate systems, leading to a structurally diverse family of well-defined nanoparticles or clusters, but surprisingly, structurally characterized chromium aggregates are few [4–9]. This is probably due to the relative kinetic inertness of Cr(III) and the inherent stability of the low nuclearity complexes—in particular, oxo-centred Cr(III) triangles—once formed [10]. although the use of carboxylate ligands has recently proved a few of high-nuclearity chromium complexes

[11–17], however, presently few inorganic multinuclear chromium clusters, to our knowledge, have been reported. Whereas tungsten and molybdenum species have already proven effective in numerous applied sciences such as catalysis and medicine, only recently more attention is being focused on chromium aggregates that offer the potential for new structures, properties and applications.

Although most of polyoxoanions with unexpected structures are discovered under hydrothermal conditions, new synthetic methods have to be explored extensively in order to discover novel chromium compounds. Recently, our group prepared successfully a novel copper chlorophosphate, $Na_3[CuO(HPO_4)Cl]$ with a novel one-dimensional structural feature under hydrothermal conditions by relying on "reagent" rather than "solvent" quantities of water [18]. In this paper, we try synthesizing new materials in chromium-phosphate system in the same way, and interestingly, lead to a novel high-nuclearity chromium-phosphate, $Na_{17}[Cr_9P_{12}O_{58}H_{12}] \cdot xH_2O$ ($x \approx 25$) **1**, which is constructed from large structural groups containing an unpresented enneanuclear core Cr_9O_{10} enclosed by 12 PO_4 tetrahedra.

*Corresponding author. Fax: +86 21 52413122.
E-mail address: jtzhao@mail.sic.ac.cn (J.-T. Zhao).

2. Experimental

2.1. General

The reagents used were commercially obtained with analytical purities and used without further purification. The products were examined by powder X-ray diffraction (Rigaku D/max 2550 V diffractometer, Cu$K\alpha$) in order to confirm their phase identity and purity. IR spectra were collected on a Digilab-FTS-80 spectrophotometer from 4000 to 400 cm^{-1} using pressed KBr pellets of the samples. Thermogravimetric analyses and differential scanning calorimetry (TGA and DSC) were performed using a STA-409PC/4/H LUXX DSC-TGA instrument at a heating rate of 10 K/min in a flow of nitrogen gas from room temperature to 1273 K. The magnetic susceptibility measurements were carried out with a SQUID magnetometer (Quantum-Design, MPMS XL-7) in the temperature range 2–300 K.

2.2. Synthesis and characterizations

The title compound was synthesized under hydrothermal conditions by relying on "reagent" rather than "solvent" quantities of water. In the typical reaction, $CrCl_3 \cdot 6H_2O$ (0.53 g) and $Na_3PO_4 \cdot 12H_2O$ (4.56 g) in a molar ratio of 1:6 were homogenized by grinding before being placed in a Teflon-lined stainless steel autoclave, and heated to 443 K for 5 days, then cooled at 2 K/h to room temperature. The large green plate crystals were found in the viscous light green gel (pH $\approx$ 12), which were washed with deionized water to remove the residual $Na_3PO_4 \cdot 12H_2O$, and the crystals of **1** were isolated as the only solid phase (yield of 90% based on $CrCl_3 \cdot 6H_2O$). Anal. Calc. for **1**: Cr, 18.20; P, 14.45; Na, 15.21. Found: Cr, 17.45; P, 14.16; Na, 15.10%. IR(KBr): v_1(H–O) (3451 cm^{-1}), v_2(H–O) (1643 cm^{-1}), v(PO_4) (1079 cm^{-1}, 1029 cm^{-1}), and v_{as}(PO_4) (995 cm^{-1}). TGA shows a mass loss of 17.8% in the range of 323–473 K with an endothermic peak, corresponding to the release of water molecules (calculated 17.5%). Further mass loss of 4.3% between 473 and 723 K with a broad exothermal peak is consistent with the removal of 6 molar equiv. of water through condensation OH groups (calcd. 4.2%).

2.3. Crystal structure determination

Crystals of **1** were selected under a polarizing microscope, glued to a thin glass fibre with cyanoacrylate (superglue) adhesive, and inspected for singularity. One of them was chosen (0.20 mm × 0.20 mm × 0.08 mm), and data sets were collected at 295 K on a Nonius Kappa CCD diffractometer equipped with a normal focus, and a 2.4 kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. The structure corrected for Lorentz and polarization effects. A multiscan absorption correction was applied. The structure was solved in the space group $C2/c$ by direct methods and refined against $|F^2|$ with the aid of the SHELX AND SHELXL programs included in WinGX package [19]. The chromium and phosphor were located from the structure solution, whereas the sodium, framework-oxygen and hydrogen atoms were found in the difference Fourier maps. The hydrogen atoms of water molecules were omitted. The conformational disorder between O42 and O43 gives rise to their unreasonable short distance (1.02 Å) in the crystal structure. Additional information about the data collection and structure refinement is presented in Table 1, and the selected bonds and angles are given in Table 2. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD 414468.

3. Results and discussion

3.1. Description of crystal structure

The crystal structure of **1** displays a centrosymmetric complex anion $[Cr_9P_{12}O_{58}H_{12}]^{17-}$, containing an unprecedented enneanucleus chromic core Cr_9O_{10} with peripheral ligations provided by eight PO_4, two HPO_4 and two H_2PO_4 groups. The symmetry around each Cr centre is distorted octahedral with bond distances from 1.89(3) to 2.04(2) Å and angles from 81.86(6) to 100.52(6)°. The overall shape of enneanucleus chromium core can be described as the butterfly-like unit of oxo-chromium with the C_i symmetry (Fig. 1). As the "hinge", two Cr_4O_4 heterocabanes constructed from edge-sharing $Cr(1)O_6$, $Cr(2)O_6$, $Cr(3)O_6$ and $Cr(4)O_6$ octahedra are bridged via the common

Table 1
Crystal data and structure refinements for **1**

Empirical formula	$H_{12}Cr_9Na_{17}O_{83}P_{12}$
Formula weight	2570.57
Wavelength (Å)	0.71073
Temperature (K)	293
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	17.002(3)
b (Å)	26.333(5)
c (Å)	16.017(4)
B (°)	96.63(3)
V (Å^3)	7123.07(2)
Z	4
D_{calc} (g cm^{-3})	2.397
μ(Mo$K\alpha$) (mm^{-1})	1.843
θ range (°)	1.55–27.12
Total data collected	7798
Unique data	5231
R_{int}	0.042
S	0.997
R indices [$I > 2\sigma(I)$], R_1, wR_2	0.056, 0.163
Final R indices, R_1^a, wR_2^a	0.084, 0.175

^{a}w = $1/[\sigma^2(F_O)^2 + (0.0882P)^2]$ where $P = [F_O^2 + 2F_C^2]/3$.

Table 2
Selected bond distances (Å) and angles (°) for **1**

Cr(1)–O(10)	1.976(4)	Cr(5)–O(22)	2.005(4)
Cr(1)–O(10)[a]	1.976(4)	Cr(5)–O(19)[a]	1.997(4)
Cr(1)–O(7)	1.988(4)	Cr(5)–O(18)	2.004(4)
Cr(1)–O(7)[a]	1.988(4)	P(1)–O(4)	1.515(4)
Cr(1)–O(11)	2.015(4)	P(1)–O(17)	1.533(4)
Cr(1)–O(11)[a]	2.015(4)	P(1)–O(24)	1.545(4)
Cr(2)–O(12)	1.895(4)	P(1)–O(2)	1.543(4)
Cr(2)–O(2)	1.979(4)	P(2)–O(23)	1.516(4)
Cr(2)–O(9)	1.979(4)	P(2)–O(13)	1.537(4)
Cr(2)–O(20)	1.997(4)	P(2)–O(15)	1.534(4)
Cr(2)–O(10)[a]	1.997(4)	P(2)–O(16)	1.549(4)
Cr(2)–O(11)	2.042(4)	P(3)–O(26)	1.505(4)
Cr(3)–O(12)	1.912(4)	P(3)–O(18)	1.542(4)
Cr(3)–O(16)	1.974(4)	P(3)–O(25)	1.554(4)
Cr(3)–O(25)	1.982(4)	P(3)–O(20)	1.552(4)
Cr(3)–O(1)	1.987(4)	P(4)–O(5)	1.512(5)
Cr(3)–O(7)	2.027(4)	P(4)–O(6)	1.519(4)
Cr(3)–O(11)	2.061(4)	P(4)–O(1)	1.556(4)
Cr(4)–O(12)	1.888(4)	P(4)–O(21)	1.561(4)
Cr(4)–O(14)	1.961(4)	P(5)–O(3)	1.502(5)
Cr(4)–O(19)	1.976(4)	P(5)–O(8)	1.529(5)
Cr(4)–O(21)	1.974(4)	P(5)–O(9)	1.561(4)
Cr(4)–O(7)	2.011(4)	P(5)–O(14)	1.562(4)
Cr(4)–O(10)[a]	2.036(4)	P(6)–O(22)	1.526(5)
Cr(5)–O(15)	1.969(4)	P(6)–O(28)	1.549(5)
Cr(5)–O(24)	1.986(4)	P(6)–O(27)	1.570(5)
Cr(5)–O(11)	2.004(4)	P(6)–O(29)	1.556(5)
O(10)–Cr(1)–O(10)[a]	180.00(18)	O(11)–Cr(5)–O(22)	176.11(17)
O(10)[a]–Cr(1)–O(7)	82.32(15)	O(22)–Cr(5)–O(19)[a]	83.40(16)
O(7)–Cr(1)–O(11)	82.76(14)	O(15)–Cr(5)–O(18)	88.01(16)
O(11)–Cr(1)–O(11)[a]	180	O(4)–P(1)–O(17)	111.0(2)
O(7)[a]–Cr(1)–O(11)	97.24(14)	O(4)–P(1)–O(24)	109.9(2)
O(10)–Cr(1)–O(11)[a]	82.32(15)	O(17)–P(1)–O(24)	107.9(2)
O(12)–Cr(2)–O(9)	91.93(16)	O(4)–P(1)–O(2)	109.0(2)
O(12)–Cr(2)–O(20)	87.88(16)	O(23)–P(2)–O(13)	112.3(2)
O(2)–Cr(2)–O(11)	100.82(16)	O(23)–P(2)–O(15)	108.9(2)
O(9)–Cr(2)–O(11)	169.87(15)	O(13)–P(2)–O(16)	108.4(2)
O(20)–Cr(2)–O(11)	94.31(15)	O(23)–P(2)–O(16)	108.0(2)
O(10)[a]–Cr(2)–O(11)	81.13(14)	O(26)–P(3)–O(18)	111.4(2)
O(12)–Cr(3)–O(16)	171.80(15)	O(26)–P(3)–O(25)	108.6(2)
O(12)–Cr(3)–O(25)	88.62(16)	O(18)–P(3)–O(25)	108.6(2)
O(16)–Cr(3)–O(1)	86.06(16)	O(26)–P(3)–O(20)	109.5(2)
O(25)–Cr(3)–O(7)	168.76(15)	O(5)–P(4)–O(6)	109.2(3)
O(1)–Cr(3)–O(7)	80.08(15)	O(5)–P(4)–O(1)	110.5(2)
O(12)–Cr(3)–O(11)	82.89(15)	O(6)–P(4)–O(1)	108.7(2)
O(12)–Cr(4)–O(19)	169.30(16)	O(5)–P(4)–O(21)	111.3(2)
O(14)–Cr(4)–O(19)	95.80(16)	O(3)–P(5)–O(8)	112.6(3)
O(12)–Cr(4)–O(21)	91.68(16)	O(3)–P(5)–O(9)	108.6(3)
O(19)–Cr(4)–O(21)	95.04(16)	O(8)–P(5)–O(9)	108.7(3)
O(12)–Cr(4)–O(7)	82.72(15)	O(3)–P(5)–O(14)	111.4(3)
O(14)–Cr(4)–O(7)	170.88(16)	O(22)–P(6)–O(28)	112.2(3)
O(15)–Cr(5)–O(24)	170.51(15)	O(22)–P(6)–O(27)	110.0(3)
O(15)–Cr(5)–O(11)	93.39(15)	O(28)–P(6)–O(27)	110.4(3)
O(24)–Cr(5)–O(11)	94.70(15)	O(22)–P(6)–O(29)	104.3(3)

[a] $-x+1/2$, $-y+1/2$ and $-z+1$.

Fig. 1. Ball-and-stick side view of the enneanucleus chromium(III) core $\{Cr_9O_{10}\}$, showing a butterfly-like motif, of which the "hinge" positions are occupied by a pair of corner-shared $\{Cr_4O_4\}$ cubanes and further two chromic centres located on the "wingtip" positions to form three-membered rings on both sides of the "hinge" (Cr, green sphere; O, red sphere).

Cr(4)) have the relatively short Cr···Cr separations ranging from 2.907 to 2.928 Å, but have the appreciably longer separations to Cr(1) ranging from 3.031 to 3.055 Å, which gives rise to a slightly distorted tetrahedral geometry. In contrast to the hinge, the Cr···Cr distances from the wingtip to the hinge [$d_{av} = 3.566$ Å] are much longer due to a single oxide linkage between these two types of chromium atoms. Six hydrogen atoms attached on two μ_3-oxygen and one μ_2-oxygen of Cr_9O_{10} cluster core, respectively.

Around the central chromium core, 12 phosphate groups are closely connected with octahedral CrO_6 units via the μ_2-oxygen bridges (Fig. 2). All P sites are four-coordinate with regular tetrahedral geometries. The $P(1)$, $P(2)$ and $P(3)$ sites at the exterior of the double-cubane bridge the Cr centre in such way that two neighbouring octahedra are linked by one tetrahedron to form a three-membered ring. The other donors of $P(1)$ and $P(2)$ sites as terminal or protonated oxygen protrude away from the hinge, whereas besides one terminal donor, the $P(3)$ also share one μ_2-oxygen with Cr(5) to further fix the wingtip on the hinge. More bridges between the wingtip and hinge simultaneously come from $P(4)O_4$ between chromic central Cr(5) and Cr(2), and $P(5)O_4$ between Cr(5) and Cr(4), respectively, by sharing two μ_2-oxygen. Additionally, $P(6)$ site at the exterior of the wingtip bound to a μ_2-oxide from Cr(5)O_6 and other donors as two hydroxyl groups and one terminal oxygen protrude away from the wingtip. All phosphates, therefore, can also be considered as the tetrahedral pseudo-shell of the chromium octahedral core to form the shell–core structure of the clusters. On the basis of bond strength calculations [20], the bond valence sums (BVS) calculated for Cr (2.86–3.07) and P (4.75–4.87), respectively, are very close to their chemical valence and confirm the reliability of the determined structure.

The aggregates form layers parallel to the *ac* plane, and due to $a \approx c$ and $\beta \approx 90°$ this leads to apseudotetragonal cluster array. As spacers, sodium ions and waters of

chromic atom Cr(1) to create a corner-sharing dicubane. Located in the "wingtip" positions, two chromium centre Cr(5) are attached on the "hinge" through sharing a μ_4-oxygen with one Cr_4O_4 cubane and a μ_2-oxygen with Cr(4) from the other cubane, respectively, forming three-membered octahedral rings. Three hinge Cr atoms (Cr(2), Cr(3),
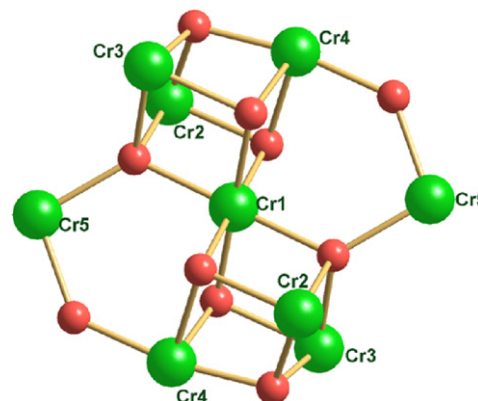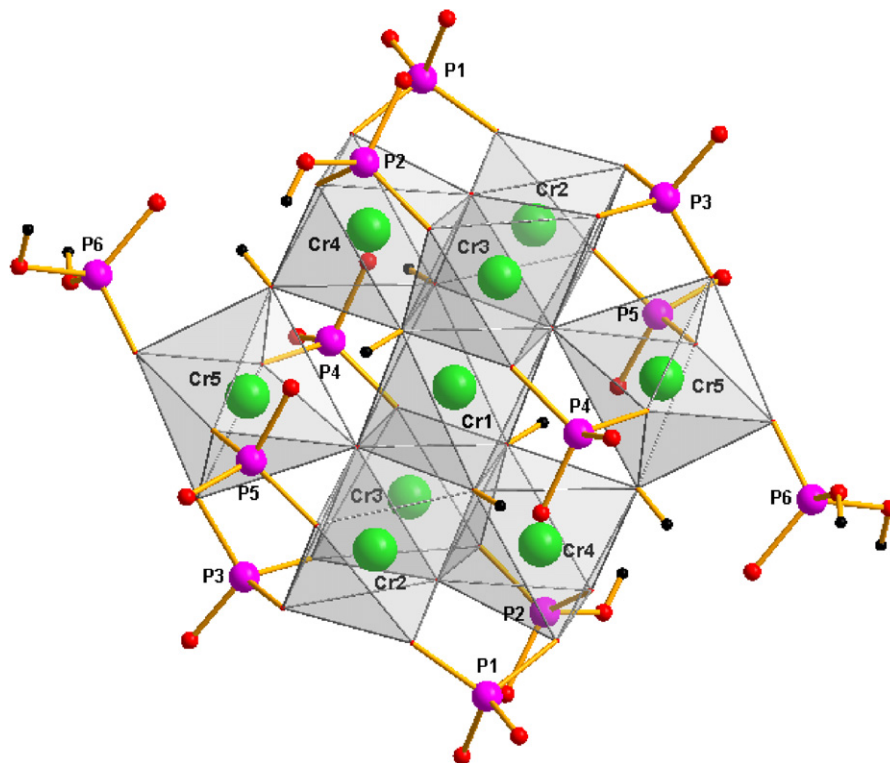
Fig. 2. Polyhedral representation of the oxo-chromium core in compound **1**, showing the bridging function of phosphate groups around the octahedral chromium core (CrO$_6$ octahedron, grey and transparent; Cr, green sphere; P, pink sphere; O, red sphere; H, small black sphere).

crystallization fill in the cavities among the clusters. Each aggregate is linked through its apices to eight surrounding species in layers above and below via hydrogen bonds, while each sodium is simultaneously associated with anions by coordinating bonds with the oxygen from the clusters. For example, Na(1) in the distorted octahedral geometry connects with two neighbouring clusters by sharing three common O-corners, respectively, while Na(2) in the distorted square pyramid links with one cluster and two sodium cations by sharing edges and corners, respectively. The complex structure of clusters, therefore, can be described by the fact that inorganic clusters suspend in the soft media composed of sodium ions and water molecules.

Presently, the use of oxo/hydroxo/aquo/carboxy ligands has proved a few chromium complexes with nuclearity > 2 including cores Cr$_3$(OH)$_2$, Cr$_4$S, Cr$_4$O$_2$, Cr$_8$F$_8$, Cr$_8$(OH)$_8$, Cr$_8$O$_4$, Cr$_{10}$O$_{10}$ and Cr$_{12}$O$_{12}$, exhibiting several unusual geometries of chromic aggregates [11–17]. Mainly besides large Cr$_n$ wheels, complex chromic cages based on Cr$_4$O$_4$ units in the Cr$_4$ tetrahedral geometry have been explored such as the isolated Cr$_4$ tetrahedron in Cr$_8$O$_4$(O$_2$CPh)$_{16}$ [10] and the edge-sharing triple Cr$_4$ tetrahedra in [Cr$_{12}$O$_8$(OH)$_4$(O$_2$CCHMe$_2$)$_{16}$(HO$_2$CCHMe$_2$)$_4$] [15]. As a new member of chromic clusters, the discovery of the enneanucleus chromic core Cr$_9$O$_{10}$ containing the novel corner-sharing double Cr$_4$ tetrahedra in complex **1** not only further completes the structural chemistry of Cr$_4$ tetra-hedral family, but also proves the inherent stability of

Cr$_4$O$_4$ unit in the formation of high nuclearity complexes, which can be thought of as building blocks in the formation of larger aggregates.

3.2. Magnetic property

The dc magnetic susceptibility data of a microcrystalline sample of **1** were collected in the range from 2.0 to 300 K in a 0.1 T magnetic field (Fig. 3). $\chi_M T$ (where χ_M is the molar magnetic susceptibility) steadily decreases with decreasing temperature from 16.15 emu K mol^{-1} at 300 K to 11.07 emu K mol^{-1} at 30 K, below which the $\chi_M T$ value decreases more rapidly to 4.08 emu K mol^{-1} at 2.0 K, demonstrating that the coupling between Cr^{III} centres is antiferromagnetic. The room temperature value of $\chi_M T$ of 16.15 emu K mol^{-1}, is a little below the expected value of $\chi_M T$ for nine non-interacting Cr^{III} centres (16.73 emu K mol^{-1}, for $g = 1.99$), which also suggests that antiferro-magnetic couplings dominate the overall intramolecular exchange interactions within the complexes. The magnetic behaviour of **1** can be explained in terms of the presence of several different monatomic oxygen bridges between the Cr atoms of corner-sharing dicubanes with Cr–O–Cr angles less than 100°. This gives rise to moderately strong antiferromagnetic interactions associated with such types of bridges. Earlier published results on magnetic studies of polynuclear Cr complexes showed that a bridging angle less than 100° in monatomic oxygen bridges in all cases give rise to antiferromagnetic coupling [10,15]. Due to the
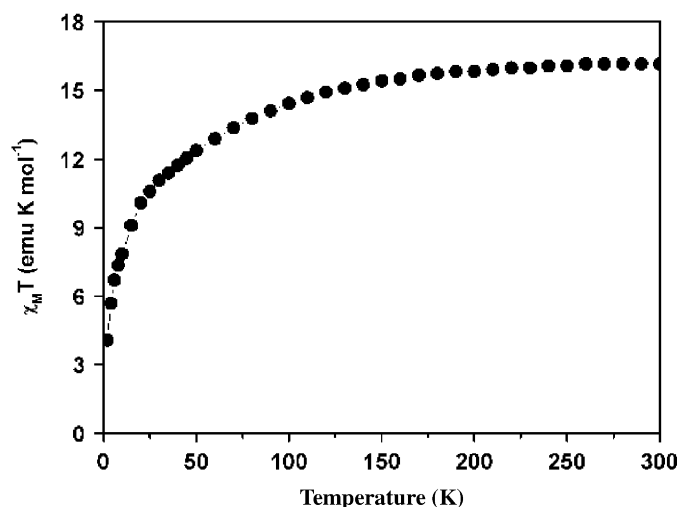
Fig. 3. Plot of the dependence of $\chi_M T$ on temperature for **1**.

complexity of the system, a detailed theoretical investigation is necessary to understand fully the magnetic exchange interaction in the title compound.

4. Conclusion

A new chromium-phosphate, $Na_{17}[Cr_9P_{12}O_{58}H_{12}] \cdot xH_2O$ ($x \approx 25$), has been synthesized by a novel hydrothermal method for the first time. The structure of the title compound contains an unpresented enneanuclear core Cr_9O_{10} with a butterfly-like topology of oxo-chromium, which is constructed from corner-sharing Cr_7O_8 dicubanes as the hinge, as well as two chromic centres are further attached on the hinge as the wingtip. Twelve phosphates around the chromic core are grafted on it via the μ_2-oxygen to lead to the tetrahedral pseudo-shell of the chromium octahedral core. The sodium ions and water as guests fill in the cavities among the clusters to satisfy the charge balance and keep the structural stability. The magnetic measurement of the title compound indicates the existence of antiferromagnetic interactions. The successful synthesis not only completes further the family of chromium-phosphate system, but also provides important information for further developing novel inorganic materials by using the low-temperature method.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.04.031.

References

[1] A. Müller, F. Peters, M.T. Pope, D. Gatteschi, Chem. Rev. 98 (1998) 239.
[2] M.T. Pope, A. Müller, Angew. Chem. Int. Ed. Engl. 30 (1991) 34.
[3] R. Sessoli, D. Gatteschi, A. Caneschi, M.A. Novak, Nature 365 (1993) 141.
[4] A. Müller, S.K. Das, P. Kögerler, H. Bögge, M. Schmidtmann, A.X. Trautwein, V. Schünemann, E. Krickemeyer, W. Preetz, Angew. Chem. Int. Ed. 39 (2000) 3413.
[5] S.W. Zhang, D.Q. Liao, M.C. Shao, Y.Q. Tang, Chem. Commun. (1986) 835.
[6] A. Müller, E. Krickemeyer, S.K. Das, P. Kögerler, S. Sarkar, H. Bögge, M. Schmidtmann, S. Sarkar, Angew. Chem. Int. Ed. 39 (2000) 1612.
[7] M. Yuan, Y. Li, E. Wang, C. Tian, L. Wang, C. Hu, N. Hu, H. Jia, Inorg. Chem. 42 (2003) 3670.
[8] R.B. Bontchev, J. Do, A.J. Jacobson, Angew. Chem. Int. Ed. 38 (1999) 1937.
[9] E. Dumas, C. Debiemme-Chouvy, S.C. Sevov, J. Am. Chem. Soc. 124 (2002) 908.
[10] I.M. Atkinson, C. Benelli, M. Murrie, S. Parsons, R.E.P. Winpenny, Chem. Commun. (1999) 285.
[11] M. Eshel, A. Bino, I. Felner, D.C. Johnston, M. Luban, L.L. Miller, Inorg. Chem. 39 (2000) 1376.
[12] A. Bino, R. Chayat, E. Pedersen, A. Schneidert, Inorg. Chem. 30 (1991) 856.
[13] R.A. Coxall, A. Parkin, S. Parsons, A.A. Smith, G.A. Timco, R.E.P. Winpenny, J. Solid State Chem. 159 (2001) 321.
[14] F.E. Mabbs, E.J.L. McInnes, M. Murrie, S. Parsons, C.C. Wilson, R.E.P. Winpenny, Chem. Commun. (1999) 643.
[15] S. Parsons, A.A. Smith, R.E.P. Winpenny, Chem. Commun. (2000) 579.
[16] P. Christian, G. Rajaraman, A. Harrison, J.J.W. McDouall, J.T. Rafterya, R.E.P. Winpenny, Chem. Commun. (2004) 1511.
[17] D.M. Low, G. Rajaraman, M. Helliwell, G. Timco, J. van Slageren, R. Sessoli, S.T. Ochsenbein, R. Bircher, C. Dobe, O. Waldmann, Chem.-A Eur. J. 12 (2006) 1385.
[18] W. Liu, M.R. Li, H.H. Chen, X.X. Yang, J.T. Zhao, J. Solid State Chem. 178 (2004) 912.
[19] G.M. Sheldrick, SHELXL-97: Program for Refining Crystal Structures, University of Göttingen, Germany, 1997.
[20] N.E. Brese, M. O'Keeffe, Acta Cryst alloys B 47 (1991) 192.