Inorganic Chemistry

ARTICLE

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Stabilization of Noncondensed $(As^{III}S_3)^{3-}$ Anions by Coordinating to $[Mn^{II}(phen)]^{2+}$ Complex Cations: a Mixed-Valent Thioarsenate (III, V) $\{[Mn(phen)]_3(As^{V}S_4)(As^{III}S_3)\}_n \cdot nH_2O$ Showing the Coexistence of Antiferromagnetic Order, Photoluminescence, and Nonlinear Optical Properties

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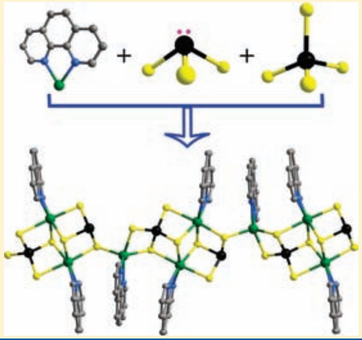
Supporting Information

ABSTRACT: A novel one-dimensional (1-D) mixed-valent thioarsenate (III, V), $\{[Mn(phen)]_3(As^{V}S_4)(As^{III}S_3)\}_n \cdot nH_2O$ (**1**), with a noncentrosymmetric (NCS) polar packing arrangement has been obtained under solvothermal conditions. The noncondensed $(As^{III}S_3)^{3-}$ anion in **1** is stabilized by coordinating to $[Mn^{II}(phen)]^{2+}$ complex cations and exhibits an unprecedented μ_3-1,2κS:2,3κS′:3κS″ linkage mode. Compound **1** represents the first example of the stabilization of noncondensed $(MQ_3)^{3-}$ (M = As, Sb; Q = S, Se) species only in the coordination of TM(II) complex cations (TM = transition-metal) and the first observation of the coexistence of the $(As^{V}S_4)^{3-}$ tetrahedron and the noncondensed $(As^{III}S_3)^{3-}$ pyramid in a single compound. Of particular interest, compound **1** is also an antiferromagnet with T_N = 31 K, and exhibits photoluminescence (PL) with a maximum emission at about 438 nm and a second harmonic generation (SHG) response.



INTRODUCTION

Considerable efforts have been devoted to developing new molecule-based multifunctional materials, that is, a single compound that displays the coexistence or synergism of two or more properties including mechanical, electronic, optical, and magnetic properties.[1] Among these multifunctional materials, molecule-based magnets exhibiting another property besides magnetism, such as nonlinear second harmonic generation (SHG)[1d−f] or ferroelectric behavior,[1j−n] have attracted the attention of material scientists because of their broad possible applications. A noncentrosymmetric (NCS) structure is the prerequisite for SHG-active magnets, while ferroelectric magnets strictly require the compound to crystallize in NCS space groups belonging to the ten polar point groups. Despite the fact that much progress has been made in the syntheses of NCS structures, there still remain great challenges in the syntheses of NCS polar materials.[1j−p,2]

The chalcogenide-based materials have been extensively investigated during the past decades because of their interesting structural chemistry and promising physical properties.[3] Group V cations, such as As(III) and Sb(III), contain lone electron pairs, which may induce NCS structures of group V chalcogenidometalates to form.[3j−l,4] The characteristic condensation of $(M^{III}Q_3)^{3-}$ (M = As, Sb; Q = S, Se) species because of their high negative charge density can lead to the formation of many novel polynuclear anions such as $(M^{III}{}_xQ_{2x+1})^{(x+2)-}$ (x = 2, 3, 4),[5] $(M^{III}{}_xQ_{2x})^{x-}$ (x = 3, 4),[6] or one-dimensional (1-D) $^{1}_{\infty}(M^{III}Q_2{}^{-})$ anions,[4c,7] which have been widely reported in the group V chalcogenidometalates. Generally, the noncondensed $(M^{III}Q_3)^{3-}$ species can be effectively stabilized by coordinating to metal cations to form dense solids[8] or isolated anionic structures charge-compensated by counter-cations.[9] It is attractive that stabilizing $(M^{III}Q_3)^{3-}$ species in the coordination of unsaturated transition-metal (TM) or rare-earth-metal (RE) complexes may produce combined properties or synergistic effects, for example, the photoluminescence (PL) and magnetic property of the TM or RE complexes may integrated with the most expected SHG property induced by the asymmetric $(M^{III}Q_3)^{3-}$ pyramids. However, research in this aspect is very limited; hitherto only 11 centrosymmetric[10] and 1 NCS[11] compounds were structurally reported, and their properties, such as magnetic, PL, and SHG (for the NCS compound) properties, have been extremely rarely investigated.[10e] From a structural point of view, the noncondensed $(M^{III}Q_3)^{3-}$ species in the 12 compounds are all stabilized by coordinating to TM complex

Received: March 18, 2011
Published: May 20, 2011

cations with a high valent state ($\geq+3$) TM ion center[10a,b,d,11] (such as Ti^{4+}, Cr^{3+}) or simultaneously coordinating to metal cations and TM(II) complexes.[10c,e−g] To the best of our knowledge, the stabilization of $(MQ_3)^{3-}$ species only in the coordination of TM(II) complexes has never been reported up to now. Our previous study indicates that $[TM^{II}(\pi\text{-conjugated-ligand})_m]^{2+}$ complex cations can stabilize well the chalcogenidometalate anion with high negative charge density by dispersing the negative charge on the chalcogenidometalate anion,[12] which motivates us to apply metal complexes with a π-conjugated-ligand in the stabilization of $(M^{III}Q_3)^{3-}$ species. As expected, by using the $[Mn^{II}(phen)]^{2+}$ complex cation (phen = 1,10-phenanthroline) as a stabilizer and a structure-directing agent, we successfully isolated a noncondensed $(As^{III}S_3)^{3-}$ anion-containing hybrid thioarsenate, $\{[Mn(phen)]_3(As^{V}S_4)(As^{III}S_3)\}_n\cdot nH_2O$ (**1**) with NCS polar packing arrangement, in which two different thioarsenate anions $(As^{III}S_3)^{3-}$ and $(As^{V}S_4)^{3-}$ coexist to exhibit a novel mixed-valent As^{3+}/As^{5+} character. Compound **1** represents the first example of the stabilization of a noncondensed $(MQ_3)^{3-}$ species only in the coordination of TM(II) complexes. Herein, we report the synthesis, structure, optical (NLO and PL), and magnetic properties of **1**.

EXPERIMENTAL SECTION

Materials and Instruments. All reagents were purchased commercially and used without further purification. Elemental analyses of C, H, and N were performed on an Elementar Vario EL III microanalyzer. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex II diffractometer using Cu Kα radiation. A NETZSCH STA 449C thermogravimetric analyzer was used to obtain thermogravimetry (TG) and differential thermal analysis (DTA) curves in N_2 with a flow rate of 20 mL/min and a ramp rate of 10 °C·min^{-1} in the temperature range 30−1000 °C. An empty Al_2O_3 crucible was used as the reference. The FT-IR spectrum was obtained on a Perkin-Elmer spectrophotometer using KBr disk in the range 4000−400 cm^{-1}. The solid-state fluorescence excitation and emission spectra were measured on an Edinberg EI920 fluorescence spectrophotometer at room temperature with a wavelength increment of 1.0 nm and integration time of 0.2 s. Optical diffuse reflectance spectrum was measured at room temperature with a PE Lambda 900 UV−vis spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. The sample was ground into fine powder and pressed onto a thin glass slide holder. The $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectrum was calculated from reflectance spectrum using the Kubelka−Munk function: $\alpha/S = (1 - R)^2/2R$,[13] where α is the absorption coefficient, S is the scattering coefficient (which is practically wavelength independent when the particle size is larger than 5 μm), and R is the reflectance. The polycrystalline magnetic study was performed on a Quantum Design PPMS-9T magnetometer. All data was corrected for diamagnetism estimated from Pascal's constants. Powder SHG measurement on sample of **1** was performed on a modified Kurtz-NLO system using 1.905 μm laser radiation. The SHG signal was collected and focused into a fiber optic bundle. The output of the fiber optic bundle was coupled to the entrance slit of a spectrometer and detected using a CCD detector. AGS powder was used as a reference to assume the second-order NLO effect. SHG efficiency has been shown to depend strongly on particle size; thus, samples of AGS as well as **1** were ground and sieved into several distinct particle size ranges (50−75, 75−100, 100−150, 150−200, 200−250, 250−300 μm).

Preparation of 1. A mixture of As (0.038 g, 0.5 mmol), $MnCl_2\cdot 4H_2O$ (0.099 g, 0.5 mmol), S (0.064 g, 2.0 mmol), and phen·H_2O (0.099 g, 0.5 mmol) in 4 mL of methylamine aqueous solution (28% in H_2O) was sealed in a stainless steel reactor with a 25-mL Teflon liner, heated at 150 °C for 5 days and then cooled to room temperature. The product consists of red block crystals of **1** and a few indefinite dark-red powders. The crystals of **1** were selected by hand and washed with ethanol and diethyl ether. The crystals are stable in air and insoluble in common solvents. (Yield: 18% based on As). Anal. Calcd for $C_{36}H_{26}As_2Mn_3N_6OS_7$ **1**: C, 39.39%; H, 2.39%; N, 7.66%. Found: C, 39.36%; H, 2.25%; N, 7.65%. FT-IR (KBr, cm^{-1}): 3425(m), 3053(m), 1621(m), 1515(m), 1421(s), 1340(w), 1143(m), 1100(w), 847(s), 775(w), 726(s), and 638(w). The experimental PXRD pattern of **1** is in good agreement with that simulated from the single-crystal X-ray data, suggesting the phase purity of **1** (Supporting Information, Figure S1).

Table 1. Crystal and Structure Refinement Data for 1

	1
formula	$C_{36}H_{26}As_2Mn_3N_6OS_7$
M_r (g mol^{-1})	1097.71
color, habit	red, block
cryst size (mm^3)	0.30 × 0.20 × 0.20
cryst syst	monoclinic
space group	$P2_1$
Flack factor	0.620(5)
D_{calcd} (g cm^{-3})	1.795
a (Å)	9.478(4)
b (Å)	20.230(9)
c (Å)	10.652(5)
β (deg)	96.11(1)
V (Å^3)	2030.8(16)
Z	2
abs coeff (mm^{-1})	2.935
$F(000)$	1090
reflns collcd/unique (R_{int})	15120/6300 (0.0439)
data/params/restraints	5933/503/4
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0385
$wR_2{}^b$ [$I > 2\sigma(I)$]	0.0829
goodness of fit	1.029
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e Å^{-3})	0.461, −0.420

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

Single-Crystal Structure Determination. The intensity data set was collected on a Rigaku Saturn 724 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω-scan technique at 293 K. The data set was reduced with the CrystalClear program.[14] An empirical absorption correction was applied using the multiscan method. The structure was solved by direct methods using the Siemens SHELXL package of crystallographic software.[15] The difference Fourier maps were created on the basis of these atomic positions to yield the other non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of phen molecules were added geometrically and refined using the riding model. The hydrogen atoms of lattice water molecules were located by different Fourier maps and refined with O−H distances to a target value of 0.85 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The crystal under investigation was a twin. The value of the Flack parameter and its standard uncertainty were determined using the TWIN/BASF commands and were refined to 0.620(5). Crystallographic data and structural refinements are summarized in Table 1. More details on the crystallographic studies as well as atom displacement parameters are given in Supporting Information, Table S1. Furthermore, crystal structures of the other four randomly picked crystals of **1** from the same crystallization were refined using single X-ray diffraction data, where the same set of positional

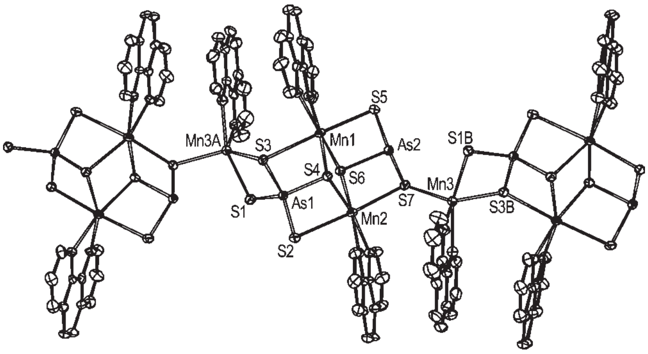


Figure 1. ORTEP view of a neutral chain $\{[Mn(phen)]_3(As^VS_4)(As^{III}S_3)\}_n$ in **1** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry codes: A ($2-x$, $1/2+y$, $2-z$); B ($2-x$, $-1/2+y$, $2-z$).

coordinates were used. The four crystals are all racemic twinning, and the Flack parameters refined by the TWIN/BASF commands are in the range of 0.239(5)−0.620(4) (Supporting Information, Table S2).

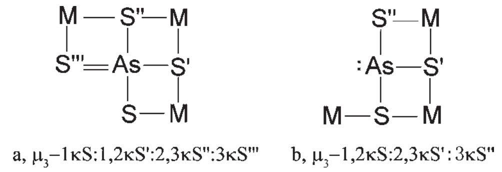
TGA for 1. Thermogravimetric analysis (TGA) for **1** revealed a small weight loss of about 1.1% between 90 and 300 °C, which corresponds to the removal of the water molecules (calcd 1.6%). The weight losses from 300 to 550 °C correspond to the decomposition of the structure with a significant weight loss of 50.2%, which is close to the removal of the phen molecules (calcd 49.3%, Supporting Information, Figures S2 and S3), and the residue may be MnS and As_2S_4 (exp. 48.7%, calcd 49.1%).

■ RESULTS AND DISCUSSION

The reaction temperature and the pH of the solution are very important for the preparation of **1**. Note that methylamine aqueous solution acting as an organic base offers the indispensable alkaline condition in the synthesis of **1**. Detailed experiments show that compound **1** cannot be obtained when the concentration of the methylamine solution is lower than 17% or the reaction temperature higher than 170 °C.

Single-crystal X-ray analysis reveals that compound **1** crystallizes in the monoclinic chiral and polar space group $P2_1$ and consists of neutral chains with composition $\{[Mn(phen)]_3(As^VS_4)(As^{III}S_3)\}_n$ and lattice water molecules. There are two crystallographically distinct As atoms in the asymmetric unit (Figure 1): As1 is coordinated by four S atoms to form a $(As^VS_4)^{3-}$ tetrahedron, while As2 is coordinated by three S atoms to form a $(As^{III}S_3)^{3-}$ pyramid. There are three structurally distinct Mn^{2+} cations in the chain. Mn1 and Mn2 are in distorted octahedral environments, each of which is coordinated by one phen ligand through two N atoms, one pyramidal $(As^{III}S_3)^{3-}$ via two S atoms, and one tetrahedral $(As^VS_4)^{3-}$ through two S atoms. While, Mn3 lies within a five-coordinated environment involving two N atoms of one phen ligand, two S atoms of one $(As^VS_4)^{3-}$ tetrahedral and one S atoms of one $(As^{III}S_3)^{3-}$ pyramid to form a distorted trigonal bipyramid. One $(As^VS_4)^{3-}$ tetrahedron and one $(As^{III}S_3)^{3-}$ pyramid connect with two $[Mn(phen)]^{2+}$ complexes to form a tetranuclear cluster $\{[Mn(phen)]_2(As^VS_4)(As^{III}S_3)\}^{2-}$ with the Mn1···Mn2 distance of 3.686(1) Å which are further linked by $[Mn3(phen)]^{2+}$ complex in a trans mode to yield a neutral $\{[Mn(phen)]_3(As^VS_4)(As^{III}S_3)\}_n$ chain extended along the [010] direction (Supporting Information, Figure S5a). It should be noted that the tetranuclear cluster in **1** showing the coexistence of As(III) in the $(As^{III}S_3)^{3-}$ unit and As(V) in $(As^VS_4)^{3-}$ unit is different from those found in $\{[Mn(L)]_3(As^VS_4)_2\}_n \cdot nH_2O$ (L = 2,2′-bipy (**2a**), phen (**2b**)),[16] each of which is formed by the connection of two tetrahedral $(As^VS_4)^{3-}$ and two $[Mn(L)]^{2+}$ complexes (Supporting Information, Figure S4). The As−S bond distances are in the normal range[10f,16,17] and can be grouped into three types: the longest $As^{III}-\mu_3$-S bond distance of about 2.274 Å, the medium $As^{III}-\mu_2$-S and $As^V-\mu_3$-S bond distance of about 2.193 Å, and the shortest $As^V-\mu_2$-S bond distance of about 2.137 Å (Supporting Information, Table S1). The distortion of the $(As^VS_4)^{3-}$ tetrahedron is evidenced by the S−As−S bond angles in the range of 103.40(4)−114.94(4)° deviating from the ideal value of 109.5°. The average Mn−N bond distance of 2.268 Å in the octahedra is about 0.032 Å longer than that in the trigonal bipyramid (2.236 Å). The Mn−N bond distances in the range of 2.222(3)−2.277(3) Å are normal.[5c,16−18] The Mn−S bond distances range from 2.433(1) to 2.713(1) Å, which are comparable with those reported in the literature (Supporting Information, Table S1).[18] The (MnS_4N_2) octahedra are significantly distorted which can be manifested by the axial trans bond angles ranging from 159.36(8) to 171.59(7)° for Mn1 and 161.34(7) to 169.46(4)° for Mn2 deviating from the ideal value of 180°. The axial trans N21−Mn3−S1 bond angle of the $(Mn3S_3N_2)$ trigonal bipyramid of 159.00(9)° deviates from the ideal value of 180°, indicating a severe distortion of the polyhedron. Within the chain, there are face-to-face $\pi\cdots\pi$ stacking interactions between the aromatic rings of phen chelating to Mn3 atom and the adjacent aromatic rings of phen ligands chelating to Mn1 and Mn2 atoms with centroid−centroid distance varying from 3.529(2) to 3.719(2) Å and dihedral angles in the range of 5.98(12)−7.54(13)° (Supporting Information, Figure S5b). The shortest centroid−centroid separation between two parallel adjacent aromatic rings belonging to different chains is 4.659(1) Å, indicating that there are no significant interchain $\pi\cdots\pi$ stacking interactions. The lattice water molecules bridge the neutral chains through the C−H···O and O−H···S hydrogen bonds to form a three-dimensional (3-D) framework (Supporting Information, Table S4 and Figure S7).

Scheme 1. Linkage Modes of the $(As^VS_4)^{3-}$ (a) and $(As^{III}S_3)^{3-}$ (b) Anions in 1



a, μ_3−1κS:1,2κS':2,3κS'':3κS'''   b, μ_3−1,2κS:2,3κS':3κS''

A prominent structural feature of **1** is the mixed-valent As^{3+}/As^{5+} character, which is in good agreement with the bond valence sum calculations As1 = 5.234, As2 = 3.086. The mixed-valent As^{3+}/As^{5+} character can also be observed in several other chalcogenoarsenates,[8,17] where the +3 valent As all exists in condensed polynuclear chalcogenoarsenates(III) species. However, the mixed-valent character observed here, where the +3 valent As in a noncondensed pyramidal $(As^{III}S_3)^{3-}$ and the +5 valent As in a tetrahedral $(As^VS_4)^{3-}$, is quite different from them.

Another interesting structural feature is the novel linkage mode of the $(As^{III}S_3)^{3-}$ anion in **1**. It has been demonstrated that in addition to the three terminal S atoms, the As(III) atom containing a 4s lone electron pair in pyramidal $(As^{III}S_3)^{3-}$ can also participate in coordination; therefore the pyramidal $(As^{III}S_3)^{3-}$ anion can display flexible linkage modes in group V chalcogenidometalates.[10f] However, to the best of our

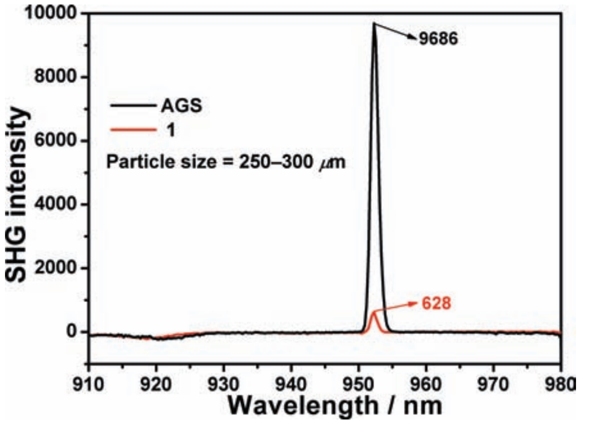


Figure 2. SHG responses of **1** (red) and AGS (black) at 1.905 μm.

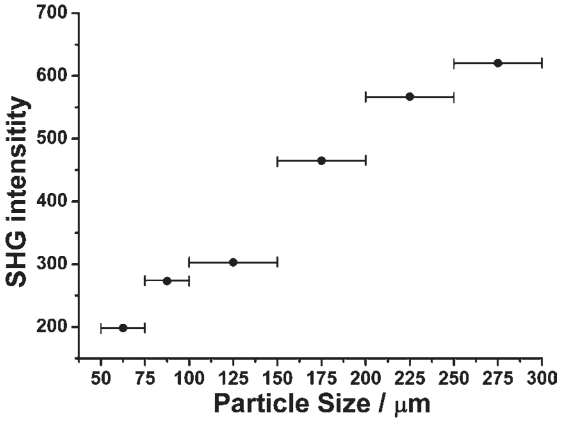


Figure 3. Phase matching curve (SHG intensity versus particle size) for **1**.

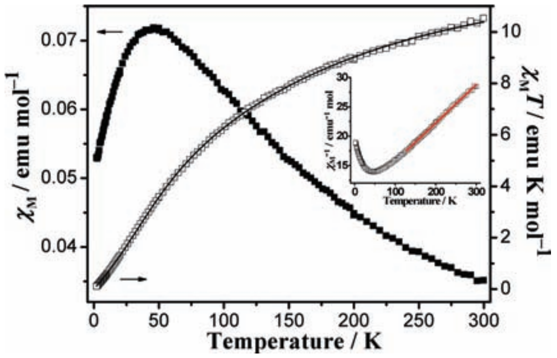


Figure 4. Temperature dependence of χ_M and $\chi_M T$ curves for **1**; the black solid line represents the best fit of the experimental data to eqs 1 and 2. Inset: temperature dependence of $\chi_M{}^{-1}$ curve for **1**; the red solid line represents the best fit of the Curie–Weiss law.

knowledge, the $(As^{III}S_3)^{3-}$ anion in **1** exhibits an unprecedented μ_3-1,2κS:2,3κS′:3κS″ linkage mode (Scheme 1).

Given that compound **1** crystallizes in the NCS space group $P2_1$, its second-order nonlinear optical effect was investigated. Preliminary studies of a powder sample indicate that compound **1** is SHG active with a response being about $^1/_{15}$ of that of AGS ($AgGaS_2$; the comparison was performed with **1** and AGS at the similar particle size of 250–300 μm, Figure 2). Furthermore, particle size dependent SHG measurements indicate that compound **1** is phase-matchable (Figure 3). On the basis of structural data, the NLO behavior of **1** should originate from the cooperation of the polarizations of the polar units in **1**, including phen molecules, $(As^{III}S_3)$ pyramids, lattice water molecules, and distorted $(As^{V}S_4)$ tetrahedra, (MnN_2S_4) octahedra, and (MnS_3N_2) trigonal bipyramids. The dipole moment of the $(As^{III}S_3)$ pyramid of 14.05 D is considerable larger than that of the other polar units in **1** (in the range of 1.80–5.04 D, Supporting Information, Table S5). It should be noticed that the dipole moments of the $(As^{III}S_3)^{3-}$ pyramid always cancel each other because of their antiparallel arrangements in structures,[10c,e,f,19] whereas those in the chains of **1** are aligned almost in the same direction (propagating spirally along the [010] direction) producing a net dipole moment, which are further arranged in the same way within the chains, and therefore cannot be canceled. Consequently, it is believed that the $(As^{III}S_3)^{3-}$ pyramids are mainly responsible for the polarization of **1**. However, three facts weaken the SHG property of **1**: (1) compound **1** exhibits significant absorption near 953 nm (The SHG wavelength is 953 nm), (2) the existence of racemic twinning in **1** will cancel part of the polarizations,[20] and (3) the spatial arrangements of the SHG-active units in the structure were not in complete alignment, working against the enhancement of macroscopic polarizabilities (Supporting Information, Figure S8).[21]

Compound **1** exhibits PL property with an emission maximum occurring around 438 nm (λ_{ex} = 350 nm) (Supporting Information, Figure S10), which is consistent with our previous investigation on the solid-state luminescence of other similar compounds.[12,16a] The photoluminescence mechanism of **1** is attributed to intraligand transition because similar emission is also observed for a pure phen ligand (Supporting Information, Figure S10). The optical diffuse-reflection spectrum of **1** is shown in Supporting Information, Figure S12 with the optical absorption edge estimated as 2.55 eV, which is consistent with its red color.

To investigate the magnetic behavior of **1**, the direct current (dc) temperature-dependence magnetic susceptibility of **1** was measured on the crystalline sample in an applied field of 1000 Oe from 300 to 2 K, and the corresponding curves of χ_M and $\chi_M T$ versus T (χ_M is the molar magnetic susceptibility per Mn_3 unit) are shown in Figure 4. The $\chi_M T$ product of 10.54 emu·K/mol at 300 K is smaller than the spin-only one expected for three isolated Mn^{2+} ions (13.13 emu·K/mol), considering g = 2.00 and S = $^5/_2$. As the temperature is lowered, the $\chi_M T$ product monotonically decreases to 0.11 emu·K/mol at 2 K, suggesting an antiferromagnetic behavior. The inverse magnetic susceptibility data in the range of 125–300 K can be fitted well to the Curie–Weiss law $1/\chi_M = (T - \theta)/C$ (Figure 4, inset), with a Curie constant C = 15.30 emu·K/mol and a Weiss constant θ = −140.1 K, which confirms an overall strong antiferromangetic interaction between the Mn^{2+} ions, and it should be mainly within the chains regarding the structure feature. The appearance of a maximum peak in the χ_M versus T curve near 46 K indicates antiferromagnetic ordering. Below this temperature, the χ_M value decreases gradually and approaches a value of 0.051 emu/mol by extrapolating the temperature to zero. This value accounts for about $^2/_3$ of the maximum χ_M value of 0.072 emu/mol, which is the typical character of an antiferromagnet.[22] The $d(\chi_M T)/dT$ versus T curve shows a maximum value at 31 K for the Neel temperature (T_N, Supporting Information, Figure S13).[23] The magnetic property of **1** shows low-dimensional character because the ratio of $T_N/T(\chi_{max})$ of 0.67 is significantly lower than that of a 3-D antiferromagnet,[24] which is consistent with the structural

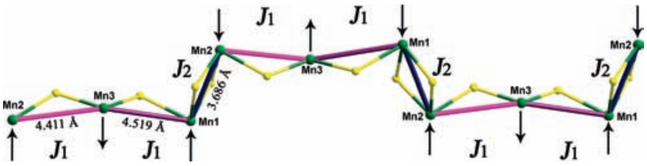


Figure 5. Magnetic structures with two J coupling between the Mn^{2+} centers in **1**.

character of **1**. The in-phase signal (χ') of the alternating current (ac) magnetic susceptibility presents a broad peak at about 45 K and the out-of-phase signal (χ'') is negligibly small (Supporting Information, Figure S14). This also supports the conclusion that compound **1** possesses a magnetic transition phase. In addition, no frequency dependence was observed in the ac measurements, which precludes the possibility of the spin glass or superparamagnetic behavior in **1**. Further evidence for **1** to be an antiferromagnet comes from the field-dependence magnetization values which increases almost linearly, reaching 3.18 $N\beta$ at 80 KOe (Supporting Information, Figure S15), far from the saturation value of 15 $N\beta$ for three magnetically decoupled Mn^{2+} ions ($S = {}^{5}/_{2}$).

According to the chain topology, there are three sets of magnetic exchange pathways within the chain: one includes two bridging μ_3-S atoms from a tetrahedral $(AsS_4)^{3-}$ and a pyramidal $(AsS_3)^{3-}$ anion; the second consists of a single bridging μ_3-S atom from a $(AsS_4)^{3-}$ tetrahedron; the third is a single μ_3-S bridge from a $(AsS_3)^{3-}$ pyramid, which alternate in the ABC sequence. The magnetic interactions through the $(AsS_3)^{3-}$ anion between Mn1 and Mn3 and the $(AsS_4)^{3-}$ anion between Mn2 and Mn3A are negligible because their Mn···Mn distances of 6.440(2) Å for the former and 6.356(3) Å for the latter are significantly longer than the Mn···Mn distances through the above-mentioned three pathways, which lie in the range of 3.686(1)−4.520(2) Å. However, it should be noted that these Mn···Mn distances through the above-mentioned three pathways are still too long for significant direct magnetic exchange to occur, suggesting that coupling occurs via the μ_3-S atoms. According to the qualitative coupling rules,[25] all these superexchange interactions which are between high-spin d^5 Mn^{2+} ions via S atoms p-orbitals will be antiferromagnetic. Compound **1** can be magnetically considered as an alternating $J_1J_2J_3$ coupling chain. However, we cannot find an analytical expression of magnetic susceptibility for such a system in the literature. To further simplify the magnetic interaction within the chain, the interactions between Mn1···Mn3 and Mn2···Mn3 are assumed to be equal taking into consideration their approximately equal Mn···Mn distances (4.520(2) Å for the former and 4.411(3) Å for the latter), and the system can be approximately treated as a 1-D Heisenberg chain with alternating $J_1J_1J_2$ interactions (Figure 5). The magnetic susceptibility of such system has been proposed by Escuer et al.[26] as

$$\chi_{\text{chain}} = \frac{Ng^2\beta^2 S(S+1)}{3KT}\left(\frac{A}{B}\right) \tag{1}$$

with

$$A = 3(1 - u_1{}^4 u_2{}^2) + 4u_1(1 - u_1{}^2 u_2{}^2) + 2u_2(1 + u_1)^2(1 - u_1{}^2) + 2u_1{}^2(1 - u_2{}^2)$$

and

$$B = (1 - u_1{}^2 u_2)^2$$

where

$$u_i = \coth\left[\frac{J_i S(S+1)}{KT}\right] - \frac{KT}{J_i S(S+1)} \quad (i = 1, 2)$$

with $S = {}^{5}/_{2}$. The interaction parameters J_1 and J_2 are based on the spin Hamiltonian $H = -J_1\Sigma(S_{3i}S_{3i+1} + S_{3i+1}S_{3i+2}) - J_2\Sigma S_{3i-1}S_{3i}$, and the S operator is treated as a classical spin. The interchain interaction (zJ') through the hydrogen bonds was treated by the molecular field approximation

$$\chi = \frac{\chi_{\text{chain}}}{1 - (2zJ'/Ng^2\beta^2)\chi_{\text{chain}}} \tag{2}$$

The least-squares fit of the experimental data above 2 K to the above expressions (eqs 1 and 2) lead to $J_1 = -9.24(2)\ \text{cm}^{-1}$, $J_2 = -27.4(4)\ \text{cm}^{-1}$, $zJ' = 2.8(1)\ \text{cm}^{-1}$ with $g = 2.02(1)$ (where J_1 and J_2 are the intrachain exchange interactions, J' is the interchain exchange interaction, and z is the number of nearest neighbors of the chains). The agreement factor R, defined as $\Sigma[(\chi_M T)_{\text{obsd}} - (\chi_M T)_{\text{calcd}}]^2/\Sigma(\chi_M T)_{\text{obsd}}{}^2$, is equal to 3.25×10^{-5}. The rather negative J_1 and J_2 values further confirm that the Mn^{II} spins connected by the double μ_3-S bridge and the single μ_3-S bridges are all strong antiferromagnetic coupling in **1**.

In **1**, Mn1, Mn2, and Mn3 atoms adopt an obtuse-triangular arrangement (Figure 1) with the Mn1···Mn3 distance being significantly longer than the Mn1···Mn2 and Mn2···Mn3 distances, which will induce very large differences between their magnetic exchange interactions. A triangular arrangement of three spins with antiferromagnetic coupling can generally induce spin frustration; however, such a geometry in **1** is not conducive to the occurrence of spin frustration. A frustration parameter defined as $f = |\theta|/T_N$, which is widely used to measure the relative degree of the spin frustration, equals 4.5. This small value indicates the absence of spin-frustration or extremely weak spin-frustration in **1** (f is about 1 for a ferromagnet and 2−4 for an antiferromagnet, but for a spin-frustrated lattice, it is usually quite larger since the long-range ordering is prohibited by the competing interactions).[27]

■ CONCLUSION

By using $[Mn^{II}(phen)]^{2+}$ complex cations as a stabilizer and a structure-directing agent, we have isolated a mixed-valent thioarsenate (III, V), $\{[Mn(phen)]_3(As^{V}S_4)(As^{III}S_3)\}_n \cdot nH_2O$, containing noncondensed $(As^{III}S_3)^{3-}$ anions under solvothermal condition, which further confirms the peculiar effect of $[TM(\pi\text{-conjugated-ligand})_m]^{n+}$ complex cations on the stabilization of the chalcogenidometalate anion with high negative charge density. The coexistence of antiferromagnetic ordering, PL, and SHG response in **1** implies that the approach of combining metal (TM or RE) complex cations with asymmetric chalcogenidometalate anionic units could be promising in the construction of NCS multifunctional hybrid materials. More SHG-active multifunctional materials combined with other properties would be expected by the effective arrangement of functional building units (e.g., magnetic and PL-active units) in polar structures through a crystal engineering strategy. Work in these directions is underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic data (CIF format), additional structural figures, TGA curve, IR spectrum, PXRD patterns, UV absorption spectrum, optical diffuse reflectance spectrum, temperature dependence of the reciprocal susceptibility (χ_M^{-1}), ac susceptibility measurements, $d(\chi_M T)/dT$ versus T curve, and field dependence of magnetization. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We gratefully acknowledge financial support by the NSF of China (90922035, 21003126), 973 program (2011CBA00505), Key Project from the CAS (KJCX2-EW-H03) and the NSF of Fujian Province (2008I0026, 2008F3115).

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