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# Ionic Crystals of $\{[Ni(phen)_3]_2Ge_4S_{10}\}\cdot x$Sol, Showing Solid-State Solvatochromism and Rapid Solvent-Induced Recrystallization

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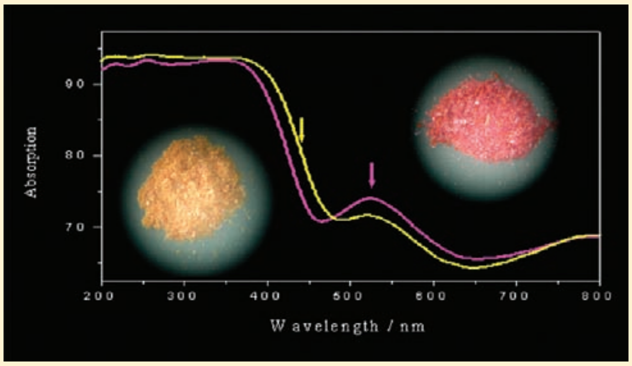
*Supporting Information*

**ABSTRACT:** Thiogermanates, $\{[Ni(phen)_3]_2Ge_4S_{10}\}\cdot x$Sol (Sol = $4MeOH\cdot 12H_2O$ (**1**) and $24H_2O$ (**2**)) were prepared and characterized by single-crystal structure analysis. There are large quantities of the solvent molecules that cocrystallize with the anions and cations and form a strong hydrogen bonding network (O—H···S and O···H—O—H···O). Reversible yellow-pink color change with fast speed was found for these compounds, when the crystals were immersed in alcohol solvents and water alternately. The time of the solvent-induced color change relates to the molecular size and structure of the alcohols. The smaller the molecule is, the faster the color change will be. The fastest color change was found by using the methanol solvent that took only about one second. The color change also relates to the ratio of water/alcohol. The solvatochromism phenomenon is accompanied with a rapid solvent-induced recrystallization that is verified by the XRD patterns.



## INTRODUCTION

Groups 13 and 14 metal (Ga, In, Ge, Sn) chalcogenometalates with secondary building units (SBU) of supertetrahedral clusters denoted as T*n* ($2 \leq n \leq 5$) are promising solid materials endowed with intrinsic structural diversity and interesting properties[1−3] and might find applications in optical,[1a,4] electronic,[1b,5] adsorption,[1a,6] ion-exchange,[1a,3a,6b] and photocatalytic fields.[7] The large T*n* clusters are even in nanoscale sizes being considered as quantum dots.[8] These chalcogenides or chalcogenometalates are usually prepared by hydro/solvothermal methods with organic amines as templates or directing reagents, and the T*n* clusters are joined together with corner $S^{2-}$ (or $Se^{2-}$) bridges forming porous framework solids. Lately, the transition metal (TM) complexes of chelating amines have been introduced into the structures of such T*n* chalcogenometalates, which can act as charge-balance cations,[9] metal complex linkages,[10] and terminated groups.[11] In comparison with TM complexes of aliphatic chelating amines, TM complexes of π-conjugated imine ligands, such as 1,10-phenanthroline (phen) and 2,2′-bipyridine, are seldom used as directing agents in the solvothermal synthesis of chalcogenometalates. We are devoted to preparing compounds in which the TM-phen/bpy complexes enter into the structures of the chalcogenometalates. The 0-D to 2-D supertetrahedral T3 clusters of $In_{10}S_{20}$ with TM-phen/bpy complex cations have been isolated.[12] The aromatic TM-phen/bpy complexes have π···π, *n*···π, and M···π electron transitions that are different to the aliphatic chelating amine complexes and have been interesting until now for their application in photoelectronic materials.[13]

Ion exchange is the most common property among the properties of these T*n* porous framework solids, in which protonated amine molecules can be exchanged with inorganic cations.[1a,3a,7] The ion's exchange in the rigid open frameworks of such materials is not an easy process and usually needs a long time (>24 h) to reach the positive result. For example, the exchange of amine molecules with $Cs^+$ ions from UCR-20GaGeS-TAEA took 60 h.[1a] Herein, we report two simple T2 thiogermanates, $\{[Ni(phen)_3]_2Ge_4S_{10}\}\cdot x$Sol, which are composed of discrete $[Ni(phen)_3]^{2+}$ cations, $[Ge_4S_{10}]^{4-}$ anions, and a large quantity of solvent molecules. Reversible color conversion between yellow and pink is found with fast speed when the crystals are immersed in aliphatic alcohol and water alternately. Such solid-state solvatochromism should be one of the key functions for preparing environmentally responsive materials.[14]

## EXPERIMENTAL SECTION

**General Remarks.** Starting materials $[(CH_3)_4N]_4Ge_4S_{10}$[15] and $[Ni(phen)_3]Cl_2$[16] were prepared by the literature method. All other analytically pure reagents were purchased commercially and used without further purification. The IR spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. Elemental

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analyses of C, H, and N were performed using an VARIDEL III elemental analyzer. Solid-state room-temperature optical diffuse reflectance spectra of the microcrystal samples were obtained with a Shimadzu UV-3150 spectrometer. Thermal analysis was conducted on a TGA-DCS 6300 microanalyzer. The samples were heated under a nitrogen stream of 100 mL·min$^{-1}$ with a heating rate of 20 °C·min$^{-1}$. Room-temperature X-ray diffraction data were collected on a D/MAX-3C diffractometer using a Cu tube source (Cu K$\alpha$, $\lambda$ = 1.5406 Å).

**Synthesis of [Ni(phen)$_3$]$_2$Ge$_4$S$_{10}$·4MeOH·12H$_2$O (1).** Diffusion of a methanol solution (2 mL) of [Ni(phen)$_3$]Cl$_2$ (0.0073 g, 0.01 mmol) in superstratum into an aqueous solution (2.5 mL) of $[(CH_3)_4N]_4Ge_4S_{10}$ (0.0045 g, 0.005 mmol) in an underlayer of a glass tube over a 12 h period gave yellow crystals in 65% yield based on Ge. The crystals are environment-sensitive and easily lose the methanol molecules. The compound was found to be insoluble in aqueous and common nonaqueous media except DMSO. Elemental analysis ($C_{72}H_{72}Ge_4N_{12}Ni_2O_{12}S_{10}$, MW 2025.78, loss of methanol). Found: C 42.81%, H 3.62%, N 8.27%. Calcd: C 42.69%, H 3.58%, N 8.30%. IR (cm$^{-1}$): 1651 (m), 1622 (m), 1516 (m), 1423 (s), 1143 (w), 1103 (m), 848.7 (s), 725 (s), 447.5 (m).

**Synthesis of [Ni(phen)$_3$]$_2$Ge$_4$S$_{10}$·24H$_2$O (2).** Starting materials of Ni(phen)$_3$Cl$_2$ (0.0145 g, 0.02 mmol) and $[(CH_3)_4N]_4Ge_4S_{10}$ (0.0091 g, 0.01 mmol) were dissolved in 10 mL of a mixed solvent of water and DMF (8:2 by v/v). The mixture was stirred and then filtered. Pink crystals were obtained from the filtrate under ambient condition for 14 h in 58% yield based on Ge. The crystals are air-stable and insoluble in aqueous and common nonaqueous media except DMSO. Elemental analysis ($C_{72}H_{96}Ge_4N_{12}Ni_2O_{24}S_{10}$, MW 2241.96). Found: C 39.10, H 3.92%, N 7.89%. Calcd C 38.57, H 4.32, N 7.50%. IR (cm$^{-1}$): 3451 (w), 1651 (m), 1624 (m),1514 (m), 1423 (s), 1144 (w), 1103 (m), 848.7 (s), 725 (s), 445.6 (m).

**X-ray Crystallographic Study.** The measurement was carried out on a Rigaku Mercury CCD diffractometer at low temperature with graphite monochromated Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation. X-ray crystallographic data for both compounds were collected and processed using CrystalClear (Rigaku).[17] The structures were solved by direct methods using SHELXS-97, and the refinement against all reflections of the compounds was performed using SHELXL-97.[18] The hydrogen atoms of the phen were positioned with idealized geometry and refined with fixed isotropic displacement parameters. The hydrogen atoms of the solvent were not dealt with. Relevant crystal data, collection parameters, and refinement results can be found in Table 1.

**Table 1. Crystal Data and Structural Refinement Parameters for 1 and 2**

| | 1 | 2 |
|---|---|---|
| formula | $C_{151}H_{175.5}Ge_8N_{24}Ni_4O_{33}S_{20}$ | $C_{144}H_{190}Ge_8N_{24}Ni_4O_{47}S_{20}$ |
| fw | 4311.41 | 4465.96 |
| cryst size (mm$^3$) | 0.10 × 0.30 × 0.35 | 0.13 × 0.20 × 0.30 |
| cryst syst | monoclinic | monoclinic |
| space group | $C2/c$ | $C2/c$ |
| $a$ (Å) | 45.425(4) | 50.563(4) |
| $b$ (Å) | 18.7598(13) | 14.6406(11) |
| c (Å) | 24.955(2) | 25.0692(19) |
| $\alpha$ (deg) | 90.00 | 90.00 |
| $\beta$ (deg) | 121.731(2) | 95.380(2) |
| $\gamma$ (deg) | 90.00 | 90.00 |
| $V$ (Å$^3$) | 18087(3) | 18476(2) |
| $Z$ | 4 | 4 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.554 | 1.605 |
| $F(000)$ | 8806 | 9144 |
| $\mu$ (mm$^{-1}$) | 2.020 | 1.986 |
| $T$ (K) | 193(2) | 193(2) |
| reflns collected | 44101 | 45614 |
| unique reflns | 15851 | 16194 |
| observed reflns | 12587 | 12175 |
| no. params | 1068 | 1104 |
| GOF on $F^2$ | 1.179 | 1.161 |
| $R_1$ [$I > 2\sigma(I)$] | 0.1045 | 0.0972 |
| $_{W}R_2$ | 0.1956 | 0.1582 |

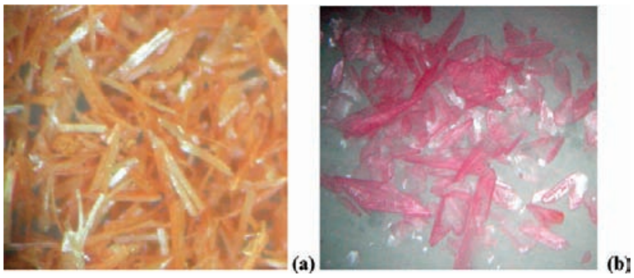

**Figure 1.** Crystals of compounds **1** (a) and **2** (b).

## RESULTS AND DISCUSSION

**Synthesis.** Compound **1** was obtained as yellow crystals by the diffusion method at the methanol−water interface, while compound **2** was prepared as pink crystals in an aqueous solution with a small amount of DMF (Figure 1). The purity of the samples **1** and **2** was ensured by elemental analyses and comparing the experimental XRD patterns with the calculated patterns from the crystal data (Supporting Information, Figure S1). The concentration of DMF is the key point to controlling the growth of crystals of **2**. When adding less DMF, it is easy to get microcrystals, and on the contrary, there might not be any crystals separated from the solution. Temperature also affects the speed and quality of crystal growth, and the optimized one is about 25−30 °C. Although the methods mentioned above are widely used and provide an effective method for crystal growth in coordination chemistry and supramolecular chemistry, it is uncommon to be used in the synthesis of chalcogenometalates. Because the discrete T$n$ clusters of main group metals are not thermostable species due to their higher ionic charge, such as $[In_4S_{10}]^{8-}$ and $[In_{10}S_{20}]^{10-}$, they usually tend to be polymeric structures that are generally obtained by hydro/solvothermal synthesis.[1−8] The $[Ge_4S_{10}]^{4-}$ is a thermostable bare T$n$ cluster due to the higher valence charge of Ge(IV) that compensates for most of the negative charge of the sulfur ions. The compound $[(CH_3)_4N]_4Ge_4S_{10}$ can be easily dissolved in water and is used as a precursor in solution synthesis.

**Structures of Compounds 1 and 2.** The fundamental structure of compound **1** consists of a discrete T2 cluster of $[Ge_4S_{10}]^{4-}$ and two $[Ni(phen)_3]^{2+}$ cations that was shown in Figure 2. The crystal belongs to a $C2/c$ space group with eight formulas in one crystal unit. The germanium atoms are tetrahedrally coordinated by sulfur atoms that exhibit terminal and bibridging modes. The bond distances and the angles are in accordance with a typical T2 cluster of $[Ge_4S_{10}]^{4-}$.[19] The Ge−S(terminal) distances, 2.119(3)−2.134(3) Å, are shorter than the Ge−S(bridged) distances, 2.207(3)−2.252(3) Å (Table 2), indicating the terminal sulfur atoms are not protonated.[20] The molecular packing is shown in Figure 3a and Supporting Information Figure S2a. There are 12 water and 4 methanol molecules cocrystallized per anion in the unit cell. The anions of $[Ge_4S_{10}]^{4-}$ connect with water by O−H···S (average distance 3.227 Å) and O···H−O−H···O hydrogen bonds, forming a 2-D network viewed from the $c$ axis (Figure 4). There are also a lot of C−H···S interactions between the cations and anions.

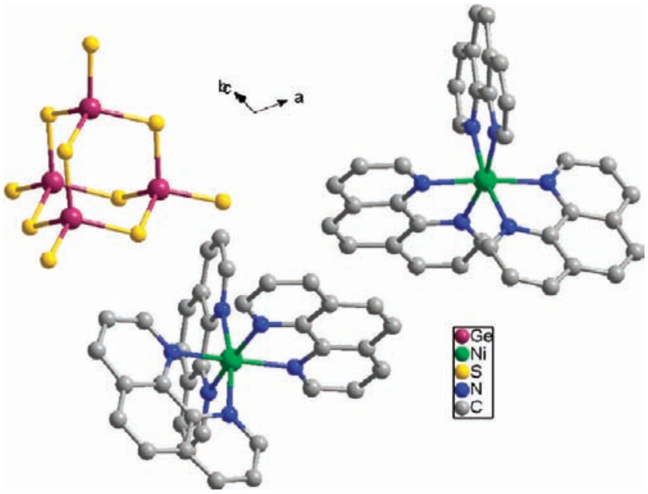

**Figure 2.** Structure of compound **1**; the uncoordinated solvent molecules in **1** and hydrogen atoms of phen were omitted for clarity.

### Table 2. Important Ge−S and Ni−N Bond Lengths (Å) and Angles (deg) for 1 and 2

| | | | |
|---|---|---|---|
| **1** | | | |
| Ge1−S1(t[a]) | 2.134(3) | Ge1−S3(b[b]) | 2.230(3) |
| Ge1−S2(b) | 2.236(3) | Ge1−S4(b) | 2.245(3) |
| Ge2−S5(t) | 2.131(3) | Ge2−S2(b) | 2.237(3) |
| Ge2−S7(b) | 2.241(3) | Ge2−S6(b) | 2.244(3) |
| Ge3−S8(t) | 2.119(3) | Ge3−S9(b) | 2.216(3) |
| Ge3−S6(b) | 2.236(3) | Ge3−S3(b) | 2.252(3) |
| Ge4−S10(t) | 2.130(3) | Ge4−S9(b) | 2.207(3) |
| Ge4−S7(b) | 2.231(3) | Ge4−S4(b) | 2.247(3) |
| Ni1−N2 | 2.076(8) | Ni1−N1 | 2.078(9) |
| Ni1−N5 | 2.078(9) | Ni1−N6 | 2.079(9) |
| Ni1−N3 | 2.090(9) | Ni1−N4 | 2.089(10) |
| Ni2−N8 | 2.082(8) | Ni2−N10 | 2.082(8) |
| Ni2−N12 | 2.090(8) | Ni2−N11 | 2.093(9) |
| Ni2−N9 | 2.095(8) | Ni2−N7 | 2.097(8) |
| N1−Ni1−N4 | 175.0(4) | N2−Ni1−N5 | 169.0(4) |
| N3−Ni1−N6 | 168.0(4) | N7−Ni2−N10 | 169.3(3) |
| N8−Ni2−N11 | 170.4(3) | N9−Ni2−N12 | 172.0(3) |
| **2** | | | |
| Ge1−S1(t) | 2.123(2) | Ge1−S3(t) | 2.231(b) |
| Ge1−S2(b) | 2.238(3) | Ge1−S4(b) | 2.251(2) |
| Ge2−S5(t) | 2.129(3) | Ge2−S2(b) | 2.223(3) |
| Ge2−S7(b) | 2.229(2) | Ge2−S6(b) | 2.240(3) |
| Ge3−S8(t) | 2.126(3) | Ge3−S9(b) | 2.234(2) |
| Ge3−S6(b) | 2.238(3) | Ge3−S3(b) | 2.234(2) |
| Ge4−S10(t) | 2.121(2) | Ge4−S9(b) | 2.234(2) |
| Ge4−S7(b) | 2.233(2) | Ge4−S4(b) | 2.236 (2) |
| Ni1−N2 | 2.097(7) | Ni1−N1 | 2.085(7) |
| Ni1−N5 | 2.092(7) | Ni1−N6 | 2.083(7) |
| Ni1−N3 | 2.103(7) | Ni1−N4 | 2.101(7) |
| Ni2−N8 | 2.094(7) | Ni2−N10 | 2.082(7) |
| Ni2−N12 | 2.078(7) | Ni2−N11 | 2.099(7) |
| Ni2−N9 | 2.064(7) | Ni2−N7 | 2.071(7) |
| N1−Ni1−N4 | 168.5(4) | N2−Ni1−N5 | 173.3(3) |
| N3−Ni1−N6 | 166.4(3) | N7−Ni2−N10 | 169.7(3) |
| N8−Ni2−N11 | 172.8(3) | N9−Ni2−N12 | 168.6(3) |

[a] Terminal sulfur atom. [b] Bridged sulfur atom.

The fundamental structure of compound **2** also consists of a discrete T2 cluster of $[Ge_4S_{10}]^{4-}$ and two $[Ni(phen)_3]^{2+}$ cations (Supporting Information Figure S3). The crystal belongs to a $C2/c$ space group with 8 anions and 16 cations in a unit cell. There are a lot of cocrystallized water molecules in compound **2** (24 water molecules per anion), more than that in **1**, but no organic solvent. The bond distances and the angles are in accordance with those of **1**. The Ge−S(terminal) distances, 2.121(2)−2.129(3) Å, are shorter than the Ge−S(bridged) distances, 2.223(3)−2.240(3) Å (Table 2). The molecular packing of **2** is showed in Figure 3b and Supporting Information Figure S2b. Comparing to the crystal data of **1**, the $\beta$ angle of **2** changes from 121.7° to 95.4° with elongated $a$ axis and shortened $b$ axis. The most remarkable structural feature of **2** is that the arrangement of anions and cations forms tunnels along the $c$ direction (Figure 5b). Most of the water molecules reside in the holes and are assembled by hydrogen bonds to a square water tunnel with side length of about 1/2 $b$, while such a tunnel in **1** is very narrow (Figure 5a). The hydrogen bonding network (O−H···S and O···H−O−H···O) in **2** is more complicated than that in **1**. In comparison with the previously reported structures containing isolated $[Ge_4S_{10}]^{4-}$ anions,[19,21] it is found that no or only a few solvent molecules cocrystallized in the crystals. The unusual cavity structure constructed by the T2 cluster and $[Ni(phen)_3]^{2+}$ cations is presumably the key to understanding the matter of solvent exchange.

**Studies of the Reversible Color Change.** The open and highly solvated structures of **1** and **2** suggest that the crystals are dynamically metastable and their composition is sensible to the solvent used in the synthesis and the atmosphere they stayed. It was discovered that the yellow crystal of **1** easily turns to a pink color upon exposure in moisture (about 90% humidity); therefore, the sample has to be stored in a sealed vessel and treated quickly in physical measurements. Experiments also show that pink crystals of **2** in microcrystals can be transformed to a yellow form and then reversiblely returned to a pink form when the sample is immersed alternately in ethanol and water. A similar phenomenon is also found for the yellow crystals of **1**. The solvent exchange in most porous polymers usually takes about one or several days or even needs the help of a vacuum technique. The solvent-induced reversible pink-yellow color change is very sharp and fast for compounds **1** and **2**. A video is provided in Supporting Information to show the experiments. Figure 6 illustrates the time of the change from the pink form to the yellow form for a microcrystal sample of **2**, when it was immersed in different concentration of water/ethanol mixed solvent. The color change is very quick in pure ethanol, about 1 s. The time is prolonged when the percent of water increased, and it is about 1 min in 50% ethanol. The time of solvent-induced color change is also related to the structures of alcohols. The smaller the molecule is, the faster the solvent-induced color change will be. The color change of **2** in pure methanol is very fast, less than 1 s, and the time is about 5 s for a 58% methanol−water mixed solvent. Figure 7 shows the minimum percent of alcohol in water/alcohol mixed solvent needed for the complete color change of **2** from pink to yellow within 5 s. The solvent-induced color change of $i$-propanol is faster than that of $n$-propanol, while the color of **2** cannot be completely changed to yellow in pure $i$-butanol in contrast to the complete color change of **2** in pure $n$-butanol.

Figure 8 displays the XRD patterns of the microcrystal sample of **2** that was immersed alternately in ethanol and water solvents. When the sample was immersed in ethanol, the pink form (line a) immediately turned to the yellow form (line b). The yellow sample was immersed in water and in ethanol,

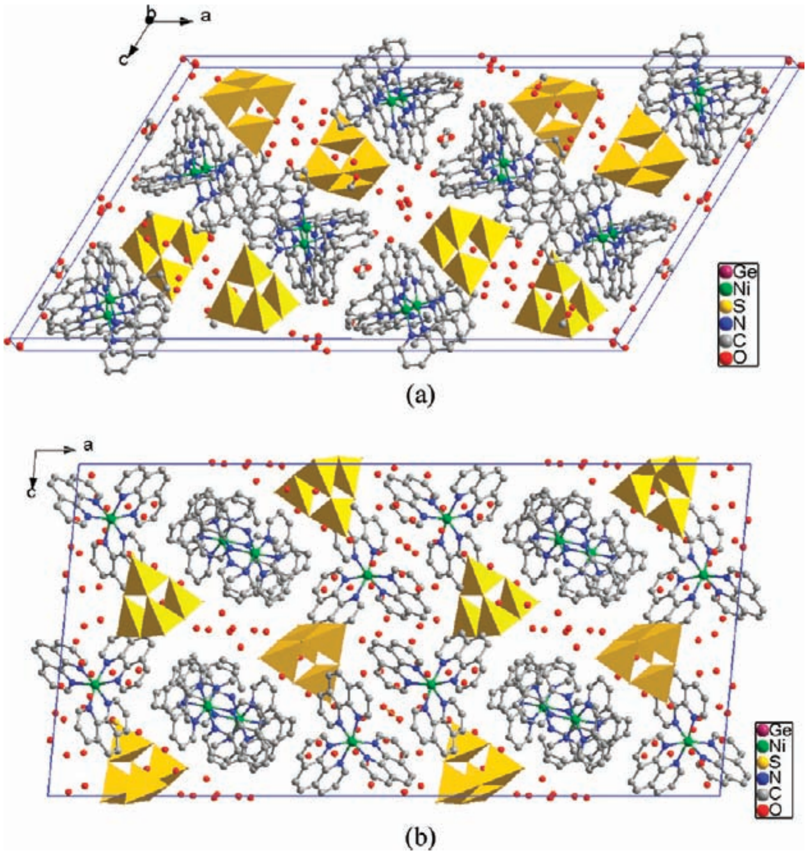

**Figure 3.** Molecular packing of **1** (a) and **2** (b) viewed along the *b* axis, showing the cocrystallized solvent molecules in the unit cell.

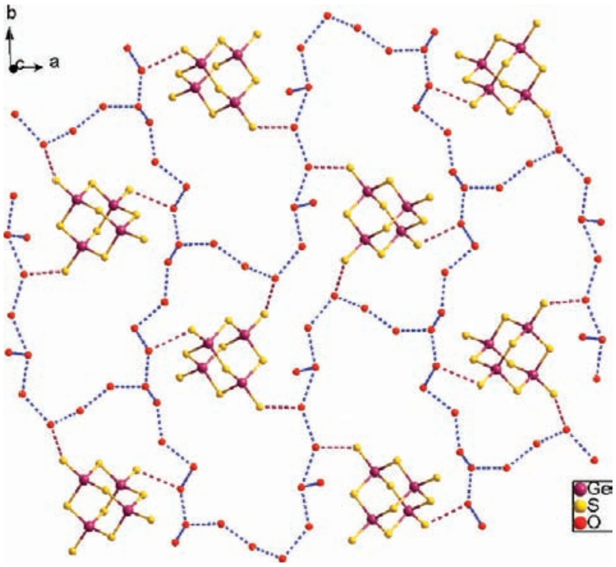

**Figure 4.** Anions $[Ge_4S_{10}]^{4-}$ connected by O−H···S hydrogen bonds with water and methanol into a 2-D net viewed from the *c* axis.

alternately, which represents one round. After the second round (c), the fourth round (d), and the sixth round (e), all the XRD patterns are similar to b. The XRD pattern (f) shows that the sample returned to the pink form after finally being immersed in water. A similar reversible change is also found for compound **1** (Supporting Information Figure S4 and video).

The good reversible solvent-induced phase change is verified by the microcrystal XRD patterns. The XRD pattern of the yellow form obtained from the solvent-induced color change of **2** is very close to that of compound **1** (Figure S1a). The phenomenon is not a single-crystal to single-crystal exchange. When a large crystal of **1** is immersed in water or **2** is immersed in ethanol, cracks appear in the crystal surface examined by microscope. For this reason, we consider that this phenomenon should be a rapid solvent-induced recrystallization.

**Optical Property and Thermal Stability.** Optical diffuse-reflection spectra of **1** and **2** were measured at room temperature using $BaSO_4$ as a standard reference (Figure 9). The absorption data was calculated from the reflectance. As shown in Figure 9, the absorption spectra of **1** and **2** are very similar, and there are two peaks at about 790 and 525 nm. These absorption bands can be assigned to the *d*−*d* transition of the Ni-phen complex cations in octahedral coordination (Supporting Information Figure S5). According to the Orgel diagram,[20] there are three *d*−*d* transition bands for the $Ni^{2+}$ ($d^8$) complex, $^3T_{2g} \leftarrow {}^3A_{2g}$ (790 nm), $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (525 nm), and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$, respectively. The band $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ is hidden in the intense absorption bands of the ligand and the anion (<450 nm). Compound **2** shows stronger intensity at peak 525 nm than that of **1**. At about 450 nm the absorption dramatically increases and forms an absorption platform with the onset point 470 nm for **1** and 454 nm for **2**, respectively. These differences in absorption causes the different colors of compounds **1** and **2**, because the absorption center of a yellow color is 470 nm and a red color is 550 nm. The phenomena are most probably attributed to the solvent effect.

Thermal behaviors of compounds **1** and **2** were conducted on a TGA microanalyzer under nitrogen. The decomposition of the two compounds showed three steps in the range of 25 to

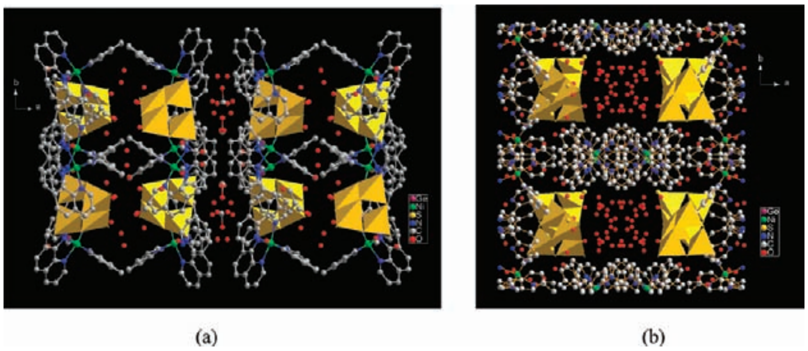

**Figure 5.** Molecular packing of **1** (a) and **2** (b), showing that the water occupied tunnels penetrated the crystal of **2** along the *c* direction.

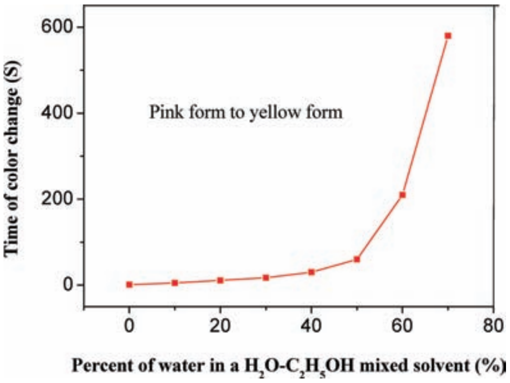

**Figure 6.** Time needed for a complete color change of a microcrystal sample of **2**, when it is immersed in different percentages of water/ethanol mixed solvent.

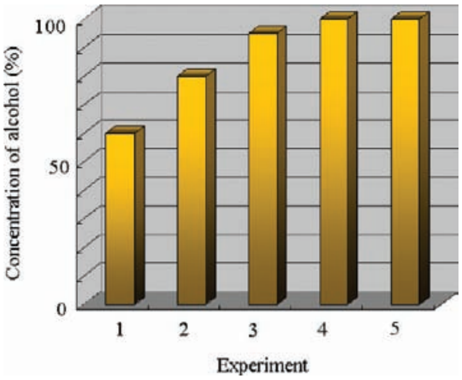

**Figure 7.** Minimum percent of alcohol in a mixed solvent with water for the complete color change of **2** from pink to yellow within 5 s (the color change will be quicker if the ratio is higher than this percent). (1) Methanol, (2) ethanol, (3) *i*-propanol, (4) *n*-propanol, and (5) *n*-butanol.

1000 °C (Figure 10). Both the compounds lose the solvent molecules even at room temperature. In the first step, the mass loss of 12.8 and 18.7% for **1** and **2**, respectively, corresponds with the removal of the all the water molecules, calcd 10.7% for **1** (12$H_2O$) and 19.3% for **2** (24$H_2O$) at about 150 °C. The total loss of methanol and water molecules for **1** should be 16.0%. This experiment result indicated that the methanol molecules are easy to lose when the crystals move out of the solvent. The compounds begin to remove organic ligands at 230–240 °C and finished at about 830 °C with multistep decomposition, and the detailed mechanism is complicated.

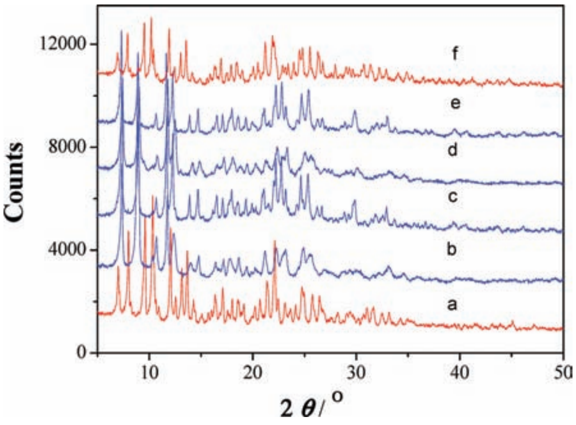

**Figure 8.** XRD patterns of microcrystal samples: sample of **2** (pink form) (a), after immersed in ethanol (yellow form) (b), after the second round (c), the fourth round (d), and the sixth round (*e*), and finally immersed in water (f).

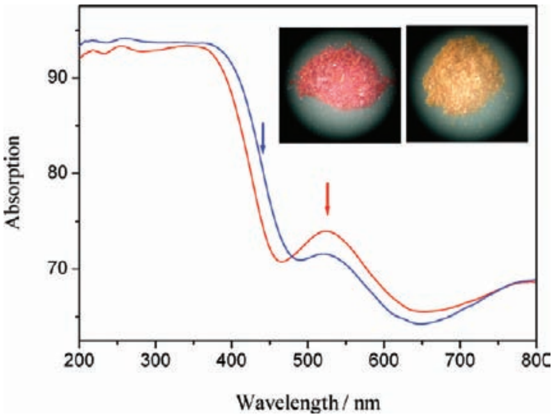

**Figure 9.** Optical absorption spectra of **1** (blue line; inset, yellow sample) and **2** (red line; inset, pink sample) in solid state.

## ■ CONCLUSIONS

In summary, two ionic thiogermanates, $\{[Ni(phen)_3]_2Ge_4S_{10}\}\cdot x$Sol, were obtained recently. The cation and anion assembled open structures are cocrystallized with a large quantity of solvent molecules. The remarkable phenomenon is that reversible color change between yellow and pink was found with fast speed when the crystals were immersed in alcohol solvents and water alternately. The time of the color change relates to the size, structure, and concentration of the solvents. The fastest color change happened in the solvent of methanol. The solvatochromism phenomenon is companied

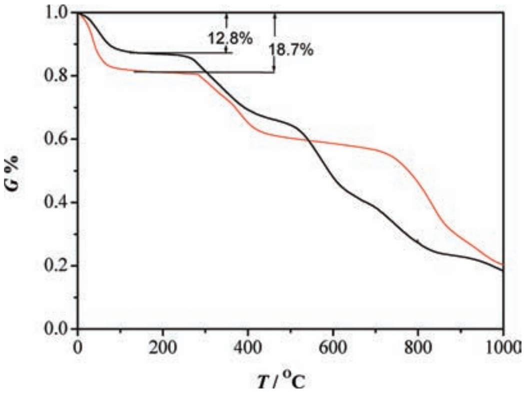

**Figure 10.** Thermal gravimetric results of **1** (black line) and **2** (red line).

with a rapid solvent-induced recrystallization that is verified by the XRD patterns. The solvent-rich ionic open structures are the key point of this phenomenon. The solid-state solvatochromism is one of the key functions for environmentally responsive materials.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Crystallographic data of **1** and **2** in CIF format, figures of molecular packing, XRD, and UV−vis spectra of starting materials, and experiment videos showing the reversible color changes. This material is available free of charge via the Internet at http://pubs.acs.org.

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