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# Synthesis, crystal structure and magnetic property of a new nickel selenite chloride: $Ni_5(SeO_3)_4Cl_2$

Yue-Ling Shen, Jiang-Gao Mao*, Hai-Long Jiang

*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, and the Graduate School of the Chinese Academy of Sciences, Fuzhou 350002, PR China*

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## Abstract

The new nickel selenite chloride, $Ni_5(SeO_3)_4Cl_2$, was obtained by high-temperature solid state reaction of $NiCl_2$, $Ni_2O_3$ and $SeO_2$ in a 1:2:4 molar ratio at 700 °C in an evacuated quartz tube. Its structure was established by single-crystal X-ray diffraction. $Ni_5(SeO_3)_4Cl_2$ crystallizes in the triclinic system, space group *P*-1 (No. 2) with cell parameters of $a = 8.076(2)$, $b = 9.288(2)$, $c = 9.376(2)$ Å, $\alpha = 101.97(3)$, $\beta = 105.60(3)$, $\gamma = 91.83(3)^\circ$ and $Z = 2$. All nickel(II) ions in $Ni_5(SeO_3)_4Cl_2$ are octahedrally coordinated by selenite oxygens or/and chloride anions (([Ni(1)$O_5$Cl], [Ni(2)$O_4Cl_2$], [Ni(3)$O_5$Cl], [Ni(4)$O_6$] and [Ni(5)$O_4$Cl]). The structure of the title compound features a condensed three-dimensional (3D) network built by Ni(II) ions interconnected by $SeO_3^{2-}$ anions as well as $Cl^-$ anions. Magnetic property measurements show strong antiferromagnetic interaction between nickel(II) ions.

*Keywords:* Nickel selenite chloride; Crystal structure; Solid state reaction; Open framework; Magnetic property

## 1. Introduction

During the past two decades, metal selenites and tellurites have been of research interest to scientists in chemistry and materials [1]. The asymmetric coordination polyhedron adopted by Se(IV) or Te(IV) atom may result in noncentrosymmetric structures with consequent interesting physical properties, such as nonlinear optical second harmonic generation (SHG) [2–5]. Furthermore, lone-pair elements such as Se(IV) and Te(IV), when mixed with a transition metal in the presence of halogen ions, can be regarded as "chemical scissors" [6–9]. Transition metal Te(IV) or Se(IV) oxohalogenides have also been proved to be promising new low-dimensional magnets [6–9]. A number of transition metal oxohalogenides containing lone-pair elements have been reported [6–20], some of which are similar to natural minerals [21–24].

As far as the NiO–$NiX_2$–$QO_2$ (X = Cl, Br, I; Q = Se, Te) system is concerned, several nickel tellurite halides have been reported [9–10]. For example, $Ni_5(TeO_3)_4Cl_2$ with a layered structure has been found to be a new two-dimensional (2D) $S = 1$ quantum spin system with antiferromagnetic super-exchange interaction. To the best of knowledge, there are no structural reports on nickel selenite halides. Our exploration of compounds in Ni–$SeO_2$–Cl system lead to a new nickel(II) selenite chloride, $Ni_5(SeO_3)_4Cl_2$, whose structure differs significantly from the layered $Ni_5(TeO_3)_4Cl_2$ with a comparable formula [9]. Herein we report its synthesis, crystal structure and magnetic property.

## 2. Experimental

### 2.1. Synthesis

All chemicals were obtained from commercial sources and used without further purification. $Ni_5(SeO_3)_4Cl_2$

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*Corresponding author. Fax: +86 591 371 4946.
*E-mail address:* mjg@ms.fjirsm.ac.cn (J.-G. Mao).

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was prepared by solid state reaction of 0.4 mmol of $NiCl_2$, 0.8 mmol of $Ni_2O_3$ and 1.6 mmol of $SeO_2$. The reaction mixture was thoroughly ground and pressed into a pellet, which was subsequently put into a quartz tube, evacuated and sealed. The quartz tube was heated at 700 °C for 6 days and then cooled to 350 °C at 4 $^\circ C\,h^{-1}$ before switching off the furnace. Two major phases were observed, namely, $Ni_5(SeO_3)_4Cl_2$ (brick, orange) and $NiSeO_3$ (plate, red). Efforts to make a single-phase product were tried but unsuccessful. The sample used for magnetic measurements is composed of single crystals of $Ni_5(SeO_3)_4Cl_2$ selected based on its unique color and shape.

### 2.2. *Single-crystal structure determination*

An orange brick-shaped single crystal with dimension of $0.30 \times 0.20 \times 0.16$ mm was mounted on Rigaku Mercury CCD using MoK$\alpha$ radiation ($\lambda = 0.71073$ Å), and a graphite monochromator at room temperature. The data were corrected for Lorenz factor, polarization, air absorption and absorption due to variations in the path length through the detector faceplate. Absorption correction based on Multi-scan technique was also applied [25]. The space group was determined to be *P*-1 (No. 2). The structure was solved by direct methods (SHELXTL) and refined by least-square methods with atomic coordinates and anisotropic thermal parameters [25]. O(10) atom was refined with isothermal parameters. Final difference Fourier maps were essentially featureless with residual peaks of 1.967 and $-1.792$ e Å$^{-3}$, which are less than 0.9 Å from Se(4) and Se(2), respectively. The crystallographic data collection and refinement parameters are summarized in Table 1. Selected bond lengths are listed in Table 2.

### 2.3. *Magnetic susceptibility measurements*

Magnetic susceptibility measurements for $Ni_5(SeO_3)_4Cl_2$ (0.0231 g, single crystals) were performed with a PPMS-9T magnetometer at 200 Oe and 1.0 T in the range of 2.0–300 K, respectively. Zero-field-cooling (ZFC) measurements were also performed. The raw data were corrected for the susceptibility of the container and the diamagnetic contributions of the sample using Pascal's constants.

## 3. Results and discussion

$Ni_5(SeO_3)_4Cl_2$ exhibits a different structure from $Ni_5(TeO_3)_4Cl_2$ with a similar formula [9]. $Ni_5(TeO_3)_4Cl_2$ (monoclinic $C2/c$) is layered while $Ni_5(SeO_3)_4Cl_2$ (triclinic, *P*-1) has a 3D structure.

Table 1
Crystal data and structure refinement for $Ni_5(SeO_3)_4Cl_2$

| | |
|---|---|
| Empirical formula | $Ni_5(SeO_3)_4Cl_2$ |
| Formula weight | 872.29 |
| $T$ (K) | 293 |
| Crystal system | Triclinic |
| Space group | *P-1*(No. 2) |
| $a$ (Å) | 8.076(2) |
| $b$ (Å) | 9.288(2) |
| $c$ (Å) | 9.376(2) |
| $\alpha$ (°) | 101.97(3) |
| $\beta$ (°) | 105.60(3) |
| $\gamma$ (°) | 91.83(3) |
| $V$ (Å$^3$) | 659.8(2) |
| $Z$ | 2 |
| $D_c$ (g cm$^{-3}$) | 2.195 |
| $\mu$ (MoK$\alpha$) (mm$^{-1}$) | 9.251 |
| $F$(000) | 406 |
| Colour, habit | Orange, brick |
| Crystal size (mm) | $0.30 \times 0.20 \times 0.16$ |
| Data collected | 5409 |
| Independent data | 3225 ($R_{int} = 0.0296$) |
| Observed data [$I > 2\sigma(I)$] | 2830 |
| Data/restraints/parameters | 3225/0/209 |
| Goodness-of-fit on $F^2$ | 1.035 |
| $R_1$, w$R_2$ [$I > 2\sigma(I)$]$^a$ | 0.0324, 0.0759 |
| $R_1$, w$R_2$ (all data) | 0.0364, 0.0774 |
| Largest diff. peak and hole (e Å$^{-3}$) | 1.967 and $-1.792$ |

$^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Table 2
Selected bond lengths (Å) for $Ni_5(SeO_3)_4Cl_2$

| | | | |
|---|---|---|---|
| Ni(1)–O(9)#1 | 2.001(4) | Ni(1)–O(6)#2 | 2.074(4) |
| Ni(1)–O(6) | 2.084(4) | Ni(1)–O(3) | 2.117(4) |
| Ni(1)–O(2) | 2.149(4) | Ni(1)–Cl(1) | 2.356(2) |
| Ni(2)–O(12)#3 | 2.022(4) | Ni(2)–O(10)#4 | 2.052(3) |
| Ni(2)–O(8)#4 | 2.072(3) | Ni(2)–O(1) | 2.080(3) |
| Ni(2)–Cl(1) | 2.329(2) | Ni(2)–Cl(2) | 2.493(2) |
| Ni(3)–O(3)#3 | 2.020(4) | Ni(3)–O(12) | 2.035(3) |
| Ni(3)–O(7)#5 | 2.060(4) | Ni(3)–O(5)#6 | 2.177(4) |
| Ni(3)–O(11) | 2.294(4) | Ni(3)–Cl(2) | 2.353(2) |
| Ni(4)–O(7) | 2.039(4) | Ni(4)–O(11) | 2.045(4) |
| Ni(4)–O(9) | 2.051(4) | Ni(4)–O(5)#1 | 2.054(3) |
| Ni(4)–O(5)#6 | 2.095(3) | Ni(4)–O(10) | 2.117(3) |
| Ni(5)–O(4)#1 | 1.997(4) | Ni(5)–O(11) | 1.999(4) |
| Ni(5)–O(8)#4 | 2.001(4) | Ni(5)–O(2)#1 | 2.026(3) |
| Ni(5)–O(1) | 2.111(4) | Ni(5)–Cl(2) | 2.783(2) |
| Ni(1)–Ni(1)#2 | 3.215(2) | Ni(2)–Ni(5) | 2.940(1) |
| Ni(3)–Ni(4)#5 | 3.086(1) | Ni(3)–Ni(4) | 3.211(1) |
| Ni(3)–Ni(5) | 3.444(1) | Ni(4)–Ni(4)#5 | 3.094(2) |

Symmetry transformations used to gnerate equivalent atoms: #1 $-x+1, -y, -z+1$; #2 $-x, -y, -z$; #3 $-x+1, -y+1, -z+1$; #4 $x-1, y, z$; #5 $-x+2, -y+1, -z+2$; #6 $x+1, y+1, z+1$.

There are five independent nickel atoms in $Ni_5(SeO_3)_4Cl_2$. As shown in Fig. 1, all five nickel(II) ions are six-coordinated by selenite oxygen or/and chlorine atoms in a distorted octahedral geometry. Ni(1) and Ni(3) are octahedrally coordinated by one chlorine and five oxygen atoms from four selenite anions, and Ni(2) is coordinated by two chlorine and four oxygen atoms from four selenite anions. Ni(4) is octahedrally coordinated by six oxygen atoms from four selenite anions,

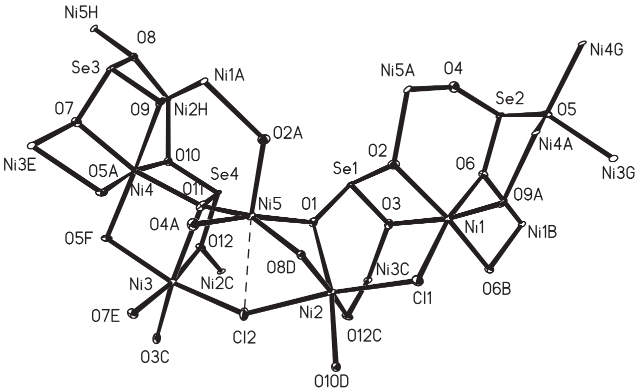

Fig. 1. ORTEP representation of the selected unit of $Ni_5(SeO_3)_4Cl_2$ showing the coordination geometries around the Ni(II) and Se(IV) ions. The thermal ellipsoids are drawn at 50% probability. Symmetry codes for the generated atoms: (a) $-x+1, -y, -z+1$; (b) $-x, -y, -z$; (c) $-x+1, -y+1, -z+1$; (d) $x-1, y, z$; (e) $-x+2, -y+1, -z+2$; (f) $x+1, y+1, z+1$; (g) $x-1, y-1, z-1$; (h) $x+1, y, z$.

Ni(5) is octahedrally coordinated by one chlorine and five oxygen atoms from five selenite anions. The Ni–O distances are in the range of 1.997(4)–2.294(4) Å and the Ni–Cl ones ranges from 2.329(2) to 2.783(2) Å, which are similar to those reported in the literatures [9]. The Ni(2) octahedron with Ni(2)–Cl(1) bond length of 2.783(2) Å has the largest distortion (Table 2). There are only $NiO_6$ and $NiO_5Cl$ octahedra in the layered $Ni_5(TeO_3)_4Cl_2$ [9]. All four selenium(IV) atoms are three-coordinated by three oxygen atoms in a distorted $\psi$-$SeO_3$ tetrahedral geometry with the fourth site occupied by the lone-pair electrons, which are similar to those of the tellurium(IV) atoms in $Ni_5(TeO_3)_4Cl_2$ [9]. The Se–O distances range between 1.657(4) and 1.782(4) Å, which are comparable to those reported in other metal selenites [1]. Results of the bond valence calculations indicate that all selenium atoms are in +4 oxidation state [26]. The calculated total bond valences are 4.04, 3.93, 3.98 and 3.91, respectively, for Se(1), Se(2), Se(3) and Se(4). Cl(1) and Cl(2) anions in $Ni_5(SeO_3)_4Cl_2$ bridge to two and three nickel(II) ions, respectively, whereas the chloride anions in $Ni_5(TeO_3)_4Cl_2$ are unidentate and are orientated toward the interlayer space [9].

The $Se(1)O_3$ group is hexadentate, chelating bidentately with a Ni(1) (O(2) and O(3)) and also bridging with 1 Ni(2), 1 Ni(3), and 2 Ni(5). The $Se(2)O_3$ group is hexadentate and bridges with 2 Ni(1), 2 Ni(4), 1 Ni(3) and 1 Ni(5). O(5) is a tridentate metal linker. The $Se(3)O_3$ group is hexadentate, chelating bidentately with a Ni(4) (O(7) and O(9)) and also bridging to four other Ni(II) ions (Ni(1), Ni(2), Ni(3) and Ni(5)). The $Se(4)O_3$ group is heptadentate, chelating bidentately with a Ni(3) (O(11) and O(12)) and chelating bidentately with a Ni(4) (O(10) and O(11)), as well as bridging to 1 Ni(5) and 2 Ni(2) atoms (Fig. 1), O(10) is tridentate metal linker and other two oxygen atoms are bidentate. These coordination modes are different from those of tellurite anion in $Ni_5(TeO_3)_4Cl_2$, in which all tellurite anions are heptadentate, two of which each chelates bidentately with a nickel(II) ion and bridges to five other nickel(II) ions whereas the remaining two each bridges to seven nickel(II) ions [9].

It is worthy to mention the particular connectivity between different nickel(II) octahedra (Fig. 2). The $Ni(1)O_6$ octahedron is edge-sharing (O6–O6) with a neighbouring $Ni(1)O_6$ octahedron, and is also corner-sharing with Ni(2), Ni(3), Ni(4) and Ni(5) octahedra (Fig. 2a). $Ni(3)O_5Cl$ octahedron is edge-sharing with one Ni(4) (O5–O7) and one Ni(5) (O11–Cl2) octahedron, corner-sharing with one Ni(1) (O3) and two Ni(2) (Cl2 and O12) octahedra. The $Ni(5)ClO_5$ octahedron connects by face-sharing with a Ni(2) (O1–Cl2–O8) octahedron and edge-sharing with a Ni(3) (Cl2–O11) octahedron, and corner-sharing with Ni(3) and Ni(4) octahedra. The $Ni(2)O_5Cl$ octahedra is face-sharing with a Ni(5) octahedron and corner-sharing with Ni(1), Ni(3)

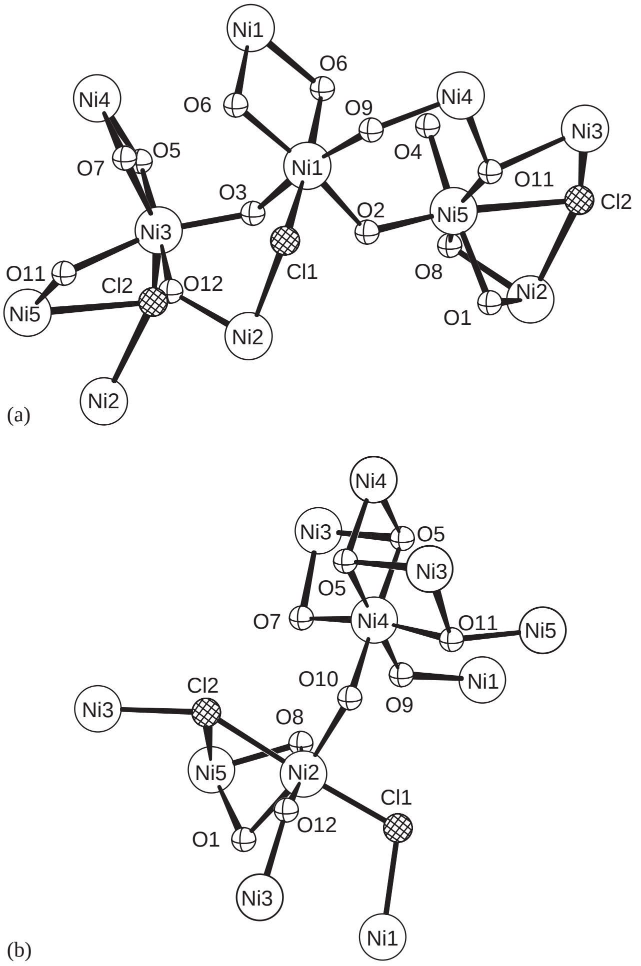

Fig. 2. (a) The connectivity scheme of Ni(1), Ni(3) and Ni(5) with their neighbouring Ni(II) ions; (b) The connectivity scheme of Ni(2) and Ni(4) with their neighbouring Ni(II) ions.

and Ni(4) octahedra (Fig. 2b). The Ni(4)$O_5$Cl octahedron is edge-sharing with two Ni(3) (O5–O11 and O5–O7) octahedra and one Ni(4) (O5–O5) octahedron, in addition to corner-sharing with the Ni(1), Ni(2) and Ni(5) octahedra (Fig. 2b). The two nickel octahedra interconnected via face-sharing have the shortest Ni…Ni separation (2.934(2) Å), followed by those via O–O edge-sharing (in the range of 3.086(1)–3.215(1) Å) and via O–Cl edge-sharing (3.444(1) Å) (Table 2). The Ni…Ni distances between nickel(II) centres bridged by a selenite oxygen are at least 3.657(1) Å.

The interconnection of the Ni(II) ions by $SeO_3^{2-}$ anions as well as $Cl^-$ anions results in a 3D network with cavities occupied by the lone-pair electrons of the $Se^{4+}$ ions (Fig. 3). The 3D network can also be viewed as formed by the interconnection of nickel(II) octahedra via corner-, edge- and face-sharing with $Se^{4+}$ ions capping on the cavities (Fig. 3).

Magnetic property of $Ni_5(SeO_3)_4Cl_2$ has also been studied. The $\mu_{eff}$ of 6.1 $\mu_B$ at room temperature measured at 1 T is slightly smaller than 6.33 $\mu_B$ expected for five spin-only $Ni^{2+}$ ions ($Ni^{2+}$, $S = 1$, $\mu_{eff} = 2.83\,\mu_B$). It is decreased with cooling and reaches 1.7 $\mu_B$ at 2.5 K, indicating antiferromagnetic interaction between nickel(II) centres. Plot of the inverse of molar susceptibility ($\chi^{-1}$) versus temperature shows that it obeys the Curie–Weiss law above 50 K, but it deviates significantly from the Curie–Weiss law below 50 K (Fig. 4). Nonlinear fitting of the susceptibility data above 50 K according to $\chi = C/(T - \theta) + \chi_0$ gave a Weiss constant of −143 (2) K, indicating very strong antiferromagnetic interactions between nickel ions. Such strong antiferromagnetic interactions are expected since the Ni…Ni separation between face-sharing or edge-sharing nickel octahedra are very short (ranging from 2.940(1) to 3.444(1) Å, Table 2) and the structure of $Ni_5(SeO_3)_4Cl_2$ is a very condensed 3D network. ZFC measurements and low field-cooling (FC) measurements at 200 Oe have also been performed to detect the possible existence of a weak ferromagnetic contribution. As shown in Fig. 5, the ZFC and FC (200 Oe) $\chi - T$ curves are almost identical, both show a maximum of molar susceptibility at around 4.5 K ($T_N$), which provides further evidence of antiferromagnetic interactions between magnetic centres. Based on these results we think that a weak ferromagnetic contribution is unlikely. Further detailed magnetic studies are still needed to establish the magnetostructural correlations.

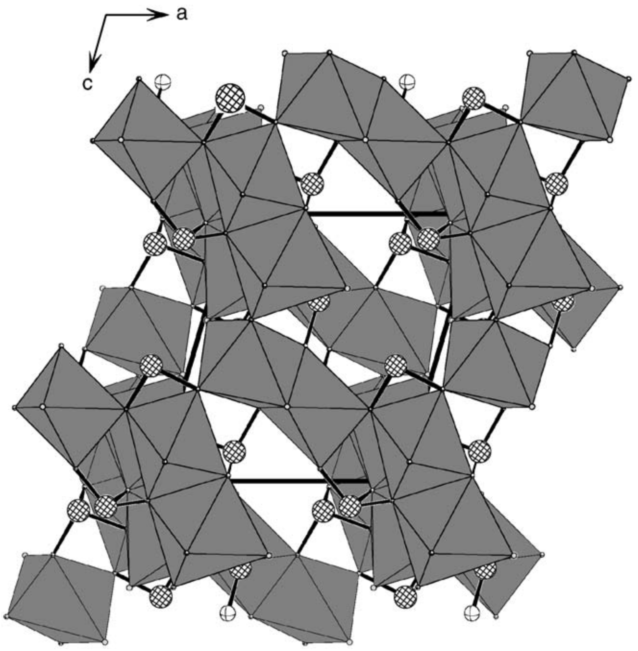

Fig. 3. View of the structure of $Ni_5(SeO_3)_4Cl_2$ down the *b*-axis. The nickel(II) octahedra are shaded in grey. The Se and O atoms are represented by hatched and crossed circles, respectively.

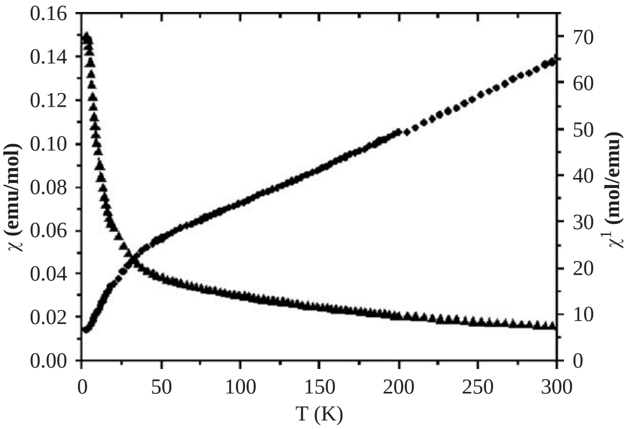

Fig. 4. Plot of $\chi$ and $\chi^{-1}$ versus temperature (10,000 Oe).

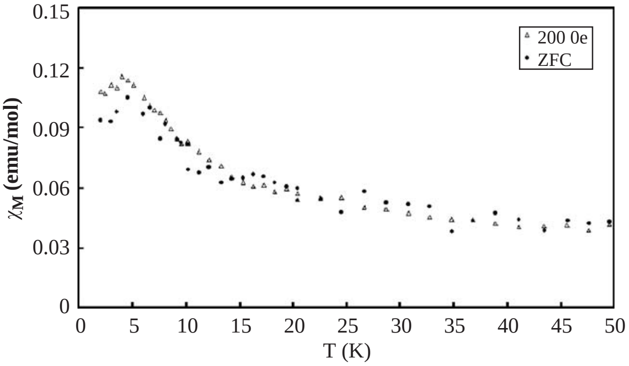

Fig. 5. Plot of $\chi_M$ versus temperature under ZFC and FC (200 Oe).

## 4. Conclusions

In summary, a novel nickel(II) selenite chloride $Ni_5(SeO_3)_4Cl_2$ has been synthesized successfully by solid state reaction. Its structure features a complex condensed 3D network. Future efforts will be devoted to syntheses and magnetic studies of other compounds in similar systems.

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