



Crystal structures, magnetic and electrical properties of two new two-dimensional bis(2-thioxo-1, 3-dithiole-4, 5-dithiolato)nickelate salts



Xin Sun^a, Hao Yang^a, Hai-Yan Xu^a, Jian-Lan Liu^{a,*}, Lan-Cheng Zhou^a, Xiao-Ming Ren^{a,b,c,*}

^a State Key Laboratory of Materials-Oriented Chemical Engineering and College of Science, Nanjing Tech University, Nanjing 210009, People's Republic of China

^b College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, People's Republic of China

^c State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

ARTICLE INFO

Article history:

Received 31 May 2015

Received in revised form 3 July 2015

Accepted 7 July 2015

Available online 23 July 2015

Keywords:

Nickel-bis-dithiolene charge-transfer salt

Crystal structure

Magnetic property

Dielectric behavior

Electrical conduction

ABSTRACT

Two new salts of bis(2-thioxo-1, 3-dithiole-4, 5-dithiolato) nickelate monoanion with 4-amino-1-heptylpyridinium (**1**) and 4-amino-1-nonylpyridinium (**2**) were prepared and characterized. Two isostructural salts with anion/cation = 1:1 crystallize in space group *P*-1 with similar cell parameters and packing structures. The anions and cations form alternating layered arrangements, which are connected via charge-assisted S...H H-bonds. Within an anion layered alignment, the magnetic exchange is transmitted between the neighboring anions via three types of pathways (face-to-face π - π stack, lateral-to-lateral and head-to-tail S...S contacts), where the stronger antiferromagnetic coupling occurs between the face-to-face stacked anions, owing to π -type magnetic orbitals efficiently overlapped, than others and dominates the magnetic nature of **1** and **2**. The dielectric and conducting properties were also investigated for two salts in the temperature range of 175–375 K.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

During the past decades, transition metal-bis(1, 2-dithiolene) complexes have been widely studied [1] due to their novel properties and potential application in the areas of conducting, superconducting [2], magnetic materials [3–7] and catalysis and so on [8–10]. A great deal of evidences indicated that the novel functional properties arise from the specific planar geometries with extended electronic structure and intermolecular interactions of bis(1, 2-dithiolene) metalate anions [11].

The $[M(dmit)_2]^-$ ($M = Ni, Pd$ and Pt , $dmit = 2$ -thioxo-1, 3-dithiole-4, 5-dithiolate), species is an excellent molecular building block for constructing the molecule-based magnetic and conducting materials. The diverse packing structures have been observed in $[M(dmit)_2]^-$ salts, where the $[M(dmit)_2]^-$ anions form one-dimensional (1-D) chain [12], two-dimensional (2-D) sheet [13] or three-dimensional (3-D) lattice [14], and this is due to that the dithiolene unit in $dmit^{2-}$ ligand extends with SR groups, leading to the presence of versatile S...S interactions between the neighboring $[Ni(dmit)_2]^-$ moieties in crystal. On the other hand, the electron

transport and the magnetic coupling can be transmitted through non-bonded interatomic contacts, especially through contacted sulfur atoms between the neighboring $[Ni(dmit)_2]^-$ moieties owing to the unpaired electron delocalizing over the whole skeleton of the $[M(dmit)_2]^-$ anion. Thus, the conducting and magnetic natures of $[Ni(dmit)_2]^-$ salt is quite sensitive to the alignment of $[Ni(dmit)_2]^-$ anions in crystal [15].

It is noteworthy that the alignment of $[Ni(dmit)_2]^-$ anions is strongly dependent on the geometric nature of the counterion in crystal. Working with this line, our recent research has involved the incorporation of flexible cations, such as 4-amino-1-alkylpyridinium (C_n -Apy⁺), into the $[Ni(dmit)_2]^-$ lattice in an effort to systematically study the stacking pattern of $[Ni(dmit)_2]^-$ and conducting and magnetic properties of salts, we achieved two mixed-valence molecular crystals, $[C_8\text{-Apy}]_2[Ni(dmit)_2]_3$ and $[C_3\text{-Apy}][Ni(dmit)_2]_3$ ($C_8\text{-Apy}^+ = 4$ -amino-1-octylpyridinium; $C_3\text{-Apy}^+ = 4$ -amino-1-propylpyridinium). Interestingly, the salt $[C_8\text{-Apy}]_2[Ni(dmit)_2]_3$ shows rapid, clear and stable response of photoconductivity under UV irradiation [16], and the salt $[C_3\text{-Apy}][Ni(dmit)_2]_3$ exhibits a magnetic phase transition around 77 K with a ca. 6 K thermal hysteresis loop but absence of electrical response in the corresponding temperature interval [17].

In this paper, we report on crystal structures, magnetic, dielectric and conduction features for two new salts of $[Ni(dmit)_2]^-$ with

* Corresponding authors. Fax: +86 25 58139481.
E-mail address: xmren@njtech.edu.cn (X.-M. Ren).

4-amino-1-heptylpyridinium ($C_7\text{-Apy}^+$) and 4-amino-1-nonylpyridinium ($C_9\text{-Apy}^+$), respectively.

2. Experimental

2.1. Materials and general methods

All chemicals and reagents were purchased from commercial sources and directly used without additional purification. 4,5-di(thiobenzoyl)-1,3-dithiole-2-thione was prepared in accordance to the published procedure [18]; $[C_7\text{-Apy}]\text{Br}$ and $[C_9\text{-Apy}]\text{Br}$ were synthesized following the similar procedure for preparation of $[C_6\text{-Apy}]\text{Br}$ [19].

2.2. Chemical and physical characterizations

Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance powder diffractometer operating at 40 kV and 40 mA with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Samples were scanned from $2\theta = 5 - 50^\circ$ with $0.1^\circ/\text{step}$ and 1.0 s/step . FT-IR spectra were recorded on an IF66 V FT-IR ($4000\text{--}400 \text{ cm}^{-1}$) spectrophotometer with KBr pellets. Magnetic susceptibility data were measured for polycrystalline samples on a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer over the temperature range of $1.8\text{--}400 \text{ K}$, and the diamagnetism correction was not made. Temperature, frequency dependent dielectric permittivity were measured using a concept 80 system (Novocontrol, Germany) in the ranges of $273\text{--}373 \text{ K}$ (from -100 to 100°C) and the ac electrical field frequencies span from 1 Hz to 10^7 Hz . The samples were prepared in the form of a pellet with a 10.0 mm in diameter and ca. 0.85 mm in thickness for **1** versus 10.0 mm in diameter and ca. 0.73 mm in thickness for **2**, and sandwiched between two parallel copper electrodes.

2.3. Syntheses of **1** and **2**

2.3.1. Synthesis of $[C_7\text{-Apy}][\text{Ni}(\text{dmit})_2]$ (**1**)

To 4,5-di(thiobenzoyl)-1,3-dithiole-2-thione (812 mg, 2 mmol) suspended in methanol (10 mL), sodium methoxide (prepared from 184 mg of sodium in 10 mL of methanol) was added under argon atmosphere and at ambient temperature within 30 min, which gave a dark red solution. And then $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (238 mg, 1 mmol) was added to this solution. After strongly stirred for 30 min, a solution of $[C_7\text{-Apy}]\text{Br}$ (273 mg, 1 mmol) in methanol (20 mL) was added to the above mixture. After 120 min, a solution of I_2 (127 mg, 0.5 mmol) and NaI (150 mg, 1 mmol) in methanol (20 mL) was added. The mixture was strongly stirred for 30 min and allowed to stand overnight. The resultant dark green microcrystals were collected by filtration, and washed with MeOH and dried in vacuum. Yield: $\sim 65\%$. Anal. Calc. for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{S}_{10}\text{Ni}$: C, 33.53; H, 3.28; N, 4.35%. Found: C, 33.58; H, 2.98; N, 4.45%. IR bands (KBr pellet, cm^{-1}): $1347(\nu_{\text{C}=\text{C}})$, $1058(\nu_{\text{C}=\text{S}})$, $516(\delta_{\text{S}-\text{C}-\text{S}})$.

2.3.2. Synthesis of $[C_9\text{-Apy}][\text{Ni}(\text{dmit})_2]$ (**2**)

A procedure similar to **1** was used for preparation of $[C_9\text{-Apy}][\text{Ni}(\text{dmit})_2]$ (**2**) instead of $[C_7\text{-Apy}]\text{Br}$ by $[C_9\text{-Apy}]\text{Br}$. Yield: 70%. Anal. Calc. for $\text{C}_{20}\text{H}_{25}\text{N}_2\text{S}_{10}\text{Ni}$: C, 35.70; H, 3.75; N, 4.16%. Found: C, 35.57; H, 3.67; N, 4.01%. IR bands (KBr pellet, cm^{-1}): $1347(\nu_{\text{C}=\text{C}})$, $1054(\nu_{\text{C}=\text{S}})$, $514(\delta_{\text{S}-\text{C}-\text{S}})$.

The single crystals, suitable for X-ray diffraction structure analyses, were obtained by slow evaporation of the solution of **1** (or **2**) in acetone at ambient temperature for 7–10 days.

2.4. X-ray data collection and structure determinations

The single-crystal X-ray diffraction data were collected for **1** and **2** on a Bruker Smart Apex II CCD detector with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $296(2) \text{ K}$ using the ω -scan technique. The diffraction intensity data were integrated corrected using the SAINT program. An empirical absorption correction was applied using the SADABS program [20]. The structures were solved by direct methods using the program SHELXS-97 and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [21]. All hydrogen atoms were placed at the calculated positions and refined as riding on the parent atoms. Details about data collection, structure refinement and crystallography are summarized in Table 1.

3. Results and discussion

3.1. Descriptions of crystal structures

3.1.1. $[C_7\text{-Apy}][\text{Ni}(\text{dmit})_2]$ (**1**)

Salts **1** and **2** are isostructural to each other, and crystallize in the triclinic space group $P-1$ with quite analogous cell parameters (ref. Table 1) and packing structure. As shown in Fig. 1a and b, an asymmetric unit contains one pair of $C_7\text{-APy}^+$ (or $C_9\text{-APy}^+$) and $[\text{Ni}(\text{dmit})_2]^-$ anion in **1** (or **2**). The $[\text{Ni}(\text{dmit})_2]^-$ monoanion shows an approximately planar geometry, and the typical bond lengths and angles in the $[\text{Ni}(\text{dmit})_2]^-$ anion are summarized in Table 2. The Ni—S bond lengths range from $2.1535(9)$ to $2.1720(9) \text{ \AA}$ in **1** versus $2.1536(9)$ to $2.1713(9) \text{ \AA}$ in **2**. These bond parameters are comparable to the reported values in $[\text{Ni}(\text{dmit})_2]^-$ salts [22]. The hydrocarbon chain shows an almost completely trans-planar conformation in both $C_7\text{-APy}^+$ and $C_9\text{-APy}^+$ cations, where the bond length and angle values in pyridyl rings and the hydrocarbon

Table 1
Crystallographic data and structure refinement parameters for **1** and **2**.

Compound	1	2
Temp./K	296(2)	296(2)
Wavelength/ \AA	0.71073	0.71073
Formula	$\text{C}_{18}\text{H}_{21}\text{N}_2\text{S}_{10}\text{Ni}$	$\text{C}_{20}\text{H}_{25}\text{N}_2\text{S}_{10}\text{Ni}$
Formula weight	644.66	672.71
Space group	$P-1$	$P-1$
CCDC no.	1047283	1047284
Crystal system	Triclinic	Triclinic
$a/\text{\AA}$	8.5107(9)	8.5973(9)
$b/\text{\AA}$	12.1950(13)	12.2146(11)
$c/\text{\AA}$	14.2376(16)	14.6102(14)
$\alpha/^\circ$	111.004(3)	102.421(3)
$\beta/^\circ$	103.102(3)	105.313(3)
$\gamma/^\circ$	99.608(3)	100.443(3)
$V/\text{\AA}^3$	1292.6(2)	1398.2(2)/2
$\rho/\text{g cm}^{-3}$	1.656	1.598
μ/mm^{-1}	1.570	1.455
$F(000)$	662	694
θ Range for data collection ($^\circ$)	1.89–27.51	1.76–27.51
Index ranges	$-11 \leq h \leq 11$ $-15 \leq k \leq 15$ $-18 \leq l \leq 18$	$-11 \leq h \leq 11$ $-15 \leq k \leq 15$ $-18 \leq l \leq 18$
R_{int}	0.0448	0.0602
Independent reflect./restraints/parameters	5909/0/282	6396/0/300
Refinement method	The least square refinement on F^2	
Goodness-of-fit on F^2	1.029	1.015
$R_1^a, wR_2^b [I > 2\sigma(I)]$	0.0479, 0.0962	0.0496, 0.0886
R_1^a, wR_2^b [all data]	0.0877, 0.1037	0.1090, 0.1058
Residual/ $e \text{ nm}^{-3}$	0.466/−0.356	0.420/−0.421

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

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

Download English Version:

<https://daneshyari.com/en/article/1440480>

Download Persian Version:

<https://daneshyari.com/article/1440480>

[Daneshyari.com](https://daneshyari.com)