



Crystal structures and dielectric properties of two salts of nickel-bis-1,2-dithiolene with noncentrosymmetric organic cations

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ARTICLE INFO

Article history:

Received 10 May 2018

Accepted 10 August 2018

Available online 20 August 2018

Keywords:

Nickel-dithiolene salt

Noncentrosymmetric cations

Crystal structure

Dielectric permittivity

Dielectric relaxation

ABSTRACT

Two nickel-bis-1,2-dithiolene salts, [1,4-dimethyl-DABCO][Ni(mnt)₂] (**1**) and (TMSF)₂[Ni(mnt)₂] (**2**) (mnt²⁻ = maleonitriledithiolate, 1,4-dimethyl-DABCO²⁺ = 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane and TMSF⁺ = trimethylsulfonium), were synthesized and characterized by elemental analysis, IR spectra, thermal analysis and single crystal structures. Both **1** and **2** crystallize in monoclinic space group *C2/c*, with a formula and cell parameters of C₁₆H₁₈N₆NiS₄, a = 16.9688(8) Å, b = 9.3003(5) Å, 13.4090(6) Å and β = 103.244(2)° for **1** at 293 K versus C₁₄H₁₈N₄NiS₆, a = 17.108(3) Å, b = 10.2932(16) Å, 14.071(2) Å and β = 118.845(4)° for **2** at 293 K. Moreover, two salts show similar packing structure, with the arrangements of alternating layer of anions and cations, and the layers are parallel to the crystallographic *ab*-plane. Both **1** and **2** display analogous dielectric behavior, which dielectric permittivity is almost a constant with ε' ≈ 12 at the temperature below 270 K for **1** versus 215 K for **2**, and two steps of dielectric relaxations appear in the higher temperature regime, which originate from the molecular dipole orientation and the ion migration.

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1. Introduction

Bis-1,2-dithiolene complexes of transition metals have been widely studied since 1960s. This type of complex has planar and electronically delocalized core, which is comprised of the central metal, four sulfurs and the C=C units (in most cases, the central metal is Ni, Pd or Pt ion), and the unique molecule geometry and electronic structure endow a bis-1,2-dithiolene complex of transition metal with lots of distinctive properties and promising application in the areas of conducting and magnetic materials, dyes, non-linear optics, catalysis and others [1–19].

In the family of bis-1,2-dithiolene complexes of transition metals, it is well known that the salts of [M(mnt)₂]⁻ (mnt²⁻ = maleonitriledithiolate) show diverse and novel magnetic and conducting natures [20–28]. The salt [NH₄][Ni(mnt)₂].H₂O exhibits Heisenberg antiferromagnetic chain behavior around room temperature and

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the singlet ground state with the monoanions associated as dimer at low temperatures [20]. Interestingly, this salt, with localized spins, shows long-range ferromagnetic order at the temperatures below 4.5 K and the Curie temperature demarcating the transition to ferromagnetic order abruptly disappears at 6.8 kbar applied pressure [20]. A series of one-dimensional salts, [R-BzPy][M(mnt)₂] (BzPy⁺ and R represent the benzylpyridinium and substituent; M = Ni or Pt), display spin-Peierls instability in a wide temperature ranges [29–31], and the significant isotopic effect of spin-Peierls transition temperature is observed in this series of salts [32,33]. In addition, the salt, [H₃O]_{0.33}Li_{0.8}[Pt(mnt)₂].1.67H₂O, shows metallic properties at room temperature but undergoes the Peierls instability at ca. 220 K to become a semiconductor [34,35] and the non-stoichiometric salt, Cs_{0.82}[Pd(mnt)₂].0.5H₂O, is the first palladium dithiolene complex to exhibit metallic behavior under pressure [21]. In recent years, some novel physical properties have been found in the transition metal bis-1,2-dithiolene complexes [36–38]. For instance, the quantum coherence was observed in (PPh₄)₂[Cu(mnt)₂] (mnt²⁻ = maleonitriledithiolate) doped into the diamagnetic isostructural host (PPh₄)₂[Ni(mnt)₂] as a very promising quantum bit, and very long quantum coherence times was found of 68 s at low temperature (qubit figure of merit QM = 3400) and 1 s at room temperature,

much higher than previously reported values for such systems [36].

With respect to $[M(\text{mnt})_2]^-$ ($M = \text{Ni}$ or Pt) salts widely studied, the $[M(\text{mnt})_2]^{2-}$ salts have been rarely investigated. Recently, we have synthesized and characterized a series of salts of $[\text{Ni}(\text{mnt})_2]^{2-}$ with pyridinium derivatives, and found that the molecule structure and charge of the counter cation strongly influence on the crystal structure and dielectric properties and ionic liquid crystal nature of $[\text{Ni}(\text{mnt})_2]^{2-}$ salts [39,40]. The dielectric phase transition is one of the most attractive features of material since the conversion between the distinct high and low dielectric states has succeeded in photoelectronic fields. As one of the most promising strategies to assemble such a functional material, usually, to design and synthesize molecule compounds with structural transformations effectively acquires the typically temperature-dependent dielectric states. To continuously explore this context, herein, we present our study of the crystal structures and dielectric properties of two $[\text{Ni}(\text{mnt})_2]^{2-}$ salts containing noncentrosymmetric organic cations 1,4-dimethyl-DABCO $^{2+}$ and TMSF $^+$. The two cations maybe show order–disorder structural transformation in their crystals with the temperature changes. Two new salts show similar packing structure and novel dielectric properties.

2. Experimental

2.1. Chemicals and materials

All reagents and chemicals, including 1,4-diazoniabicyclo[2.2.2]octane (abbr. DABCO), trimethylsulfonium bromide (abbr. [TMSF]Br) and iodomethane, were purchased from commercial sources and used without further purification.

Disodium maleonitriledithiolate (Na_2mnt) was synthesized following the procedure published [41].

The typical process is described for the preparation of (1,4-dimethyl-DABCO) $_2$. 1,4-diazabicyclo[2.2.2]octane (112 mg, 1 mmol) was solved in 20 mL acetone, and iodomethane (300 mg, 2.1 mmol) was added into the above solution drop by drop and stirring at room temperature. The white precipitate formed gradually, and the mixture was further stirred for 30 min, and the precipitate was separated by suction and washing by absolute ethanol for three times, and dried at 60 °C overnight. Yield ca. 85% (based on DABCO). The final product was characterized by ^1H NMR (D_2O , 400 MHz; ref. Fig. S1) with δ : 4.8 (s, D_2O -D), 4.13 (s, 12H, H-CH_2), 3.43 (s, 6H, H-CH_3).

2.2. Preparation of **1** and **2**

2.2.1. [1,4-Dimethyl-DABCO][Ni(mnt) $_2$] (**1**)

A H_2O solution of Na_2mnt (186 mg, 1 mmol) was added to a H_2O solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (120 mg, 0.5 mmol), the mixture was stirred at room temperature for 10 min, and then filtered. To the filtrate was added dropwise a H_2O solution of (1,4-dimethyl-DABCO) $_2$ (200 mg, 0.5 mmol), the immediately formed dark red precipitate was filtered out, washed with H_2O up to the filtrate being colorless. The precipitate was collected and dried at 60 °C in vacuum for 2 h. Yield ca. 58% (calculation based on $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$). Calc. for $\text{C}_{16}\text{H}_{18}\text{N}_6\text{NiS}_4$: C, 39.93; H, 3.770; N, 17.46%; Found: C, 40.00; H, 3.86; N, 17.85%.

2.2.2. (TMSF) $_2$ [Ni(mnt) $_2$] (**2**)

This salt was prepared following a similar process for preparation of **1**, just replaced (1,4-dimethyl-DABCO) $_2$ by [TMSF]Br. Yield ca. 77%. Calc. for $\text{C}_{14}\text{H}_{18}\text{N}_4\text{NiS}_6$: C, 34.08; H, 3.677; N, 11.36%; Found: C, 33.33; H, 3.73; N, 11.33%.

The single crystals suitable for X-ray analysis for **1** and **2** were achieved via a diffusion process, namely, the powdered sample of **1** or **2** were dissolved in the minimum amount of DMF, and absolute ethanol diffuses into the DMF solution of **1** or **2** to give the corresponding crystals.

2.3. Physical measurements

Elemental analyses (C, H and N) were carried out on a Perkin Elmer 240C analytical instrument. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{-1} region. The UV–vis–NIR absorption spectra in solid state were taken using a Shimadzu UV-3100 spectrometer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku/max-2550 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Thermogravimetric (TG) experiments were performed with a TA2000/2960 thermogravimetric analyzer from 293 K to 1063 K at a heating rate of 20 K min^{-1} under a nitrogen atmosphere, and the polycrystalline samples were placed in an aluminum crucible. Differential scanning calorimetry (DSC) was carried out for **1** and **2** on a Pyris 1 power-compensation differential scanning calorimeter with a warming rate of 10 K min^{-1} during the heating process. Temperature- and frequency-dependent dielectric permittivity and AC impedance measurements were carried out on a Concept 80 system (Novocontrol, Germany) in 153–403 K and 153–373 K for **1** and **2**, respectively. The powdered disc, with a thickness of ca. 1.68 mm (for **1**) and 1.36 mm (for **2**) as well as a diameter of 7.0 mm, was coated by gold films on the opposite surfaces and sandwiched by platinum electrodes and the AC frequencies span from 1 to 10^7 Hz.

2.4. X-ray single crystallography

The single crystal X-ray diffraction data were collected for **1** and **2** with graphite monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) on a CCD area detector (Bruker-SMART). Data reductions and absorption corrections were performed with the SAINT [42] and SADABS [43] software packages, respectively. Structures were solved by direct methods using the SHELXL-97 software package [44]. The non-H atoms were anisotropically refined using the full-matrix least squares method on F^2 . All H atoms were placed at calculated positions and refined riding on the parent atoms. The crystallographic details about data collection and structure refinement are summarized in Table 1.

3. Results and discussion

3.1. Crystal structure analysis

Salt **1** crystallizes in monoclinic space group $C2/c$. As shown in Fig. 1a, an asymmetric unit of **1** contains one half of $[\text{Ni}(\text{mnt})_2]^{2-}$ dianion and one half of divalent 1,4-Dimethyl-1,4-diazoniabicyclo[2.2.2]octane (abbr. $\text{Me}_2\text{-DABCO}^{2+}$) cation. The Ni^{2+} ion locates at an inversion center, which lead to the NiS_4 core being cofacial in $[\text{Ni}(\text{mnt})_2]^{2-}$. The $[\text{Ni}(\text{mnt})_2]^{2-}$ has C_i point group symmetry, and the planar mnt^{2-} ligand makes a dihedral angle of 7.8° with the plane of NiS_4 core. Two crystallographically inequivalent Ni–S bond lengths are 2.1753(6) and 2.1780(6) Å , respectively; and the S–Ni–S bite angle is $92.59(2)^\circ$. These bond parameters in $[\text{Ni}(\text{mnt})_2]^{2-}$ are comparable to that in other $[\text{Ni}(\text{mnt})_2]^{2-}$ salts reported [39,40]. The $\text{Me}_2\text{-DABCO}^{2+}$ shows the C_2 point group symmetry, and the twofold rotation axis is parallel to the b -axis and passes through the midpoint of a segment connecting N3 and N3#1 with the symmetric code $\#1 = 1 - x, y, 0.5 - z$.

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