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# Crystal structures, electronic spectra and magnetic properties of homoleptic and heteroleptic metal-dithiolate molecular solids

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ABSTRACT

Two nickel-bis-(1,2-dithiolate) molecular solids, (4-ClBzEt$_3$N)[Ni(dmit)$_x$(mnt)$_{2-x}$] ($x$ = 0 (**1**) and 1 (**2**)) (where 4-ClBzEt$_3$N$^+$ = 4-chloro-benzyltriethylammonium; dmit$^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate; mnt$^{2-}$ = maleonitriledithiolate) were synthesized and characterized structurally. The infrared (IR) spectra, powder X-ray diffraction (PXRD), UV–Vis absorption and magnetic properties have been investigated for **1** and **2**. The homoleptic metal-dithiolene complex **1** crystallizes in monoclinic system with space group $P\bar{1}$. The anions of **1** are aligned into columnar stacks along $a$-axis direction. The neighboring anions are connected via lateral-to-lateral S...S contacts of mnt$^{2-}$ ligands are observed between the cations and the anions. The powder X-ray diffraction patterns are in good agreement with the simulated patterns based on the crystal structures, indicating the purity of the as-grow crystals. FT-IR and UV–Vis absorption spectra were recorded and analyzed for **1** and **2**. The variable-temperature magnetic susceptibility analysis shows that **1** follow the Curie–Weiss law below 50 K and a spin-gap between 50 and 205 K, and **2** exhibits a weak antiferromagnetic exchange interaction as the temperature is lowered and the magnetic susceptibility data follows the $S = {}^1/_2$ Heisenberg alternating linear-chain model in the temperature range 109–400 K and a spin gap below 109 K for **2**.



## 1. Introduction

The transition metal-bis-1,2-dithiolene complexes have been investigated intensively during the past decades, regarding their magnetic [1–4], conducting [5–7], and were shown to being processable by thin film methods [8,9]. In recent years, some novel physical properties been found in the transition metal dithiolate complexes. For instance, quantum coherence was observed in (PPh$_4$)$_2$[Cu(mnt)$_2$] (mnt$^{2-}$ = maleonitriledithiolate) doped into the diamagnetic isostructural host (PPh$_4$)$_2$[Ni(mnt)$_2$] as a very promising quantum bit. It was found that this complex has very long quantum coherence times of 68 μs at low temperature (qubit figure of merit $Q_M$ = 3400) and 1 μs at room temperature, much higher than previously reported values for such systems [10]. Since then, a series of qubits have been designed and millisecond coherence time could be achieved through chemical tuning of nuclear spin content in the molecular electronic spin qubit (Ph$_4$P)$_2$[V(C$_8$S$_8$)$_3$] and the species ($d_{20}$-Ph$_4$P)$_2$[V(C$_8$S$_8$)$_3$], with a coherence time ($T_2$) of ~1 ms for the deuterated species [11]. Besides, a simple first-principles methodology was to applied to a highly coherent complex [Cu(mnt)$_2$]$^{2-}$, and to determine the modulation that vibrations exert on spin energy levels [12].

It is well known that many [M(mnt)$_2$]$^-$ and [M(dmit)$_2$]$^-$ (M = Ni, Pd, Pt etc.; mnt$^{2-}$ = maleonitriledithiolate; dmit$^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate) complexes with various organic cations have been widely reported [13–24] and their magnetic and electric properties and structure–functionality relationships have been investigated. In recent years, Nishihara et al. prepared a functional molecular crystal, (ethyl-4-bromothiazolium)$_2$[Pt(mnt)$_2$]$_3$, constructed by a novel two-dimensional cation···anion supramolecular structure via sulfur's $\sigma$-holes. And it is showed that sulfur-based $\sigma$-hole bonds are rigid enough to contribute to modulating the physical properties and structural transition through regulating the displacement of molecules [25]. In addition, some systematical studies are made for the influence of dithiolate ligand structure on the arrangement of [M(dithiolato)$_2$]$^-$ anions in the crystal and the physical properties of the salts and some heteroleptic

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metal-bis-1,2-dithiolene complexes have been reported [26–29]. For example, a heteroleptic nickel-bis-1,2-dithiolene complex (BzQl)[Ni(dmit)(mnt)] (where $BzQl^+$ = 1-(benzyl) quinolinium) has an unusual hysteretic magnetic transition and the relationship between the crystal structure and magnetic feature has been investigated in the reported paper [30]. Another complex (4-ClBz-1-APy)[Ni(dmit)(mnt)] (where $4\text{-ClBz-1-APy}^+$ = 4-chloro-benzyliden-1-aminopyridinium) exhibits antiferromagnetic magnetic behavior in the temperature range of 40–300 K and Curie–Weiss type magnetic behavior below 40 K in the temperature dependent magnetic susceptibility [31]. Recently, three nickel-bis-dithiolate salts $(Bz\text{-}Et_3N)[Ni(dmit)_x(mnt)_{2-x}]$ (where $x$ = 0–2) have been prepared and characterized and the molecular structure of dithiolate ligand dependent crystal structures and magnetic properties have been explored [32].

Up to date, the investigations on the crystal structure and magnetic properties of the heteroleptic metal-bis-1,2-dithiolene complexes are still rare and it is essential to expand the research in this area and systematic study its physical properties such as magnetism, electrical properties, and so on, and structure–functionality relationship. Therefore, more heteroleptic metal-bis-1,2-dithiolene complexes with novel physical properties maybe obtained by changing the structure and electronic properties of the couterions. In this paper, we reported two novel one-dimensional molecular solids $(ClBzEt_3N)[Ni(dmit)_x(mnt)_{2-x}]$ ($x$ = 0 (**1**) and 1 (**2**)), and explored the crystal structures, UV–Vis absorption spectra and magnetic properties.

## 2. Experimental

### 2.1. Chemicals and materials

The staring materials $Na_2mnt$ [33], 4,5-bis(thiobenzoyl)-1,3-dithiol-2-thione [34] and $[4\text{-}ClBzEt_3N]Cl$ [35] were respectively synthesized using the methods described in the literatures. $[4\text{-}ClBzEt_3N]_2[Ni(mnt)_2]$ was prepared employing the similar procedure reported in the literature [32].

### 2.2. Preparation

#### 2.2.1. [4-ClBzEt$_3$N][Ni(mnt)$_2$] (**1**)

A MeOH solution (10 $cm^3$) of $I_2$ (205 mg, 0.80 mmol) was slowly added to a MeCN solution (25 $cm^3$) of $[4\text{-}ClBzEt_3N]_2[Ni(mnt)_2]$ (793 mg, 1.0 mmol), the mixture was allowed standing overnight after stirred for 25 min. The dark powder formed were filtered off, washed with MeOH and dried under vacuum. Yield ca. 71 % (based on $[4\text{-}ClBzEt_3N]_2[Ni(mnt)_2]$). *Anal.* Calc. for $C_{21}H_{21}ClN_5NiS_4$: C, 44.57; H, 3.74; N, 12.38. Found: C, 44.38; H, 3.34; N, 12.35%.

#### 2.2.2. [4-ClBzEt$_3$N][Ni(dmit)(mnt)] (**2**)

Compound **2** was obtained by ligand-exchange reaction between $[4\text{-}ClBzEt_3N][Ni(mnt)_2]$ (170 mg, 0.3 mmol) and $[4\text{-}ClBzEt_3N][Ni(dmit)_2]$ (202 mg, 0.3 mmol) in refluxing acetone (100 mL) under vigorous stirring for two days. The mixture was filtered and the filtrate was concentrated under reduced pressure over-night, whereupon micro-crystals were formed. Yield: ca. 69% (based on $[4\text{-}ClBzEt_3N][Ni(dmit)_2]$). Elemental analysis calcd. (%) for $C_{20}H_{21}ClN_3NiS_7$: C, 38.62; H, 3.40; N, 6.76. Found: C, 38.76; H, 3.78; N, 6.55%.

Crystals of **1** and **2** suitable for single crystal X-ray diffraction were obtained by slow evaporation of the saturated acetonitrile or acetone of the corresponding compound at ambient temperature for 5–7 days.

### 2.3. Physical measurements

Elemental analyses for C, H and N were performed with an Elementar Vario EL III analytic instrument. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 diffractometer with Cu Kα radiation ($\lambda$ = 1.5418 Å) with a scanning range from 5 to 50° at a scanning rate 2° $min^{-1}$. FT-IR spectra were recorded on a Bruker Vertex 80 FT-IR (4000–400 $cm^{-1}$) spectrophotometer with KBr pellets. UV-visible-NIR spectra measurements in the solution were taken using a PerkinElmer Lambda 950 UV/VIS/NIR spectrometer. Magnetic susceptibilities were measured on a Quantum Design MPMS-5 superconducting quantum interference device (SQUID) magnetometer over the temperature range 1.8–400 K.

### 2.4. X-ray crystallography

The single-crystal X-ray diffraction data were collected for **1** at 293 K with graphite monochromated Mo Kα ($\lambda$ = 0.71073 Å) on a CCD area detector (*Bruker-SMART*). Data reductions and absorption corrections were performed with the SAINT and SADABS software packages [36], respectively. Structures were solved by a direct method using the SHELXL-97 software package [37]. The non-hydrogen atoms were anisotropically refined using the full-matrix least-squares method on $F^2$. All hydrogen atoms were placed at the calculated positions and refined riding on the parent atoms. Unfortunately, the final crystal structure for **2** was not obtained, thus the detailed discussion about crystal structure could not be given. The details about data collection, structure refinement and crystallography are summarized in Table 1.

## 3. Results and discussion

### 3.1. Synthesis and IR spectrum

The heteroleptic compound **2** was synthesized through the ligand exchange reaction between the $[4\text{-}ClBzEt_3N][Ni(mnt)_2]$ (**1**)

**Table 1**
Crystal data and structural refinement of **1**.

| Compound | **1** |
|---|---|
| $T$ (K) | 293(2) |
| Chemical formula | $C_{21}H_{21}ClN_5NiS_4$ |
| Formula weight | 565.83 |
| Wavelength (Å) | 0.71073 |
| CCDC number | 1579265 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 7.4196(10) |
| $b$ (Å) | 11.8953(16) |
| $c$ (Å) | 15.4505(19) |
| $\alpha$ (°) | 96.558(4) |
| $\beta$ (°) | 93.965(4) |
| $\gamma$ (°) | 111.060(4) |
| $V$ (Å$^3$) | 1255.3(3) |
| $Z$ | 4 |
| Density (g·cm$^{-3}$) | 1.497 |
| Abs coeff. (mm$^{-1}$) | 1.231 |
| $F$(000) | 582 |
| Data collect $\theta$ range | 1.42–27.55 |
| Index range | $-9 \le h \le 9$, $-15 \le k \le 15$, $-19 \le l \le 20$ |
| Reflns collected | 19 503 |
| Independent reflns | 5726 |
| Data/restraints/parameters | 5726/0/292 |
| Refine method | The least square refinement on $F^2$ |
| $R_{int}$ | 0.0448 |
| Goodness-of-fit (GOF) on $F^2$ | 1.041 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0383<br>$wR_2$ = 0.0903 |
| $R$ indices (All data) | $R_1$ = 0.0783<br>$wR_2$ = 0.1030 |

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