



Crystal structures, magnetic and dielectric features of two new isostructural one-dimensional platinum-bis-dithiolene molecular solids



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ABSTRACT

Two new one-dimensional (1-D) molecular solids, $[\text{CH}_2 = \text{CH-BzPy}][\text{Pt}(\text{mnt})_2]$ (**1**) and $[\text{CH}_2 = \text{CH-BzPy-d}_5][\text{Pt}(\text{mnt})_2]$ (**2**) where $\text{CH}_2 = \text{CH-BzPy-d}_5^+ = 1\text{-N-(4-vinylbenzyl) pyridinium-d}_5$ and $\text{mnt}^{2-} = \text{maleonitriledithiolate}$, were synthesized and characterized. A structural phase transition undergoes with $T_C \approx 335\text{ K}$ in the crystals of **1** and **2**, which were confirmed by variable-temperature magnetic susceptibility and DSC measurements. Crystals of **1** and **2** are isostructural in both high- and low-temperature phases. Besides the strong similarity in crystal structures, they show quite analogous magnetic and dielectric features. Above T_C , the magnetic behavior is failed to follow the $S = 1/2$ Heisenberg linear chain model; below T_C , a spin gap is opened for **1** and **2**. The thermally-assisted dielectric relaxation occurs above ca. 280 K for **1** and **2**, and this relaxation process is related to the dipole motion of the disordered $\text{CH}_2 = \text{CH}$ groups in the cation under an ac electrical field.

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1. Introduction

The planar metal-bis-maleonitriledithiolate (abbr. as $[\text{M}(\text{mnt})_2]^-$, where $\text{M} = \text{Ni, Pd and Pt}$) salts have been widely studied since 1960s owing to displaying a versatile set of structural and physical properties [1–9]. For instance, the insulator salt $[\text{NH}_4][\text{Ni}(\text{mnt})_2] \cdot \text{H}_2\text{O}$ exhibits Heisenberg antiferromagnetic (AFM) chain behavior around room temperature and the ground state is a singlet with the monoanions associated as dimer at low temperatures [10,11]. It is very interesting that this salt, with localized spins, shows long-range ferromagnetic order below 4.5 K and the Curie temperature demarcating the transition to ferromagnetic order abruptly disappears at 6.8 kbar applied pressure [1]. The salt, $[\text{H}_3\text{O}]_{0.33}\text{Li}_{0.8}[\text{Pt}(\text{mnt})_2] \cdot 1.67\text{H}_2\text{O}$, shows metallic properties at room temperature but undergoes the Peierls instability at ca. 220 K to become a semiconductor [12,13] and the non-stoichiometric salt, $\text{Cs}_{0.82}[\text{Pd}(\text{mnt})_2] \cdot 0.5\text{H}_2\text{O}$, is the first palladium dithiolene complex to exhibit metallic behavior under pressure [2].

The ion-pair arrangement in the $[\text{M}(\text{mnt})_2]^-$ ($\text{M} = \text{Ni, Pd and Pt}$) crystal, directly related to the physical properties of the salts, is strongly affected by the nature of counteraction. Besides this, the ion-pair arrangement and the physical properties are also sensitive to the metal ion in $[\text{M}(\text{mnt})_2]^-$. In the series of one-dimensional (1-D) salts, $[\text{R-BzPy}][\text{M}(\text{mnt})_2]$ (where BzPy^+ and R represent the benzylpyridinium and substituent, $\text{M} = \text{Ni, Pd or Pt}$), it was observed that most $[\text{Ni}(\text{mnt})_2]^-$ -based salts [14] and a few of $[\text{Pt}(\text{mnt})_2]^-$ -based salts [15,16] experience a spin-Peierls-type transition, however, all 1-D $[\text{Pd}(\text{mnt})_2]^-$ -based salts displayed diamagnetism owing to the neighboring $[\text{Pd}(\text{mnt})_2]^-$ anions being strongly dimerized [17,18]. In addition, the critical temperature of spin-Peierls-type transition, T_C , is much higher in $[\text{Pt}(\text{mnt})_2]^-$ -based salt than the corresponding $[\text{Ni}(\text{mnt})_2]^-$ -based analogue [14–16]. Most recently, we investigated the isotopic effect of the $[\text{R-BzPy}][\text{M}(\text{mnt})_2]$ ($\text{M} = \text{Ni or Pt}$) series via replacing the pyridine moiety by pyridine- d_5 in the benzylpyridinium derivatives, and observed that the R-BzPy^+ replaced by R-BzPy-d_5^+ leads to the critical temperature of magnetic phase transition, T_C , up shifting 2–8 K in the $[\text{R-BzPy}][\text{Ni}(\text{mnt})_2]$ family [19,20], while there is no sizable isotopic effect in the $[\text{R-BzPy}][\text{Pt}(\text{mnt})_2]$ family [16].

To better understand the issue of metal ion dependent magnetic and phase transition behaviors in the $[\text{M}(\text{mnt})_2]^-$ salts ($\text{M} = \text{Ni, Pd}$

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or Pt), from more studies and using other examples, is desirable. Herein, we report the crystal structures, magnetic and dielectric features for two new 1-D $[\text{Pt}(\text{mnt})_2]^-$ -based spin-Peierls-type transition slats, $[\text{CH}_2=\text{CH-BzPy}][\text{Pt}(\text{mnt})_2]$ and $[\text{CH}_2=\text{CH-BzPy-d}_5][\text{Pt}(\text{mnt})_2]$.

2. Experimental

2.1. Chemicals and materials

All reagents and chemicals were purchased from commercial sources and used without further purification. Na_2mnt was prepared following the approach in literature [21]. $[\text{CH}_2=\text{CH-BzPy}]\text{Br}$, $[\text{CH}_2=\text{CH-BzPy-d}_5]\text{Br}$, $[\text{CH}_2=\text{CH-BzPy}]_2[\text{Pt}(\text{mnt})_2]$ and $[\text{CH}_2=\text{CH-BzPy-d}_5]_2[\text{Pt}(\text{mnt})_2]$ were synthesized utilizing a similar procedure for preparation of $[\text{Br-BzPy}]_2[\text{Pt}(\text{mnt})_2]$ [19], instead of 1-*N*-(4'-bromobenzyl) pyridinium by 1-*N*-(4'-vinylbenzyl) pyridinium or 1-*N*-(4'-vinylbenzyl) pyridinium- d_5 .

2.2. Preparation of $[\text{CH}_2=\text{CH-BzPy}][\text{Pt}(\text{mnt})_2]$ (1)

A methanol solution (10 cm^3) of I_2 (150 mg, 0.59 mmol) was slowly added to the methanol solution (20 cm^3) of $[\text{CH}_2=\text{CH-BzPy}]_2[\text{Pt}(\text{mnt})_2]$ (868 mg, 1.0 mmol), the mixture was stirred for 15 min and allowed to stand overnight, and then 450 mg of black microcrystals were filtered off, washed with methanol and dried under vacuum. Yield: ca. 67%. Elemental microanalysis calculated for $\text{C}_{22}\text{H}_{14}\text{N}_5\text{PtS}_4$ (1): C, 39.34; H, 2.10; N, 10.43%. Found: C, 39.39; H, 2.32; N, 10.55%. IR spectrum (KBr pellet, cm^{-1}) and the assignments for the listed bands [22,23]: 3128(w), 3085(w) and 3065(w), 3050(w) attributed to the $\nu_{\text{C-H}}$ of the pyridyl and phenyl rings; 2205(vs) assigned to the $\nu_{\text{C}\equiv\text{N}}$ of the mnt^{2-} ligands; 1631(s) 1560(w), 1496(s), 1456(s) attributed to the ring stretching vibration of the pyridyl and phenyl rings in the cation; 1485(s) arose from the $\nu_{\text{C-C}}$ of the mnt^{2-} ligands; 1158(vs) arose from the $\nu_{\text{C-S}} + \nu_{\text{C-C}}$ of mnt^{2-} ligands; 1117(w) attributed to $\pi_{\text{C-CN}}$ of mnt^{2-} ligands.

A similar procedure was used for preparation of $[\text{CH}_2=\text{CH-BzPy-d}_5][\text{Pt}(\text{mnt})_2]$ (2) instead of $[\text{CH}_2=\text{CH-BzPy}]_2[\text{Pt}(\text{mnt})_2]$ by $[\text{CH}_2=\text{CH-BzPy-d}_5]_2[\text{Pt}(\text{mnt})_2]$. The yield is more than 75%. Microanalysis calculated for $\text{C}_{22}\text{H}_9\text{D}_5\text{N}_5\text{PtS}_4$ (2): C, 39.04; H and D, 2.83; N, 10.35%. Found: C, 39.15; H and D, 2.50; N, 10.58%. IR spectrum (KBr pellet, cm^{-1}) and assignments for the listed bands [22]: 3080(w), 3048(w) attributed to the $\nu_{\text{C-H}}$ of phenyl rings; 2307(w), 2303(w) assigned to the $\nu_{\text{C-D}}$ of phenyl rings and 2205 (vs) attributed to the $\nu_{\text{C}\equiv\text{N}}$ of the mnt^{2-} ligands; 1585(vs) and 1552(m) assigned to the ring stretching vibration of the pyridyl and phenyl rings in the cation; 1465(s) arose from the $\nu_{\text{C=C}}$ of the mnt^{2-} ligands; 1160(vs) arose from the $\nu_{\text{C-S}} + \nu_{\text{C-C}}$ of mnt^{2-} ligands; 1115 (w) and 536(vs) attributed to $\pi_{\text{C-CN}}$ of mnt^{2-} ligands.

The single crystals, being suitable for X-ray diffraction structure analyses, were obtained by slow evaporation of the solutions of 1 and 2 in MeCN at ambient temperature for two weeks, respectively.

2.3. Physical measurements

Elemental analyses (C, H and N) were performed with an Elementar Vario EL III analytical instrument. IR spectra at room temperature were recorded on a Bruker VERTEX80V Fourier transform infrared spectrometer (KBr disc) under vacuum. Power X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance powder diffractometer operating at 40 kV and 40 mA for Cu $\text{K}\alpha$ radiation with $\lambda = 1.54018 \text{ \AA}$. Samples were scanned from $2\theta = 5-50^\circ$ with $0.02^\circ/\text{step}$ and 1.2 s/step. The measurements of the temperature, frequency dependent dielectric permittivity was carried out by employing a concept 80 system (Novocontrol, Germany) in the ranges of 223–373 K (from -50 to 100°C), the sample prepared in the form of a pellet with a 10.0 mm diameter and ca. 0.60 mm thickness for 1 (10.0 mm diameter and ca. 0.25 mm thickness for 2) was sandwiched between two parallel copper electrodes and the ac electrical field frequencies span from 1 Hz to 10^7 Hz. Magnetic susceptibility data were measured for polycrystalline samples over a temperature range of 1.8–400 K

Table 1
Crystallographic data and refinement parameters for 1 and 2 in HT and LT phases.

Compound	1		2	
Temp. (K)	296(2)	373(2)	296(2)	373(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Formula	$\text{C}_{22}\text{H}_{14}\text{N}_5\text{PtS}_4$	$\text{C}_{22}\text{H}_{14}\text{N}_5\text{PtS}_4$	$\text{C}_{22}\text{H}_9\text{D}_5\text{N}_5\text{PtS}_4$	$\text{C}_{22}\text{H}_9\text{D}_5\text{N}_5\text{PtS}_4$
Formula weight	671.70	671.70	676.71	676.71
Space group	P-1	P2 ₁ /c	P-1	P2 ₁ /c
CCDC no.	1023555	1023556	1023557	1023558
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
a (Å)	7.2846(14)	12.446(6)	7.2810(8)	12.3629(8)
b (Å)	12.351(3)	27.608(14)	12.3070(13)	27.5731(19)
c (Å)	27.395(6)	7.456(4)	27.366(3)	7.3942(4)
α (°)	88.902(7)	90	88.810(4)	90
β (°)	86.374(6)	104.006(15)	86.287(4)	104.220(6)
γ (°)	75.433(6)	90	75.704(3)	90
V (Å ³)/Z	2380.7(9), 4	2486(2), 4	2371.3(4), 4	2443.3(3), 4
ρ (g cm ⁻³)	1.874	1.795	1.896	1.840
F (000)	1292	1292	1292	1268
Abs. coeff. (mm ⁻¹)	6.265	6.000	6.290	6.104
θ Range for data collection (°)	0.74 – 27.56	1.69 – 27.42	0.75 – 27.47	2.94 – 28.59
Index ranges	–9 ≤ h ≤ 9 –15 ≤ k ≤ 16 –35 ≤ l ≤ 35	–15 ≤ h ≤ 16 –35 ≤ k ≤ 35 –9 ≤ l ≤ 9	–9 ≤ h ≤ 9 –15 ≤ k ≤ 15 –35 ≤ l ≤ 35	–13 ≤ h ≤ 15 –36 ≤ k ≤ 18 –9 ≤ l ≤ 9
R_{int}	0.0524	0.0682	0.0643	0.0643
Independent reflect./restraints/parameters	10897/0/597	5593/0/299	10799/0/597	5478/0/299
Refinement method	The least square refinement on F^2			
Goodness of fit on F^2	1.122	1.024	1.079	0.934
R_1, wR_2^a [$I > 2\sigma(I)$]	0.0572, 0.1351	0.0445, 0.0854	0.0362, 0.0742	0.0541, 0.0585
R_1, wR_2^a [all data]	0.0845, 0.1441	0.0909, 0.0983	0.0665, 0.0833	0.1464, 0.0840
Residual (e Å ⁻³)	1.764/–2.330	1.106/–0.756	0.853/–1.447	0.729/–0.807

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