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Strong antiferromagnetic exchange interactions in quasi-one-dimensional (quasi-1D) compounds based on $[Pd(mnt)_2]^-$ anions: Crystal structures, magnetic properties, and spin dimer analyses

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Abstract

Four ion-pair compounds that are based on the $[Pd(mnt)_2]^-$ anion were synthesized and structurally characterized. Crystal structure determinations revealed that, in all four cases, the anions and cations stack as segregated columns, and that adjacent $[Pd(mnt)_2]^-$ anions exhibit a strong tendency of dimerization within an anionic column. Values of $\chi_m(T)$ in 2–350 K indicated that these compounds are nearly diamagnetic. Results of the spin dimer analyses for the magnetic exchange interactions between the nearest-neighbor spins qualitatively illustrated the magnetic behaviors of these compounds.

Keywords: Bis(maleonitriledithiolato)palladium compound; Crystal structure; Magnetic property; Molecular orbital calculation and analysis

1. Introduction

Significant amounts of research have been directed towards the study of the magnetism and conductivity characteristics of $[M(mnt)_2]^-$ (M = Ni, Pd, or Pt ions; mnt^{2-} = maleonitriledithiolate) compounds [1–4]. Recently, using benzylpyridinium derivatives ($[RBzPy]^+$) as the counter-cation of $[M(mnt)_2]^-$ (M = Ni or Pt), a series of ion-pair compounds that show segregated columnar stacks of cations and anions have been prepared [5]. The quasi-one-dimensional (quasi-1D) magnetic nature of these compounds was attributed to intermolecular π-orbital interactions within the anionic columns. Furthermore, for some compounds, spin-Peierls-like phase transition was observed [5]. Herein, we describe syntheses, crystal structures, magnetic properties, and molecular orbital calculations for [1-(4′-R-benzyl)pyridinium][$Pd(mnt)_2$] (R = Cl, Br, I, or NO_2).

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2. Experiment

1-(4′-R-benzyl)pyridinium bromide ([RBzPy]Br) and disodium maleonitriledithiolate (Na_2mnt) were synthesized following published procedures [6]. The four types of [RBzPy][$Pd(mnt)_2$], in which R = Cl (**1**), Br (**2**), I (**3**), and NO_2 (**4**), were prepared using similar procedures as in the syntheses of [RBzPy][$Ni(mnt)_2$] and [RBzPy][$Pt(mnt)_2$]. Elemental analysis: Calcd. for $C_{20}H_{11}N_5ClS_4Pd$ (**1**): C, 40.6%; N, 11.8%; H, 1.87%. Found: C, 40.4%; N, 11.9%; H, 1.97%. $\nu_{C\equiv N}$ (KBr disc): 2207(s), 2218(sh) cm^{-1}. Calcd. for $C_{20}H_{11}N_5BrS_4Pd$ (**2**): C, 37.8%; N, 11.0%; H, 1.74%. Found: C, 37.8%; N, 11.1%; H, 1.81%. $\nu_{C\equiv N}$ (KBr disc): 2205(s), 2219(sh) cm^{-1}. Calcd. for $C_{20}H_{11}N_5IS_4Pd$ (**3**): C, 35.2%; N, 10.3%; H, 1.62%. Found: C, 35.1%; N, 10.1%; H, 1.75%. $\nu_{C\equiv N}$ (KBr disc): 2207(s), 2216(sh) cm^{-1}. Calcd. for $C_{20}H_{11}N_6O2S_4Pd$ (**4**): C, 39.9%; N, 14.0%; H, 1.84%. Found: C, 39.1%; N, 13.4%; H, 2.01%. $\nu_{C\equiv N}$ (KBr disc): 2206(s), 2220(sh) cm^{-1}.

The single crystals suitable for X-ray analysis were obtained by dispersing Et_2O into the MeCN solu-

Table 1
Crystal and structural refinement data for **1**–**4**

	1	**2**	**3**	**4**
Chemical formula	$C_{20}H_{11}ClN_5S_4Pd$	$C_{20}H_{11}BrN_5S_4Pd$	$C_{20}H_{11}IN_5S_4Pd$	$C_{20}H_{11}N_6O_2S_4Pd$
Formula weight	591.43	635.89	682.88	601.99
Temperature (K)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71075	0.71075	0.71075	0.71075
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	P-1 (#2)	$P2_1/c$ (#14)
a (Å)	7.2672(15)	7.3390(15)	7.5762(15)	7.1392(14)
b (Å)	26.120(5)	26.225(5)	12.354(3)	26.440(5)
c (Å)	12.729(3)	12.634(3)	14.253(3)	12.711(3)
α (°)	90	90	111.64(3)	90
β (°)	105.63(3)	105.26(3)	90.14(3)	105.88(3)
γ (°)	90	90	103.07(3)	90
V (Å^3), Z	2326.9(8), 4	2345.9(8), 4	1202.5(4), 2	2307.9(8), 4
Density (calc) (g/cm^3)	1.688	1.800	1.886	1.733
Abs coeff. (mm^{-1})	1.289	2.868	2.421	1.197
F(0 0 0)	1172.00	1244.00	658.00	1196.00
θ range for data collection	3.01–27.48	3.02–27.48	3.04–25	3.06–27.48
Index ranges	$-9 \le h \le 8$ $-33 \le k \le 33$ $-16 \le l \le 16$	$-9 \le h \le 9$ $-34 \le k \le 34$ $-16 \le l \le 16$	$-9 \le h \le 8$ $-14 \le k \le 14$ $-16 \le l \le 16$	$-9 \le h \le 9$ $-34 \le k \le 34$ $-16 \le l \le 16$
Reflns collected	5289	5374	4050	5258
Independent reflns	3584 (R_{int} = 0.0299)	3281 (R_{int} = 0.0480)	2607 (R_{int} = 0.0306)	3662 (R_{int} = 0.0393)
Refinement method on F^2	Full-matrix least-squares			
Data/restraints/params	3584/0/280	3281/0/280	2607/0/269	3662/0/298
Goodness-of-fit on F^2	0.877	1.021	1.305	0.938
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0268 wR_2 = 0.0524	R_1 = 0.0470 wR_2 = 0.1329	R_1 = 0.0830 wR_2 = 0.2760	R_1 = 0.0257 wR_2 = 0.0547
R indices (all data)	R_1 = 0.0459 wR_2 = 0.0559	R_1 = 0.0768 wR_2 = 0.1409	R_1 = 0.1120 wR_2 = 0.3069	R_1 = 0.0445 wR_2 = 0.0687
Residual (eÅ^{-3})	0.534 and −0.389	2.017 and −1.896	3.622 and −3.041	0.400 and −0.324

tion of the corresponding [RBzPy][Pd(mnt)$_2$] for ∼1 week.

2.1. X-ray crystallography

Crystallographic details on the data collection and structure refinement are summarized in Table 1. Diffraction data were collected at 293 K on a Rigaku R-AXIS RAPID IP area detector. Structures were solved by direct methods using SHELX-97 and refined by the full-matrix least-squares method on F^2 using SHELXL-97 [7]. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were introduced at calculated positions.

2.2. Magnetic susceptibility measurements and molecular orbital calculations

Magnetic susceptibility data on powder-sample were collected over the temperature range of 2–350 K using a Quantum Design MPMS XL superconducting quantum interference device (SQUID) magnetometer. Spin dimer analyses for the neighboring [Pd(mnt)$_2$]$^-$ anions were performed within the tight-binding approximation using extended Hückel molecular orbital calculations [8]. The HOMO of [Pd(mnt)$_2$]$^-$ anions were used as the basis functions. Published values of the extended Hückel parameters for Slater-type atomic orbitals were utilized [9].

3. Results and discussion

3.1. Descriptions of the crystal structures

The Oka Ridge Thermal Ellipsoid Plot (ORTEP) view of **1** in an asymmetric unit is shown in Fig. 1. The Pd ion in

Table 2
Intermolecular separations and the inter-plane distances

	1	**2**	**3**	**4**
d_1	3.4088(7)	3.4183(9)	3.4555(22)	3.3983(9)
d_2	4.2234(9)	4.2972(11)	4.5422(22)	4.0889(10)
d_3	3.3909(10)	3.3920(20)	3.4192(52)	3.3733(17)
d_4	4.2054(10)	4.2773(21)	4.5079(51)	4.0885(18)
d_5	3.595	3.612	3.705	3.540
d_6	3.418	3.428	3.459	3.301
d_7	3.545	3.506	3.722	3.367
d_8	3.513	3.480	3.681	3.452
d_9	3.889	3.946	4.008	3.995
d_{10}	4.491	4.631	4.884	4.542