

Preparation and Properties of Bis(oxalato)platinate and Bis(1,3-dithiole-2-thione-4,5-dithiolato)metallate (M = Ni, Pd, and Pt) Anion Salts with the 1,4-Diethylpyrazinium Dication

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Received August 5, 1985

Abstract

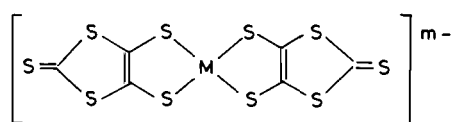
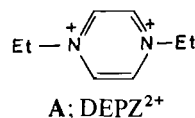
Reactions of $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$ ($\text{C}_2\text{O}_4^{2-}$ = oxalate anion) and $[\text{M}(\text{C}_3\text{S}_5)_2]^{m-}$ ($\text{C}_3\text{S}_5^{2-}$ = 1,3-dithiole-2-thione-4,5-dithiolate anion; $m = 2$ for Ni, Pd and Pt; $m = 1$ for M = Ni and Pt) with the 1,4-diethylpyrazinium dication (DEPZ^{2+}) in acetonitrile gave partially oxidized metallate-anion salts: $[\text{DEPZ}]_{0.9}[\text{Pt}(\text{C}_2\text{O}_4)_2]$ and $[\text{DEPZ}]_{0.3-0.35}[\text{M}(\text{C}_3\text{S}_5)_2]$ (M = Ni, Pd and Pt). They behave as typical semiconductors in the temperature range of -30 – $+40$ °C; electrical resistivities of the $[\text{Pt}(\text{C}_2\text{O}_4)_2]$ and $[\text{M}(\text{C}_3\text{S}_5)_2]$ salts are 3.7×10^5 and 13–620 Ω cm, respectively, at 25 °C for compacted pellets. IR and X-ray photoelectron spectra indicate that the partial oxidation of $[\text{M}(\text{C}_3\text{S}_5)_2]^{m-}$ by DEPZ^{2+} occurs essentially at the dithiolato ligand.

Introduction

Some square-planar nickel(II) and platinum(II) complexes are partially oxidized by oxidants or electrochemically to give one-dimensional, highly conductive metal complexes, such as $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$, $\text{K}_{1.64}\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{C}_2\text{O}_4^{2-}$ = oxalate anion) [1], and $\text{Ni}(\text{L})\text{I}$ (L = phthalocyanine ligands) [2]. On the other hand, partially oxidized bis(dithiolato)metallate-anion salts, $[\text{NBu}^n_4]_{0.29}[\text{Ni}(\text{C}_3\text{S}_5)_2]$ [3] and $[\text{NEt}_4]_{0.5}[\text{Ni}(\text{C}_3\text{S}_5)_2]$ ($\text{C}_3\text{S}_5^{2-}$ = 1,3-dithiole-2-thione-4,5-dithiolate anion) [4], obtained by an electrocrystallization method, have the electrical conduction pathway through the two-dimensional π -systems (predominantly sulfur orbitals). However, partial oxidation of the oxalato- and dithiolato-metallate anions by organic oxidants has not been reported. In addition, introduction of organic cations as a counterpart into the partially oxidized metallate-anion salts by chemical reactions seems to be of interest because of possibilities of a new arrangement of the anions in the crystals, as well as a new interanionic interaction. We have undertaken

to study the reactions of some metallate-anions with the 1,4-diethylpyrazinium dication (DEPZ^{2+} , A), which is a very strong oxidant [5].

This paper reports electrical properties of partially oxidized metallate-anion salts obtained by the reaction of DEPZ^{2+} with $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$ and $[\text{M}(\text{C}_3\text{S}_5)_2]^{m-}$ (B) ($m = 2$ for M = Ni, Pd and Pt; $m = 1$ for M = Ni and Pt) anions. Their electronic states are discussed based on IR, electronic reflectance, X-ray photoelectron, and ESR spectra.



$m = 1$ for M = Ni and Pt;

$m = 2$ for M = Ni, Pd and Pt;

Experimental

Materials

$[\text{DEPZ}][\text{BF}_4]_2$ (DEPZ^{2+} = 1,4-diethylpyrazinium dication) [5], $[\text{NBu}^n_4]_2[\text{Pt}(\text{C}_2\text{O}_4)_2]$ [6], $[\text{NBu}^n_4]_2 \cdot [\text{Pt}(\text{C}_2\text{O}_4)\text{Cl}_2]$ ($\text{C}_2\text{O}_4^{2-}$ = oxalate anion) [7], $[\text{NBu}^n_4]_2[\text{Pt}(\text{CN})_4]$ [6], and $[\text{NBu}^n_4]_m[\text{M}(\text{C}_3\text{S}_5)_2]$ ($\text{C}_3\text{S}_5^{2-}$ = 1,3-dithiole-2-thione-4,5-dithiolate anion; $m = 2$ for M = Ni, Pd and Pt; $m = 1$ for M = Ni and Pt) [8] were prepared according to the literature.

Preparation of 1,4-Diethylpyrazinium Metallate-anion Salts

To an acetonitrile (20 cm^3) solution of $[\text{NBu}^n_4]_2 \cdot [\text{Pt}(\text{C}_2\text{O}_4)_2]$ (50 mg, 58 μmol) was added $[\text{DEPZ}][\text{BF}_4]_2$ (55 mg, 175 μmol) dissolved in acetonitrile (10 cm^3) with stirring under nitrogen atmosphere. Blue-black microcrystals of the partially oxidized salt $[\text{DEPZ}]_{0.9}[\text{Pt}(\text{C}_2\text{O}_4)_2]$ (1), which precipitated

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TABLE I. Colors and Elemental Analyses of the DEPZ²⁺ Salts

Number	Salt	Color	Anal. Found (calc.)		
			%C	%H	%N
1	[DEPZ] _{0.9} [Pt(C ₂ O ₄) ₂]	blue-black	26.65(27.12)	2.87(2.56)	5.10(5.08)
2	[DEPZ] _{0.35} [Ni(C ₃ S ₅) ₂]	black	21.12(21.15)	1.38(0.99)	1.91(1.96)
3	[DEPZ] _{0.35} [Pd(C ₃ S ₅) ₂]	black	19.20(19.31)	1.11(0.92)	1.85(1.79)
4	[DEPZ] _{0.3} [Pt(C ₃ S ₅) ₂]	black	15.82(16.02)	0.84(0.67)	1.33(1.33)
5	[DEPZ][Pt(C ₂ O ₄)Cl ₂]	blue-black	24.07(24.38)	2.99(2.86)	5.64(5.69)
6	[DEPZ][Pt(CN) ₄]	yellow	33.13(32.95)	3.30(3.23)	19.13(19.21)

immediately, were separated by centrifugation, washed with acetonitrile, and dried *in vacuo* (52% yield). Similarly, the reactions of [NBuⁿ₄]₂[M(C₃S₅)₂] (M = Ni, Pd and Pt) with [DEPZ][BF₄]₂ in acetonitrile gave partially oxidized salts, [DEPZ]_{0.35}[Ni(C₃S₅)₂] (2), [DEPZ]_{0.3}[Pt(C₃S₅)₂] (4) and [DEPZ]_{0.35}[Pd(C₃S₅)₂] (3) (51, 48 and 53% yields, respectively). Reactions of [NBuⁿ₄]₂[M(C₃S₅)₂] (M = Ni and Pt) with [DEPZ][BF₄]₂ yielded the metallate-anion salts with essentially the same chemical formula as 2 and 4, respectively. On the other hand, the reaction of [DEPZ][BF₄]₂ with [NBuⁿ₄]₂[Pt(C₂O₄)Cl₂] or [NBuⁿ₄]₂[Pt(CN)₄] gave [DEPZ][Pt(C₂O₄)Cl₂] (5) or [DEPZ][Pt(CN)₄] (6) (40 or 25% yield). Colors and elemental analyses for salts 1–6 are summarized in Table I.

Physical Measurements

Electrical resistivities of the salts were measured for compacted pellets by the conventional two-probe technique [9]. Electronic absorption, powder reflectance [10], and X-ray photoelectron spectra [11] were measured as described elsewhere. IR absorption spectra were recorded on a Hitachi 215 (4000–650 cm⁻¹) spectrophotometer. Spin concentrations of the salts were determined at 77 K by comparing integrated ESR signal intensities of the salts with that of 2,2-diphenyl-1-picrylhydrazyl (DPPH), using the ESR spectrometer described previously [11].

Cyclic voltammetric measurements were performed in acetonitrile containing [NBuⁿ₄]ClO₄ as a supporting electrolyte, using a conventional cell consisting of two platinum wires as working and counter electrodes and a saturated calomel electrode (SCE) as a reference.

Results and Discussion

Reactions of the DEPZ²⁺ Dication with some Square-planar Metallate-anions

The DEPZ²⁺ dication is reduced at +0.39 V vs. SCE in acetonitrile to give the DEPZ^{•+} radical cation, suggesting a strong oxidizing ability. In fact, the DEPZ²⁺ dication reacts with [Pt(C₂O₄)₂]²⁻,

[M(C₃S₅)₂]²⁻ and [M(C₃S₅)₂]⁻ (M = Ni, Pd and Pt) anions to yield blue-black and black DEPZ²⁺ salts containing partially oxidized metallate-anions. The ESR spectra of these salts have given a weak sharp signal (g = 2.004) due to the DEPZ^{•+} radical cation. However, the spin concentrations were estimated at less than 2% from the comparison of the signal intensities with that of DPPH. Thus, the salts may essentially involve the DEPZ²⁺ dication as a counter part.

On the other hand, the [Pt(CN)₄]²⁻ and [Pt-(C₂O₄)Cl₂]²⁻ anions have not been oxidized by the DEPZ²⁺ dication because of high oxidation potentials of these anions; +1.01 and 1.04 V vs. SCE in acetonitrile, respectively. Although the [Pt(C₂O₄)₂]²⁻ anion also has a high oxidation potential (+1.07 V vs. SCE in acetonitrile), it has been slightly oxidized by the DEPZ²⁺ dication to yield blue-black microcrystals of the partially oxidized DEPZ²⁺ salt. On the other hand, [NBuⁿ₄]₂[M(C₃S₅)₂] (M = Ni and Pt) has low oxidation potentials: -0.03 and +0.17 V for M = Ni [3], and -0.08 and +0.11 V vs. SCE in acetonitrile for M = Pt, corresponding to [M(C₃S₅)₂]²⁻/[M(C₃S₅)₂]⁻ and [M(C₃S₅)₂]⁻/[M(C₃S₅)₂]⁰, respectively, while a cyclic voltammogram of [NBuⁿ₄]₂[Pd(C₃S₅)₂] has shown only one redox wave at +0.05 V vs. SCE in acetonitrile. These complexes react with the DEPZ²⁺ dication to form the partially oxidized salts 2–4.

Electrical Properties

Temperature dependences of electrical resistivities (ρ) for the salts, except for 5 and 6 which exhibit large values (>10⁹ Ω cm), are illustrated in Fig. 1. They behave as typical semiconductors in the temperature range from -30 to +40 or 55 °C, while salt 3 exhibits a small refraction in the linear relationship near 15 °C, probably because of a phase transition. Table II summarizes their electrical properties together with those of tetrabutylammonium metallates. The $\rho_{25\text{ }^\circ\text{C}}$ value of 1 lies in the order of 10⁵ Ω cm, which is 10⁴ lower than that of [NBuⁿ₄]₂[Pt(C₂O₄)₂]. In contrast, salts 2–4 exhibit very small $\rho_{25\text{ }^\circ\text{C}}$ values (13–620 Ω cm), which are decreased by ca. seven powers compared with those of [NBuⁿ₄]₂[M(C₃S₅)₂]

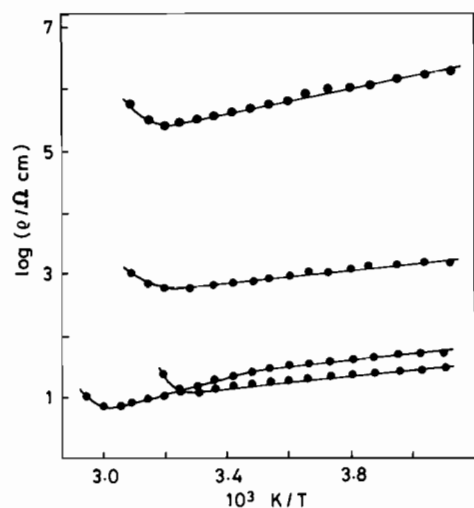


Fig. 1. Temperature dependence of electrical resistivities of the partially oxidized salts.

TABLE II. Electrical Resistivities (ρ)^a and Activation Energies (E_a)^b of the DEPZ²⁺-Metallate Anion Salts and the Tetrabutylammonium Salts

Salt	$\rho_{25^\circ\text{C}}$ ($\Omega \text{ cm}$)	E_a (eV)
[NBu ⁿ ₄] ₂ [Pt(C ₂ O ₄) ₂] 1	> 10 ⁹ 3.7 × 10 ⁵	
[NBu ⁿ ₄] ₂ [Ni(C ₂ O ₄) ₂] 2	4.4 × 10 ⁸ 6.2 × 10	0.65 0.11
[NBu ⁿ ₄] ₂ [Pd(C ₂ O ₄) ₂] 3	1.5 × 10 ⁸ 1.3 × 10	0.50 0.11
[NBu ⁿ ₄] ₂ [Pt(C ₂ O ₄) ₂] 4	2.7 × 10 ⁷ 1.8 × 10	0.41 0.29
5	> 10 ⁹	
6	> 10 ⁹	

^a Compacted samples. ^b Calculated from the equation $\rho = \rho_0 \exp(E_a/kT)$.

($M = \text{Ni}, \text{Pd}$ and Pt). These results indicate that effective conduction pathways are formed in these partially oxidized metallate-anions.

Electronic States of Partially Oxidized Metallate-Anion Salts

Figure 2 shows the electronic reflectance spectra of salt 1 and the tetrabutylammonium salt; the former exhibits a broad band around 10 000 cm^{-1} , but the latter does not. This band may be ascribed to an interanionic interaction through a columnar structure caused by the partial oxidation of the anion moiety. This is consistent with the considerable decrease of the electrical resistivity of 1 compared with the corresponding tetrabutylammonium salt, as described above. The powder reflectance spectrum of $\text{K}_{1.6}[\text{Pt}(\text{C}_2\text{O}_4)_2] \cdot x\text{H}_2\text{O}$ also displays a broad band around 10 000 cm^{-1} [6].

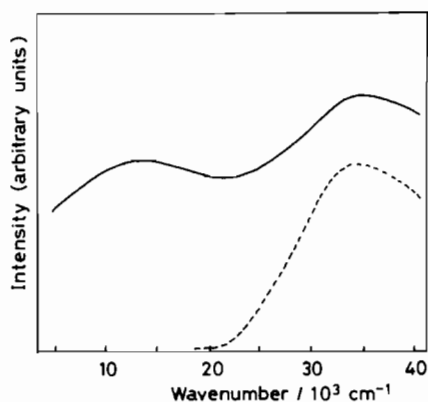


Fig. 2. Powder reflectance spectra of salt 1 (—) and [NBuⁿ₄]₂[Pt(C₂O₄)₂] (---).

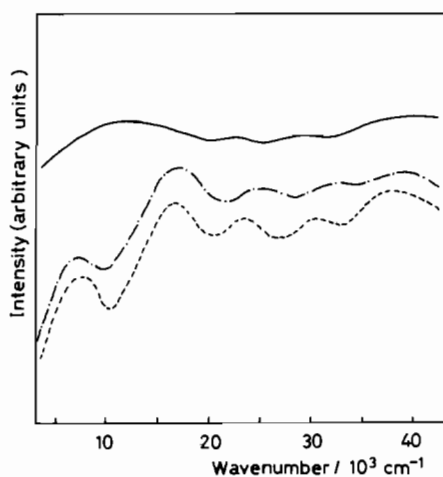


Fig. 3. Powder reflectance spectra of salt 2 (—), [NBuⁿ₄][Ni(C₃S₅)₂] (---) and [NBuⁿ₄]₂[Ni(C₃S₅)₂] (-·-).

The spectrum of salt 2, as well as those of [NBuⁿ₄][Ni(C₃S₅)₂] and [NBuⁿ₄]₂[Ni(C₃S₅)₂], are illustrated in Fig. 3. For all the salts, bands observed at higher frequencies than 15 000 cm^{-1} are assigned to the intramolecular transitions of the anionic moiety, and a band around 8000 cm^{-1} for [NBuⁿ₄][Ni(C₃S₅)₂] and [NBuⁿ₄]₂[Ni(C₃S₅)₂] may be explained as due to an association of the anionic moieties [12]. Salt 2 exhibits a broad band around 10 000 cm^{-1} , the tail-broadening bands in the IR region, as described below. This is caused by conducting electrons through the columns or networks constructed by bis(dithiolato)metallate-anions. Essentially the same spectral behavior was observed for the palladium and platinum analogs.

The IR spectrum of salt 2 as well as those [NBuⁿ₄][Ni(C₃S₅)₂] and [NBuⁿ₄]₂[Ni(C₃S₅)₂] are shown in Fig. 4, which indicates that the $\nu(\text{C}=\text{C})$ band of [NBuⁿ₄]₂[Ni(C₃S₅)₂] at 1430 cm^{-1} is shifted to 1350 cm^{-1} upon the one-electron oxidation. In salt 2 the $\nu(\text{C}=\text{C})$ band occurs at 1250 cm^{-1} ,

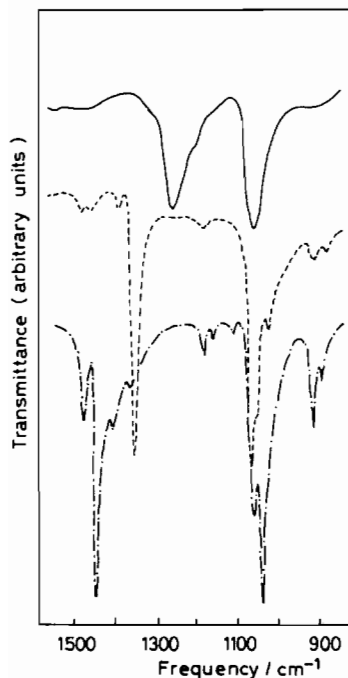


Fig. 4. IR spectra of salt 2 (—), $[\text{NBu}^n_4][\text{Ni}(\text{C}_3\text{S}_5)_2]$ (---) and $[\text{NBu}^n_4]_2[\text{Ni}(\text{C}_3\text{S}_5)_2]$ (-·-·).

TABLE III. The $\nu(\text{C}=\text{C})$ Frequencies (cm^{-1})^a of the $[\text{M}(\text{C}_3\text{S}_5)_2]^{m-}$ Anion Salts (M = Ni, Pd and Pt)

Salt	m	$\nu(\text{C}=\text{C})$
$[\text{NBu}^n_4]_2[\text{Ni}(\text{C}_3\text{S}_5)_2]$	2	1430
$[\text{NBu}^n_4][\text{Ni}(\text{C}_3\text{S}_5)_2]$	1	1350
2	0.7	1250
$[\text{NBu}^n_4]_2[\text{Pd}(\text{C}_3\text{S}_5)_2]$	2	1430
3	0.7	1290
$[\text{NBu}^n_4]_2[\text{Pt}(\text{C}_3\text{S}_5)_2]$	2	1440
$[\text{NBu}^n_4][\text{Pt}(\text{C}_3\text{S}_5)_2]$	1	1340
4	0.6	1270

^a Measured in KBr disks.

and is accompanied by the broadening which is characteristic of the salts with a high electrical conductivity. Salts 3 and 4 also show similar low-frequency shifts of the $\nu(\text{C}=\text{C})$ bands compared with those of the corresponding di(tetrabutylammonium) salts, as shown in Table III. These noticeable low-frequency shifts on the oxidation suggest that the oxidation occurs essentially on the dithiolato ligands.

Binding energies of the 2p, 3d, or 4f-electrons of the $[\text{M}(\text{C}_3\text{S}_5)_2]^{m-}$ (2p, 3d and 4f for Ni, Pd and Pt, respectively; $m = 2-0.6$) salts determined from the X-ray photoelectron spectra are summarized in Table IV, which indicates that the binding energies are almost constant irrespective of variation in the formal oxidation number of each metal. This finding suggests that the oxidation occurs essentially on the dithiolato

TABLE IV. Binding Energies (E_b) of the $[\text{M}(\text{C}_3\text{S}_5)_2]^{m-}$ Salts (M = Ni, Pd and Pt; $m = 0.6-2$) (eV)

Salts	m	E_b
$[\text{NBu}^n_4]_2[\text{Ni}(\text{C}_3\text{S}_5)_2]$	2	853.1 (Ni 2p _{3/2})
$[\text{NBu}^n_4][\text{Ni}(\text{C}_3\text{S}_5)_2]$	1	853.2 (Ni 2p _{3/2})
2	0.7	853.2 (Ni 2p _{3/2})
$[\text{NBu}^n_4]_2[\text{Pd}(\text{C}_3\text{S}_5)_2]$	2	340.4 (Pd 3d _{3/2}) 335.1 (Pd 3d _{5/2})
3	0.7	340.6 (Pd 3d _{3/2}) 335.4 (Pd 3d _{5/2})
$[\text{NBu}^n_4]_2[\text{Pt}(\text{C}_3\text{S}_5)_2]$	2	74.3 (Pt 4f _{5/2}) 71.1 (Pt 4f _{7/2})
$[\text{NBu}^n_4][\text{Pt}(\text{C}_3\text{S}_5)_2]$	1	74.5 (Pt 4f _{5/2}) 71.2 (Pt 4f _{7/2})
4	0.6	74.4 (Pt 4f _{5/2}) 71.2 (Pt 4f _{7/2})

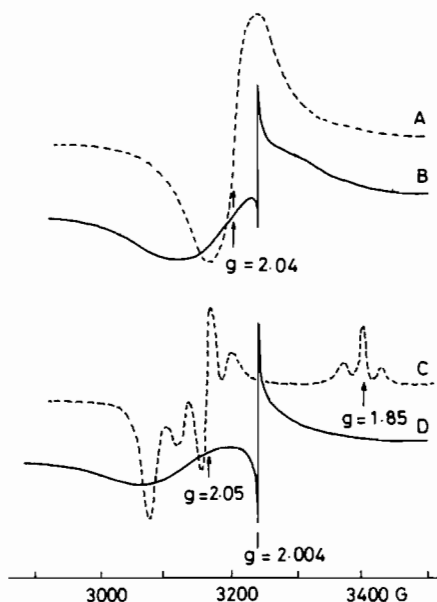


Fig. 5. Powder ESR spectra of: (A) $[\text{NBu}^n_4][\text{Ni}(\text{C}_3\text{S}_5)_2]$, (B) salt 2, (C) $[\text{NBu}^n_4][\text{Pt}(\text{C}_3\text{S}_5)_2]$ and (D) salt 4 at 77 K.

ligands of $[\text{M}(\text{C}_3\text{S}_5)_2]^{m-}$, as reported for bis(dithiolato)metallate-anion salts of the $[\text{MS}_4\text{C}_4\text{R}_4]^{m-}$ (M = Ni, Pd and Pt; R = C₆H₅ and CN; $m = 0, 1$ and 2) [13] and $[\text{PtS}_4\text{C}_4(\text{CN})_4]^{m-}$ ($m = 0.75, 1$ and 2) types [14].

The powder ESR spectrum of $[\text{NBu}^n_4][\text{Ni}(\text{C}_3\text{S}_5)_2]$ is illustrated in Fig. 5, which shows an apparently isotropic, broad signal at $g = 2.04$ assignable to the free radical essentially located on the dithiolato ligand. The palladium analog, 3, also has shown a broad signal ($g = 2.05$) at 77 K. On the other hand, $[\text{NBu}^n_4][\text{Pt}(\text{C}_3\text{S}_5)_2]$ exhibits an anisotropic signal at $g = 2.05$ accompanied with satellites at a higher field ($g = 1.85$), presumably owing to the hyperfine structure due to the ¹⁹⁵Pt coupling (63

gauss). This spectrum indicates the delocalization of an unpaired electron of the dithiolato radical around the platinum nucleus. Similar spectral behavior was observed for the *cis*-diamine α -pyridone blue compound [15]. The partially oxidized salts 2 and 4 display much broader signals at $g = 2.04$ and 2.05 , respectively, at 77 K. In addition, a weak sharp signal occurs at $g = 2.004$. This is due to the $DEPZ^{\cdot+}$ cation radical which exists to a small extent as a counterpart to the $DEPZ^{2+}$ dication. At room temperature the signals are observed as extremely broad ones at higher g values (*ca.* 2.28). This may be related to the electron-delocalization through the conductive pathways, which are presumably constructed with interligand sulfur–sulfur contacts, as reported for $[NBu^n_4]_{0.29}[Ni(C_3S_5)_2]$ [3] and $[NEt_4]_{0.5}[Ni(C_3S_5)_2]$ [4].

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