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Spectroscopic and Electrical Properties of the $Pt^{II}S_2N_2$ Type Complexes and their Iodine-doped Analogs

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Abstract

Pt(dmit)(L) ($dmit^{2-}$ = the 1,3-dithiole-2-thione-4,5-dithiolate anion; L = 2,2′-bipyridine, 1,10-phenanthroline, 4,4′-dimethyl-2,2′-bipyridine, *N*-ethyl-2-picolinaldimine, and *N*-isopropyl-2-picolinaldimine) have been prepared. They are polarized in the ground state, exhibiting a ligand-to-ligand charge transfer absorption band in the 8000–14000 cm^{-1} region. These complexes behave as semi-conductors with electrical conductivities of $1 \times (10^{-9} \sim 10^{-11})$ S cm^{-1} at 25 °C as compacted pellets. On doping iodine into the complexes, they have been partially oxidized to afford $Pt(dmit)(L) \cdot I_x$ ($x = 1.9 \sim 2.3$) containing I_3^- and I_5^- ions, whose electrical conductivities are raised by two to four powers compared with those of corresponding Pt(dmit)(L) complexes. IR, Raman, and ESR spectra of the iodine-doped complexes are discussed.

Introduction

Planar metal complexes are partially oxidized to form low-dimensional molecular stacks and often to exhibit good electrical conductivities [1]. Of those, $[M(dmit)_2]^{n-}$ anion salts ($dmit^{2-}$ = the 1,3-dithiole-2-thione-4,5-dithiolate anion; M = Ni, Pd, and Pt; $n = 0.3 \sim 2$) have recently attracted much attention because of their high conductivities [2, 3]. In particular, $TTF[Ni(dmit)_2]_2$ (TTF = tetrathiafulvalene) was reported to become a superconductor at low temperature [2].

Planar metal complexes with a polarized field in their ligands are expected to form a column through an intermolecular electrostatic interaction and to afford an electrical conduction pathway, the conducting electrons being affected by the polarized field. However, no work performed from this standpoint has been reported. Metal complexes containing both a dithiolate ligand as an electron donor and 2,2′-bipyridine as a π-electron acceptor were reported to exhibit an intramolecular ligand-to-ligand charge transfer [4–6]. Thus, the planar metal complexes with both the dmit ligand and 2,2′-bipyridine or its analog may be expected to undergo sufficient polarization to form columnar stackings through a metal–metal interaction and/or an electrostatic interaction in the polarized field.

This paper reports the preparation of Pt^{II}(dmit)(L) (L = 2,2′-bipyridine, 1,10-phenanthroline, *N*-ethyl-2-picolinaldimine, *N*-isopropyl-2-picolinaldimine, and 4,4′-dimethyl-2,2′-bipyridine) where the dmit ligand works as an electron donor and the N–N′-ligand as a π-electron acceptor. They are partially oxidized by iodine, their electrical conductivities being appreciably raised. Electronic, Raman, and ESR spectra of Pt^{II}(dmit)(L) and the iodine-doped complexes are discussed. M(dmit)(2,2′-bipyridine) (M = Ni, Pd, and Pt) and their iodine-doped complexes were previously reported [7].

Experimental

Materials

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione [8], dichloro(*N*-ethyl-2-picolinaldimine)platinum(II), $PtCl_2$(Et-pia), and the *N*-isopropyl-2-picolinaldimine (Pr^i-pia) analog [9] were prepared by the literature methods. Dichloro(2,2′-bipyridine)platinum(II), $PtCl_2$(bpy), and the 1,10-phenanthroline (phen) and 4,4′-dimethyl-2,2′-bipyridine (dmbpy) analogs were prepared according to the method similar to the case of $PdCl_2$(bpy) [10].

Preparation of (1,3-Dithiole-2-thione-4,5-dithiolato)(L)platinum(II), Pt(dmit)(L) (L = bpy, phen, dmbpy, Et-pia, and Pr^i-pia)

Sodium metal (120 mg, 5.0 mmol) and 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (610 mg, 1.5 mmol) were dissolved in methanol (50 cm^3). To the resulting dark red solution was added dropwise a dimethyl sulfoxide (50 cm^3) solution of $PtCl_2$(bpy) (420 mg, 1.0 mmol) to give a black precipitate of Pt(dmit)(bpy) immediately. After water (50 cm^3) was added to the solution to dissolve NaCl coprecipitated with the black solid, it was centrifuged. A solid

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material thus obtained was collected, washed with dimethyl sulfoxide and then methanol, and dried *in vacuo* (98% yield).

Pt(dmit)(phen) and Pt(dmit)(dmbpy) were prepared as black and red powders by reactions of Na_2-dmit with $PtCl_2$(phen) and $PtCl_2$(dmbpy), respectively, by the method similar to Pt(dmit)(bpy) (98 and 95% yields). Pt(dmit)(Et-pia) and Pt(dmit)(Pr^i-pia) were similarly prepared as black powders in methanol (98 and 97% yields).

Reactions of Pt(dmit)(L) Complexes with Iodine

Finely powdered Pt(dmit)(L) (L = bpy, phen, dmbpy, Et-pia, or Pr^i-pia) were suspended in a hexane solution containing a slight excess of iodine. The solution was stirred at room temperature for 24 h to give an iodine-doped complex, which was washed with hexane several times, collected by centrifugation, and dried *in vacuo*.

Elemental analyses for Pt(dmit)(L) and the iodine-doped complexes are summarized in Table I.

TABLE I. Elemental Analyses of Pt(dmit)(L) and Pt(dmit)(L)·I_x^{a}

Complex	Found (calc.) (%)		
	C	H	N
Pt(dmit)(bpy)	28.65	1.59	4.98
	(28.49)	(1.47)	(5.11)
Pt(dmit)(phen)	31.53	1.54	4.95
	(31.51)	(1.41)	(4.90)
Pt(dmit)(dmbpy)	31.08	2.48	4.53
	(31.29)	(2.11)	(4.87)
Pt(dmit)(Et-pia)	25.01	2.16	4.78
	(25.13)	(1.92)	(5.33)
Pt(dmit)(Pr^i-pia)	27.02	2.37	4.75
	(26.70)	(2.25)	(5.19)
Pt(dmit)(bpy)·$I_{2.2}$	18.73	1.20	3.27
	(18.88)	(0.98)	(3.39)
Pt(dmit)(phen)·$I_{1.9}$	22.11	1.27	3.77
	(22.17)	(0.99)	(3.45)
Pt(dmit)(dmbpy)·$I_{2.3}$	20.55	1.50	2.95
	(20.76)	(1.39)	(3.22)
Pt(dmit)(Et-pia)·$I_{1.9}$	17.33	1.37	3.42
	(17.23)	(1.32)	(3.65)
Pt(dmit)(Pr^i-pia)·$I_{1.7}$	19.01	1.84	3.32
	(19.05)	(1.74)	(3.70)

^{a}Melting points >300 °C for both types of the complexes and the colors are all black except for red Pt(dmit)(dmbpy).

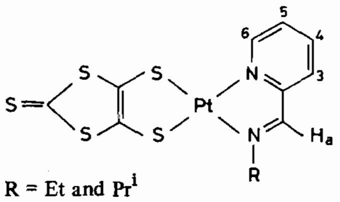
Physical Measurements

^{1}H NMR, IR [11], electronic absorption [12], powder electronic reflectance [12], and ESR spectra [13] were measured as described elsewhere. Raman spectra were recorded for the solid complexes as previously described [14], using a cut-off filter for the argon laser beam (514.5 nm) to avoid the natural scattering beams. Electrical resistivities were measured for compacted pellets as described previously [15].

Results and Discussion

Configuration and Electronic Spectra of Pt(dmit)(L)

Although Pt(dmit)(L) (L = bpy, phen, and dmbpy) were scarcely soluble in common organic solvents, both Pt(dmit)(Et-pia) and Pt(dmit)(Pr^i-pia) exhibit appropriate solubilities in dimethyl sulfoxide for the measurement of the ^{1}H NMR spectra. ^{1}H NMR spectra of these complexes show ring and imine proton signals, H_6 and H_a (shown in Structure **A**), with satellites due to the spin–spin coupling with the ^{195}Pt nucleus. The chemical shifts of H_6 and H_a protons and the proton-^{195}Pt spin–spin coupling constants are summarized in Table II, together with those of the corresponding chloride complexes $PtCl_2$(L) (L = Et-pia and Pr^i-pia) [9]. The $J(^{195}Pt-^1H)$ values of Pt(dmit)(L) (L = Et-pia and Pr^i-pia) are somewhat smaller than those of the corresponding chloride complexes, suggesting that both the platinum–nitrogen bonds of Pt(dmit)(L) are weakened to some extent by the electron-donating dithiolate ligand through some decrease of Lewis acidity of the platinum atom compared with that of $PtCl_2$(L) having the more electronegative chloride ions.



A

Figure 1 shows the electronic absorption spectra of Pt(dmit)(Pr^i-pia) in dimethyl sulfoxide and in dichloromethane as well as its powder reflectance spectrum. The intense absorption bands centered at 470 nm in dichloromethane and 480 nm in dimethyl sulfoxide are assignable to the π–π^* transition of the dmit ligand. Similar absorptions are observed in other dmit–metal complexes such as Na_2dmit (514 nm in methanol) and $[NBu^n_4]_2[Zn(dmit)_2]$ [8] (515 nm in dimethyl sulfoxide). It is to be noted that another band observed for Pt(dmit)(Pr^i-pia) in dimethyl sulfoxide (580 nm) is shifted to a higher wavelength in dichloromethane (660 nm). Such low energy shift of the absorption band in a less polar solvent is evidently shown in Fig. 2, which indicates the absorption maxima of Pt(dmit)(Pr^i-pia) plotted against the dielectric constant of the solvents. Thus, the band may be assigned to the intramolecular ligand-to-ligand

TABLE II. ^1H NMR Parameters of the *N*-Alkyl-2-picolinaldimine-platinum(II) Complexes

Complex	Chemical shift[a] δ		Coupling constant (Hz)	
	H_6	H_a	$J(^{195}Pt-H_6)$	$J(^{195}Pt-H_a)$
Pt(dmit)(Et-pia)[b]	8.90 (+0.80)	9.45 (+0.99)	34.2	78.5
Pt(dmit)(Pr^i-pia)[b]	8.98 (+0.85)	9.58 (+1.05)	33.0	82.0
$PtCl_2$(Et-pia)[c]	9.48 (+0.89)	8.80 (+0.47)	38.3	99.1
$PtCl_2$(Pr^i-pia)[c]	9.60 (+1.00)	8.90 (+0.57)	39.1	99.6

[a] $(\delta_{complexed}-\delta_{free})$ in parentheses. [b] In dimethyl sulfoxide-d_6. [c] In acetonitrile, ref. 9.

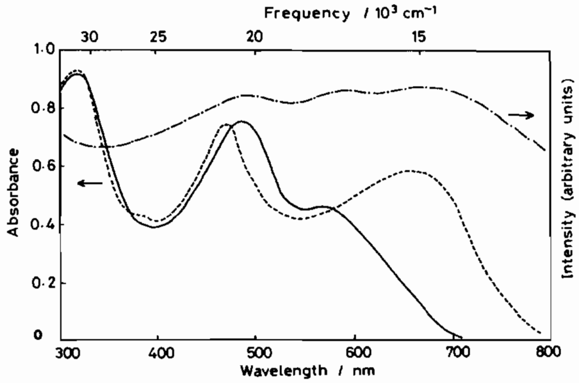


Fig. 1. Electronic absorption spectrum of Pt(dmit)(Pr^i-pia) (5.7×10^{-4} mol dm^{-3}) in dimethyl sulfoxide (———) and in dichloromethane (– – –), and its powder reflectance spectrum (— · —).

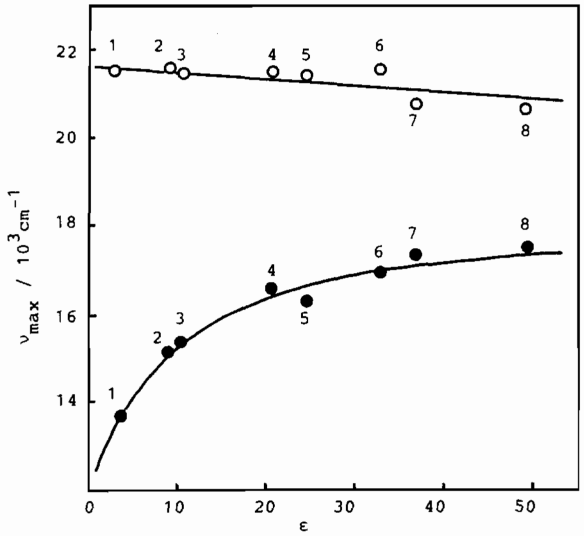


Fig. 2. Plots of absorption maxima (ν_{max}; ○: dmit π–π*, ●: LLCT transition) of Pt(dmit)(Pr^i-pia) *vs.* dielectric constants (ε) of solvents: 1, benzene; 2, dichloromethane; 3, 1,2-dichloroethane; 4, acetone; 5, ethanol; 6, methanol; 7, *N,N*-dimethylformamide; 8, dimethyl sulfoxide.

charge transfer (LLCT) transition (from electron-rich sulfur atoms to π-electron deficient nitrogen ligands), by analogy with the similarity to the solvent effect on visible region absorption spectra of several NiS_2N_2 complexes as well as the energy level calculation performed for their complexes [4]. Furthermore, this solvent effect may indicate the polarized electronic construction in the ground state of Pt(dmit)(Pr^i-pia). On the other hand, the local excitation of the dmit ligand occurs at a rather lower frequency region with increasing polarity of the solvents (see Fig. 2). The powder reflectance spectrum of Pt(dmit)(Pr^i-pia) shows a broad band at 670 nm besides those at 500 and 590 nm; the latter two bands correspond to the absorption bands observed in dimethyl sulfoxide (Fig. 1). The appearance of the 670 nm band suggests the occurrence of intermolecular interaction in the Pt(dmit)(Pr^i-pia) crystals, which is consistent with a semi-conductive behavior of this complex, as described later. Other Pt(dmit)(L) complexes also exhibit this LLCT band in the powder reflectance spectra. Table III summarizes the electronic absorption and reflectance bands of Pt(dmit)(L).

Properties of Iodine-doped Pt(dmit)(L) Complexes

The finely powdered Pt(dmit)(L) (L = bpy, phen, dmbpy, Et-pia, and Pr^i-pia) complexes suspended in hexane reacted with iodine to yield Pt(dmit)(L)·I_x ($x = 1.9 \sim 2.3$); the value of x changes depending on the nature of L. Pt(dmit)(phen) is essentially diamagnetic, although it has shown a very weak ESR signal. On the other hand, Pt(dmit)(phen)·$I_{1.9}$ exhibits an anisotropic broad ESR signal at g_{max} = 2.11, g_{int} = 2.063, and g_{min} = 1.91, as illustrated in Fig. 3. Other Pt(dmit)(L)·I_x (L = bpy, dmbpy, Et-pia,

TABLE III. Electronic Absorption [A][a] and Powder Reflectance Spectra [B] of the Platinum(II) Complexes (nm)

Complex		dmit π–π* band	Ligand-to-ligand c.t. band	Intermolecular band
Pt(dmit)(bpy)	[A][b]	490	570	
	[B]	480	560	650
Pt(dmit)(phen)	[A][b]	485	560	
	[B]	480	560	650
Pt(dmit)(dmbpy)	[A][b]	500	550	
	[B]	480	550	590
Pt(dmit)(Et-pia)	[A]	482 (4.01)	580 (3.91)	
	[B]	470	590	680
Pt(dmit)(Pr^i-pia)	[A]	482 (3.89)	570 (3.72)	
	[B]	470	580	680

[a] In dimethyl sulfoxide. Apparent log ε in parentheses. [b] log ε values have not been determined because of poor solubility.

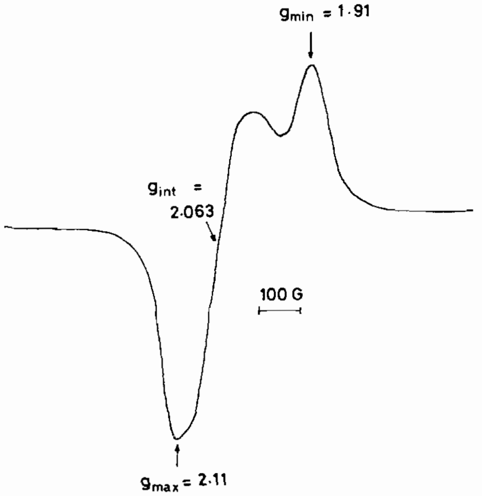


Fig. 3. Powder ESR spectrum of Pt(dmit)(phen) at room temperature.

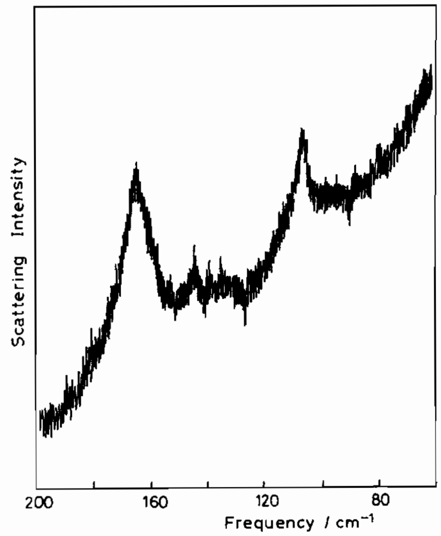


Fig. 4. Raman spectrum of Pt(dmit)(phen)·$I_{1.9}$ at room temperature.

and Pr^i-pia) complexes also displayed broad ESR signals similar to Pt(dmit)(phen)·$I_{1.9}$. Thus, the partial oxidation of Pt(dmit)(L) with iodine occurs presumably at the dmit ligand, since these complexes gave similar anisotropic signals irrespective of the co-ligand (L) of dmit.

The IR spectrum of Pt(dmit)(phen) showed a ν(C=C) band of the dmit ligand at 1425 cm^{-1}, which undergoes a remarkable shift (1280 cm^{-1}) and somewhat broadening upon iodine-doping to give Pt(dmit)-(phen)·$I_{1.9}$. Similar low-frequency shifts of the ν(C=C) band (from 1420 to 1280 cm^{-1}) were observed in iodine-doped bpy and dmbpy analogs, while in the Et-pia and Pr^i-pia complexes no ν(C=C) band which should be shifted upon iodine-doping has been observed owing to the obscuration of other bands. This is indicative of the occurrence of oxidation at the dmit ligand as well, since similar low-frequency shifts of ν(C=C) bands were reported for [M(dmit)$_2$]-[DEPZ]$_{0.3-0.35}$ (M = Ni, Pd, and Pt; DEPZ^{2+} = the diethylpyrazinium cation), where the [M(dmit)$_2$]$^{2-}$ anions are partially oxidized [3].

The doped iodine species in Pt(dmit)(L)·I_x is examined by Raman spectroscopy; the spectrum of Pt(dmit)(phen)·$I_{1.9}$ shows characteristic scatterings at 108 and 166 cm^{-1} (Fig. 4), which are attributable to I_3^- [16] and I_5^- [17, 18], respectively. In addition, there has been observed no Raman scattering due to free I_2 (ν(I–I), 250 cm^{-1}) [16]. The formation of I_3^- and I_5^- may be further support for the oxidation of Pt(dmit)(L) by iodine. Raman scattering frequencies of the Pt(dmit)(L)·I_x complexes are listed in Table IV. The partial oxidation of Pt(dmit)-(L) by iodine seems to lead to more extended intermolecular interactions of the complexes. As exemplified by the powder reflectance spectra of Pt(dmit)-(phen) and Pt(dmit)(phen)·$I_{1.9}$ (Fig. 5), the former complex shows a broad band at 650 nm due to the intermolecular interaction as described above, while

TABLE IV. Raman Scattering Frequencies (cm^{-1}) of the Iodine-doped Pt(dmit)(L) Complexes in the 80–200 cm^{-1} Region

Pt(dmit)(bpy)·$I_{2.2}$	165(m)	108(m)
Pt(dmit)(phen)·$I_{1.9}$	166(m)	108(m)
Pt(dmit)(dmbpy)·$I_{2.3}$	165(m)	106(vw)
Pt(dmit)(Et-pia)·$I_{1.9}$		106(m)
Pt(dmit)(Pr^i-pia)·$I_{1.7}$	164(w)	109(m)

m: medium, w: weak, vw: very weak.

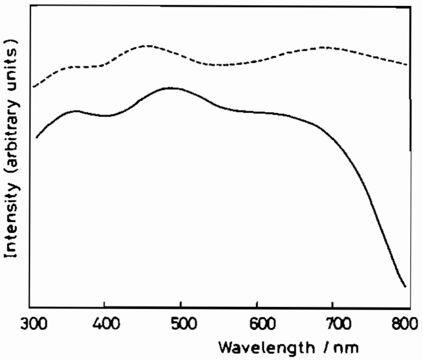


Fig. 5. Powder reflectance spectra of Pt(dmit)(phen) (——) and Pt(dmit)(phen)·$I_{1.9}$ at room temperature (- - - -).

TABLE V. Electrical Conductivities (σ) and Activation Energies (E_a) of Pt(dmit)(L) and their Iodine-doped Complexes

Complex	σ 25 °C (S cm^{-1})	E_a (eV)
Pt(dmit)(bpy)	6.2×10^{-10}	0.51
Pt(dmit)(phen)	1.5×10^{-9}	0.36
Pt(dmit)(dmbpy)	3.3×10^{-11}	0.52
Pt(dmit)(Et-pia)	5.9×10^{-10}	0.34
Pt(dmit)(Pr^i-pia)	1.4×10^{-9}	0.29
Pt(dmit)(bpy)·$I_{2.2}$	1.3×10^{-6}	0.51
Pt(dmit)(phen)·$I_{1.9}$	4.0×10^{-7}	0.67
Pt(dmit)(dmbpy)·$I_{2.3}$	1.0×10^{-7}	0.36
Pt(dmit)(Et-pia)·$I_{1.9}$	4.1×10^{-8}	0.63
Pt(dmit)(Pr^i-pia)·$I_{1.7}$	1.2×10^{-7}	0.54

the spectrum of the iodine-doped species exhibits a tail-broadening band in a longer wavelength region. This may be caused by conducting electrons through the networks constructed by partially oxidized Pt(dmit)(phen) moieties, as described below.

Both Pt(dmit)(L) and Pt(dmit)(L)·I_x complexes behave as typical semi-conductors in the −20 to +40 °C range. Electrical conductivities measured for the compacted pellets and activation energies for the electrical conduction are summarized in Table V, which indicates that the conductivities of Pt(dmit)(L) are raised by the 10^2–10^4 order of on doping iodine. Thus, effective conduction pathways may be formed in the partially oxidized complexes, as pointed out in the powder reflectance spectra.

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