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Note

# Preparation spectroscopy and conductivity of [Pt(SS)(NN)]-type complexes and their iodine oxidized complexes

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## Abstract

Complexes of the general formula [Pt(SS)(NN)] have been prepared, where SS is bbdt(1,2-bis(benzylthio)ethylene-1,2-dithiolate) or dpdt (5,6-dihydrophenyl-1,4-dithion-2,3-dithiolate) and NN is bipy (2,2'-bipyridine) or phen (1,10-phenanthroline). The UV–Vis spectra exhibit intense intramolecular ligand-to-ligand charge transfer absorption bands at 440–600 nm. Cyclic voltammograms show a reversible oxidation step assigned to [Pt(SS)(NN)]<sup>0</sup>/[Pt(SS)(NN)]<sup>+</sup>. On doping iodine into the complexes, partial oxidation occurs to afford [Pt(SS)(NN)]I<sub>x</sub> (x=1.9(2.2). IR, Raman and ESR spectra of the iodine-doped complexes are discussed. Electrical conductivities of the neutral mixed-ligand complexes ( $10^{-9}$ – $10^{-10}$  S cm<sup>-1</sup>) increase to  $10^{-6}$ – $10^{-7}$  S cm<sup>-1</sup> upon I<sub>2</sub> doping. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Charge transfer; Platinum complexes; Mixed-ligand complexes

## 1. Introduction

Partially oxidized planar metal complexes with onedimensional metal-metal interactions often exhibit high electrical conductivity [1]. For example, sulfur-rich dithiolate complexes, such as  $[M(dmit)_2]^{n-}$  (dmit=1,3-dithiole-2thione-4,5-dithiolate) have recently attracted much attention because of their high conductivities [2-6]. Another interesting set of planar complexes having the formula [Pt(SS)(NN)] contain both electron donor dithiolate and  $\pi$ -electron acceptor diimine ligands [7]. These exhibit intense electronic absorption bands due to intramolecular ligand-to-ligand charge-transfer transitions [8]. They may also assume columnar packing through S...N electrostatic interaction as well as Pt· · · Pt contacts which form an effective conducting pathway when partially oxidized [8]. Polarized, planar Pt(SS)(NN) complexes have been reported to be electrical conductors [7-9].

This paper reports the preparation of new [Pt(SS)(NN)]type complexes containing bbdt or dpdt as electron donor ligands and 2,2'-bipyridine or 1,10-phenanthroline as electron acceptor ligands. This is the first report of complexes containing both bbdt and dpdt as the SS ligands. Partial oxidation of the Pt(SS)(NN) complexes increase their electrical conductivities. Spectroscopic, electrochemical and magnetic properties as well as electrical conductivities are discussed.

## 2. Experimental

### 2.1. Materials

5H,10H-dithiolo[2,3-b][2,5]benzothionine-2-one and 4,5bis(benzylthio)-1,3-dithiole-2-one were prepared by the literature methods [10]. [PtCl<sub>2</sub>(bipy)] and [PtCl<sub>2</sub>(phen)] were prepared by procedures similar to those for [PdCl<sub>2</sub>(bipy)] [11].

# 2.2. Preparation of [Pt(dpdt)(L)] (L=bipy or phen)

Sodium metal (120 mg, 5.0 mmol) and 5H,10H-dithiolo-[2,3-b][2,5]benzothionine-2-one (436 mg,1.5 mmol) were dissolved in methanol (50 ml) under N<sub>2</sub>. To the resulting dark red solution, PtCl<sub>2</sub>(bipy) (430 mg, 1.0 mmol) in dimethyl sulfoxide (DMSO, 30 ml) was added dropwise. A dark brown solid precipitated immediately. Stirring was continued for 1 h at room temperature. Water (50 ml) was added and the solid was collected by filtration, washed with MeOH (50 ml) and dried in air. IR (KBr): 1610 m, 845 m, 746 m (aromatic), 1480 m, 1420 s, 1263 m, 1310 m,

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1105 m, 960 m, 760 w cm<sup>-1</sup>. The reactions involving this procedure are as follows:



When [PtCl<sub>2</sub>(phen)] was used in place of [PtCl<sub>2</sub>(bipy)], [Pt(dpdt)(phen)] was obtained by the same procedure. IR (KBr): 1420 m, 830 s, 710 s (phenanthroline); 1620 m, 1415 s, 1260 m, 1120 m, 1090 m, 760 w cm<sup>-1</sup>.

# 2.3. Preparation of [Pt(bbdt)(L)] (L=bipy or phen)

Sodium metal (120 mg, 5.0 mmol) and 4,5-bis(benzylthio)-1,3-dithiole-2-one (543 mg, 1.5 mmol) were allowed to react in MeOH (50 ml) under N<sub>2</sub>. The resulting dark brown solution was added dropwise to a solution of PtCl<sub>2</sub>(bipy) (430 mg, 1.0 mmol) in DMSO (30 ml). A dark brown solid precipitated immediately. Stirring was continued for 1 h at room temperature. Water (50 ml) was added and the solid was collected by filtration, washed with MeOH (50 ml) and dried in air. IR (KBr): 1600 m, 850 s, 760 m (aromatic); 1485 m, 1420 s, 1220 m, 1152 m, 920 m, 720 w cm<sup>-1</sup>. The reactions involving this procedure are as follows:



When [PtCl<sub>2</sub>(phen)] was used in place of [PtCl<sub>2</sub>(bipy)], [Pt(bbdt)(phen)] was obtained by the same procedure. IR (KBr): 1420 s, 840 m, 720 s (phenanthroline); 1620 m, 1425 s, 1240 m, 1095 m, 940 m, 720 w cm<sup>-1</sup>.

## 2.4. Reaction of Pt(dpdt)(L) or Pt(bbdt)(L) with iodine

Finely powdered Pt(dpdt)(L) (L=bipy or phen) was 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 filtration and dried in air. The iodine-doped complexes of [Pt(bbdt)(L)] (L=bipy, phen) were obtained by the same method. Elemental analyses for the [Pt(SS)(NN)] complexes and their iodine-doped products are summarized in Table 1.

#### 2.5. Physical measurements

ESR spectra were recorded on a Bruker ER 200-D-SRC spectrometer. Cyclic voltammetry (CV) was performed with a model BAX 100 V-A analyser, with an electrochemical cell containing a Pt wire as the working electrode, a Pt wire

Table 1

Elemental analyses of the  $[\mbox{Pt}(\mbox{SS})(\mbox{NN})]$  complexes and their iodine-doped analogues  $^{\rm a}$ 

Complex	Found (calc.) (%)			
	С	Н	N	
Pt(dpdt)(bipy)	39.42 (39.54)	2.52 (2.64)	4.39 (4.01)	
Pt(dpdt)(phen)	41.89 (41.84)	2.52 (2.54)	4.36 (4.44)	
Pt(bbdt)(bipy)	45.74 (45.55)	3.15 (3.21)	4.01 (4.09)	
Pt(bbdt)(phen)	47.40 (47.39)	3.25 (3.10)	4.07 (3.95)	
[Pt(dpdt)(bipy)]I <sub>2.2</sub>	26.93 (27.08)	1.80 (1.81)	3.25 (3.16)	
[Pt(dpdt)(phen)]I <sub>2.1</sub>	29.27 (29.41)	1.80 (1.78)	3.10 (3.12)	
[Pt(bbdt)(bipy)]I <sub>1.9</sub>	33.54 (33.68)	2.40 (2.38)	3.05 (3.02)	
[Pt(bbdt)(phen)]I <sub>2.2</sub>	34.03 (33.99)	2.20 (2.23)	2.65 (2.83)	

<sup>a</sup> Melting points > 260°C for both types of the complexes. Pt(SS)(NN) complexes are dark brown and Pt(SS)(NN) $I_x$  are black.

as the auxiliary electrode and a standard calomel electrode (SCE) as the reference electrode. IR spectra were recorded on an IR-450 spectrophotometer. Raman spectra were recorded on a SPEX 1403 laser spectrometer. Data were obtained on KBr pellets. Electronic spectra were recorded on an UV-1700 spectrophotometer. Electrical conductivities for compacted pellets of the complexes were measured on a HG high resistance meter by a four-probe technique. Elemental analyses were performed with a PE-2400 analytical instrument.

# 3. Results and discussion

# 3.1. Configuration, IR and electronic spectra of Pt(SS)(NN)

The four neutral mixed-ligand complexes are stable in air and water. All complexes are soluble in DMSO, dimethylformamide (DMF) and dichloromethane, though they are sparingly soluble in common organic solvents. The structures of the complexes are shown in Scheme 1.

The IR spectra of the complexes show  $\nu_{C=C}$  about 1420 cm<sup>-1</sup>, which is red-shifted compared with the corresponding value of 1460 cm<sup>-1</sup> in the uncomplexed ligand. The absorptions of [Pt(dpdt)(bipy)] and [Pt(bbdt)(bipy)] at 1600, 850, 750 cm<sup>-1</sup> confirm the presence of 2,2'-bipyr-



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Fig. 1. Electronic absorption spectrum of Pt(bbdt) (bipy)  $(1.1 \times 10^{-4} \text{ mol} \text{ dm}^{-3})$  in dimethyl sulfoxide (----) and in dichloromethane (---)

idine ligands, while the absorptions of [Pt(dpdt)(phen)] and [Pt(bbdt)(phen)] at 1420, 835, 715 cm<sup>-1</sup> can be attributed to 1,10-phenanthroline [12].

Fig. 1 shows the electronic absorption spectra of [Pt(bbdt)(bipy)] in DMSO and in CH<sub>2</sub>Cl<sub>2</sub>. The intense absorption bands centered at 450 nm in CH<sub>2</sub>Cl<sub>2</sub> and 460 nm in DMSO are assignable to the  $\pi$ - $\pi$ \* transition of the SS ligand. Note that the intense absorption band at 550 nm in DMSO is shifted to a longer wavelength (590 nm) in CH<sub>2</sub>Cl<sub>2</sub>. This band may be assigned to the intramolecular ligand-to-ligand charge transfer (LLCT) transition (from electron-rich sulfur ligand to the  $\pi$ -electron deficient nitrogen ligand) as described for the corresponding  $PtN_2S_2$  complexes [13]. The negative solvatochromism suggests the polar electronic structure of the complex in the ground state. On the other hand, the low energy shifts shown in Table 2 are smaller than those of [Pt(dmit)(Pr<sup>1</sup>pia)] (Pr<sup>1</sup>-pia=N-isopropyl-2-picolinal diimine) (580 nm in DMSO and 660 nm in CH<sub>2</sub>Cl<sub>2</sub>) [13]. Therefore, the title complexes are less polar than [Pt(dmit)(Pr<sup>1</sup>-pia)].

# 3.2. Oxidation of Pt(SS)(NN) complexes

The cyclic voltammograms of Pt(dpdt)(bipy) and Pt(bbdt)(bipy) measured in CH<sub>3</sub>CN are shown in Fig. 2. Both complexes display a reversible redox process  $[Pt(SS)(NN)]^0/[Pt(SS)(NN)]^+$ . The anodic potentials of the title complexes are summarized in Table 3.

Complexes in Table 3 are oxidized at somewhat lower potentials than their dmit, mnt, dddt and pddt analogues, suggesting that they have more suitable redox potentials for the preparation of conducting materials.

Table 2 Electronic absorptions of the [Pt(SS)(NN)] complexes

Complex	$\pi$ - $\pi$ * band (nm)		LLCT ban	LLCT band (nm)	
	DMSO	CH <sub>2</sub> Cl <sub>2</sub>	DMSO	CH <sub>2</sub> Cl <sub>2</sub>	
Pt(dpdt)(bipy)	440	435	580	614	
Pt(dpdt)(phen)	446	443	593	620	
Pt(bbdt)(bipy)	460	450	550	590	
Pt(bbdt)(phen)	458	450	600	627	



Fig. 2. Cyclic voltammograms of [Pt(dpdt)(bipy)] (top) and [Pt(bbdt)(bipy)] (bottom) measured at a Pt wire electrode in CH<sub>3</sub>CN,  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>, 0.1 mol dm<sup>-3</sup> TNAP, sweep rate: 100 mV s<sup>-1</sup>

Table 3 Electrochemical data<sup>a</sup>

Complex	eV	Ref.		
Pt(dpdt)(bipy)	0.26			
Pt(dpdt)(phen)	0.30			
Pt(bbdt)(bipy)	0.22			
Pt(bbdt)(phen)	0.24			
Pt(dmit)(bipy)	0.80	14		
Pt(mnt)(bipy)	1.32	14		
Pt(dddt)(bipy)	0.33	15		
Pt(pddt)(bipy)	0.46	15		
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 $^a$  Measured at a Pt wire electrode in CH<sub>3</sub>CN,  $1.0 \times 10^{-4} mol \ dm^{-3}$ ,  $0.1 \ mol \ dm^{-3} \ [Bu_4^n][ClO_4]$ , sweep rate: 100 mV s^{-1}.

## 3.3. Properties of iodine-doped Pt(SS)(NN) complexes

The value of *x* in iodine-doped complexes [Pt(SS)(NN)]I<sub>x</sub> is changeable depending on the nature of the SS ligand and the NN ligand. The IR spectra of the iodine complexes show remarkable low-frequency shifts and somewhat broadening of the  $\nu_{C=C}$  band (from 1420 to 1380 cm<sup>-1</sup>) compared with the neutral mixed-ligand complexes. This is indicative of the occurrence of oxidation at the dithiolate ligands, since similar low-frequency shifts of  $\nu_{C=C}$  bands were reported for [Pt(dmit)(phen)]I<sub>1.9</sub> [14]. The neutral mixed-ligand complexes [Pt(SS)(NN)] exhibit no ESR signal. On the other hand [Pt(dpdt)(bipy)]I<sub>2.2</sub> exhibits a broad ESR signal at  $g_{\parallel} = 1.93$ ,  $g_{\perp} = 2.06$ . Other iodine-doped complexes also display broad ESR signals similar to those of [Pt(dpdt)(bipy)]I<sub>2.2</sub>.

The iodine-doped complexes were investigated by Raman spectroscopy. The spectrum of  $[Pt(dpdt)(bipy)]I_{2,2}$  shows characteristic features at 108 and 165 cm<sup>-1</sup> (Fig. 3), which are attributable to  $I_3^-$  [15] and  $I_5^-$  [16]. The formation of  $I_3^-$  and  $I_5^-$  results from the oxidation of the complex by  $I_2$ . In addition, the absence of Raman bands around 250 cm<sup>-1</sup> indicates that no free  $I_2$  is present.

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Fig. 3. Raman spectrum of Pt(dpdt)(bipy)I<sub>2.2</sub> at room temperature.

The neutral mixed-ligand complexes have very small electrical conductivities  $(10^{-9}-10^{-10} \text{ S cm}^{-1})$ . However, after partial oxidation by iodine, their electrical conductivities are significantly raised into the range  $10^{-6}$ - $10^{-7}$  $S \text{ cm}^{-1}$ . On the one hand, this may be induced by more effective intermolecular: on the other hand, the rise of electrical conductivities of iodine-doped complexes may occur from the polyiodine  $(I_3^- \text{ and } I_5^-)$  species [17]. Compared with the electrical conductivities of [Pt(pddt)(NN)] complexes [18], the conductivities of [Pt(bbdt)(NN)] and [Pt(dpdt)(NN)] are similar to but somewhat larger than those of [Pt(pddt)(bipy)] and [Pt(pddt)(phen)]. Considering the difference between the title complexes and the [Pt(pddt)(biby)] complexes, it is concluded that the effective electron conducting pathways may be enhanced by the more delocalized SS ligand interactions in the title complexes.

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#### References

- [1] J.S Miller (Ed.), Extended Linear Chain Compounds, Plenum, New York, vol. 3, 1983.
- [2] L. Valade, P.P. Legros, M. Bousseau, P. Cassoux, M. Garbauskas, L.V. Interrante, J. Chem. Soc., Dalton. Trans. (1985) 783.
- [3] M. Bousseau, L. Valade, J.P. Legros, P. Cassoux, M. Garbauskas, L.V. Interrante, J. Am. Chem. Soc. 108 (1986) 1908.
- [4] P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R.A. Clark, A.E. Underhill, Coord. Chem. Rev. 110 (1991) 115.
- [5] R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, Chem. Lett. (1984) 1.
- [6] G. Matsubayashi, A. Yokozawa, J. Chem. Soc., Dalton Trans. (1990) 3535.
- [7] A. Vogler, H. Kunkely, J. Am. Chem. Soc. 103 (1981) 1559.
- [8] G. Matsubayashi, M. Hirao, T. Tanaka, Inorg. Chim. Acta 144 (1988) 217.
- [9] R. Vicente, J. Ribas, P. Cassoux, C. Sourisseau. Synth. Met. 15 (1986) 79.
- [10] S. Kalyan Kumar, B. Harkesh, P. Jasinski, J. Chem. Soc., Perkin Trans I (1991) 334.
- [11] B.J. Maccormick, E.N. Janes, R.I. Kaplan, Inorg. Synth. 13 (1972) 216.
- [12] K. Nakanshi, P.H. Solomon, Infrared Absorption Spectroscopy, 2nd ed., Holden-Day, San Francisco, 1977, p. 40.
- [13] G. Matsubayashi, M. Hirao, T. Tanaka, Inorg. Chim. Acta 144 (1988) 217.
- [14] G. Matsubayashi, Y. Yamagnchi, T. Tanaka, J. Chem. Soc., Dalton Trans. (1988) 2215.
- [15] B.N. Diel, T. Inabe, J.W. Lyding, et al., J. Am. Chem. Soc. 1059 (1983) 1551.
- [16] R.C. Teitelbaum, S.L. Ruby, T.J. Marks, J. Am. Chem. Soc. 102 (1980) 3322.
- [17] M. Forsyth, D.F. Shriver, M.A. Ratner, D.C. DeGroot, C.R. Kannewurf, Chem. Mater. 5 (1993) 1073.
- [18] Tian-Ming Yao, Jing-Lin Zuo, Xiao-Zeng You, Transition Metal. Chem. 19 (1994) 614.