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Preparations and spectroscopic properties of $Pt(C_3Se_5)(N_2\text{-chelate})$ and its oxidized complexes

Gen-etsu Matsubayashi* and **Yuji Hiroshige**

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565 (Japan)

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Abstract

$Pt(C_3Se_5)(L)$ [$C_3Se_5^{2-}$ = 4,5-di(hydroseleno)-1,3-diselenole-2-selenate; L = *N*-alkyl-2-methylpyridine-2-carbaldimine (alkyl = ethyl and i-propyl) and 2,2′-bipyridine] have been prepared. They are polarized, exhibiting an intramolecular ligand-to-ligand charge-transfer absorption band around 16 000 cm^{-1}. The Pt–Se bond order of the $Pt(C_3Se_5)(L)$ complexes is somewhat higher than the Pt–S bond order of $Pt(C_3S_5)(L)$. Oxidation of these complexes by iodine has afforded the complexes with the Pt–I bond, behaving as semiconductors with electrical conductivities of $1 \times (10^{-6}-10^{-7})$ S cm^{-1} measured for compacted pellets at room temperature. Electronic absorption, ^1H NMR, and IR spectroscopies of the complexes as well as their electrochemical properties are described.

Introduction

Previously PtS_2N_2-type complexes containing both an electron-donor dithiolate ligand and a π-electron acceptor nitrogen ligand were reported to be polarized in their ground states, exhibiting intense electronic absorption bands due to intramolecular ligand-to-ligand charge-transfer transitions [1, 2]. They assume a columnar molecular packing through S--N electrostatic interaction [2]. When adequate Pt--Pt contacts are formed and partially oxidized, effective electron conduction pathways may be formed, leading to electrical conductors. Metal complexes with the sulfur-rich dithiolate ligand, $C_3S_5^{2-}$ (4,5-dimercapto-1,3-dithiole-2-thionate), become good electrical conductors [3–5], some of which are known as superconductors at low temperatures [3, 4, 6]. Polarized, planar $Pt(C_3S_5)(N_2\text{-chelate})$ complexes have been reported to be electrical conductors [1, 2, 7].

Metal complexes with the selenium analog of the $C_3S_5^{2-}$ ligand, 4,5-di(hydroseleno)-1,3-diselenole-2-selenate, are expected to have more effective molecular interactions through Se--Se contacts in the solid state owing to diffuse and extended p and d orbitals of selenium. $Pt(C_3Se_5)(N_2\text{-chelate})$ complexes with some Pt-- Pt contacts may lead to good electrical conductors.

This paper reports the preparation of platinum(II) complexes both with the 4,5-di(hydroseleno)-1,3-diselenole-2-selenate ligand as an electron donor and with *N*-alkyl-2-methylpyridine-2-carbaldimine (alkyl = ethyl and i-propyl) or 2,2′-bipyridine as a π-electron acceptor. Their spectroscopic and electrochemical properties are discussed in comparison with those of the corresponding complexes with the $C_3S_5^{2-}$ ligand. Bondings and electrical conductivities of their complexes oxidized by iodine are also described.

Experimental

Materials

4,5-Bis(benzoylseleno)-1,3-diselenole-2-selone [8], dichloro(*N*-alkyl-2-methylpyridine-2-carbaldimine)platinum(II), $PtCl_2$(R-pa) (R = Et and Pr^i) [9], were prepared according to the literature. Dichloro(2,2′-bipyridine)platinum(II), $PtCl_2$(bpy), was prepared according to the method similar to the case of $PdCl_2$(bpy) [10].

Preparation of $Pt(C_3Se_5)(L)$ complexes (L = Et-pa, Pr^i-pa and bpy)

Bis(benzoylseleno) - 1,3 - diselenole - 2 - selone (260 mg, 400 μ mol) was dissolved into a methanol solution (20 cm^3) containing sodium metal (30 mg, 1.3 mmol) and the solution was stirred for 1 h at room temperature. To the resulting

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*Author to whom correspondence should be addressed.

solution of $Na_2C_3Se_5$ was added with stirring a dimethyl sulfoxide solution (6 cm^3) of $PtCl_2$(Et-pa) (220 mg, 550 μmol), followed by addition of water (30 cm^3). Black solids precipitated immediately, which were collected by centrifugation, washed with water and diethyl ether, and dried *in vacuo* (80% yield). By a similar procedure, $Pt(C_3Se_5)(Pr^i$-pa) and $Pt(C_3Se_5)$(bpy) were prepared (90 and 79% yields, respectively).

Reactions of $Pt(C_3Se_5)(L)$ *complexes with iodine*

Finely powdered $Pt(C_3Se_5)(L)$ (L = Et-pa, Pr^i-pa and bpy) (50 μmol) was suspended in a hexane solution (50 cm^3) containing an excess amount of iodine (150 μmol), and the suspension stirred for 24 h at room temperature under a nitrogen atmosphere. The iodine-doped complexes, $Pt(C_3Se_5)(L){\cdot}I_x$ ($x = 5.4$–6.8), obtained were washed with hexane ten times, collected by centrifugation and dried *in vacuo*. Even after adequate washings with hexane, a very small amount of iodine was continuously eluted into the solvent. This indicates the presence of iodine contaminated in the solids, which has been confirmed by electronic absorption spectra.

To an *N,N*-dimethylformamide solution (55 cm^3) of $Pt(C_3Se_5)$(Et-pa) (50 mg, 66 μmol) was added an *N,N*-dimethylformamide solution (10 cm^3) of iodine (65 mg, 250 μmol) and the solution was stirred for 1 h at room temperature, followed by addition of a water–methanol (1:1) solution (40 cm^3). Black solids of $PtI_2(C_3Se_5)$(Et-pa) precipitated, which were collected by centrifugation, washed with water and methanol, and dried *in vacuo* (30% yield). By a similar procedure, $PtI_2(C_3Se_5)(Pr^i$-pa) was obtained (35% yield). However, $Pt(C_3Se_5)$(bpy) was insoluble even in *N,N*-dimethylformamide for the reaction with iodine in solution.

TABLE 1. Elemental analyses of $Pt(C_3Se_5)(L)$ and $Pt(C_3Se_5)(L){\cdot}I_x$

Complex	Found (calc.) (%)		
	C	H	N
$Pt(C_3Se_5)$(Et-pa)	17.40 (17.37)	1.36 (1.32)	3.61 (3.68)
$Pt(C_3Se_5)(Pr^i$-pa)	19.04 (18.60)	1.56 (1.74)	3.62 (3.15)
$Pt(C_3Se_5)$(bpy)	20.35 (19.95)	1.31 (1.03)	3.50 (3.58)
$Pt(C_3Se_5)$(Et-pa)$\cdot I_{5.4}$	9.35 (9.13)	0.70 (0.70)	1.87 (1.93)
$Pt(C_3Se_5)(Pr^i$-pa)$\cdot I_{6.8}$	8.69 (8.80)	0.74 (0.74)	1.56 (1.71)
$Pt(C_3Se_5)$(bpy)$\cdot I_{6.4}$	9.03 (9.79)	0.58 (0.51)	1.69 (1.76)
$PtI_2(C_3Se_5)$(Et-pa)	13.16 (13.02)	1.02 (0.99)	2.31 (2.76)
$PtI_2(C_3Se_5)(Pr^i$-pa)	13.09 (14.01)	1.07 (1.17)	2.02 (2.72)

Elemental analyses of $Pt(C_3Se_5)(L)$ and the iodine-doped complexes are shown in Table 1.

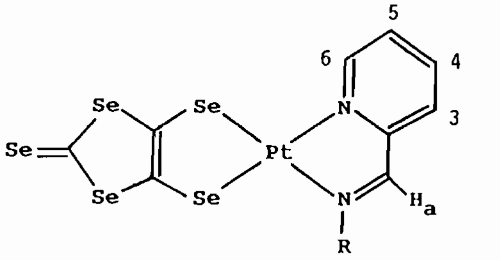
Physical measurements

^{1}H NMR spectra were measured using a JEOL JNM-GSX-400 spectrometer at 400 MHz, Faculty of Engineering, Osaka University, in dimethyl sulfoxide-d_6 against TMS as an internal standard. Far-IR [11], electronic absorption [12] and X-ray photoelectron spectra [13] were measured as described elsewhere. Cyclic voltammograms were recorded in *N,N*-dimethylformamide as described previously [14]. Electrical resistivities for compacted pellets of the complexes were measured by the conventional two-probe method [12].

Results and discussion

^{1}H NMR and electronic absorption spectra of $Pt(C_3Se_5)(L)$

The ^{1}H NMR spectra of $Pt(C_3Se_5)$(R-pa) (R = Et and Pr^i) exhibit ring and imine proton signals, H_6 and H_a (shown in **A**), having satellites due to the spin–spin coupling with the ^{195}Pt nucleus. The chemical shifts of these protons and the proton–^{195}Pt coupling constants of $Pt(C_3Se_5)$(R-pa) (R = Et and Pr^i) are summarized in Table 2, together with those of $Pt(C_3Se_5)$(R-pa). Both the $J(^{195}Pt{-}H_6)$ and $J(^{195}Pt{-}H_a)$ values of the $Pt(C_3Se_5)$(R-pa) complexes are significantly smaller than those of the corresponding C_3S_5 analogs, indicating that the Pt–N bonds of the C_3Se_5 complexes are weakened compared with those of the C_3S_5 complexes. This is consistent with the fact that the Pt–Se bond order of the complexes is raised to some extent compared with the Pt–S bond, which is deduced from the electronic absorption spectra, as described below. Similarly, the somewhat raised bond order was confirmed in metal–selenium bonds rather than metal–sulfur bonds of



Structure A (R = Et and Pr^i)

TABLE 2. ^1H NMR parameters of $Pt(C_3X_5)(R\text{-}pa)$ (X = S and Se; R = Et and Pr^i) complexes in dimethyl sulfoxide-d_6[a]

Complex	Chemical shift, δ		Coupling constant (Hz)	
	H_6	H_a	$^3J(^{195}Pt\text{-}H_6)$	$^3J(^{195}Pt\text{-}H_a)$
$Pt(C_3Se_5)(Et\text{-}pa)$	8.82 (+0.78)	9.47 (+1.02)	29.5	76.0
$Pt(C_3Se_5)(Pr^i\text{-}pa)$	8.83 (+0.70)	9.55 (+1.02)	30.0	77.0
$Pt(C_3S_5)(Et\text{-}pa)$[b]	8.90 (+0.80)	9.45 (+0.99)	34.2	78.5
$Pt(C_3S_5)(Pr^i\text{-}pa)$[b]	8.98 (+0.85)	9.58 (+1.05)	33.0	82.0

[a] ($\delta_{complexed}-\delta_{free}$) in parentheses. [b] Ref. 1.

$[M(C_3X_5)_2]^{2-}$ (M = Cu [15] and Zn [8]; X = S and Se) complexes based on X-ray crystallography.

Figure 1 illustrates the electronic absorption spectra of $Pt(C_3Se_5)(Et\text{-}pa)$ in dimethyl sulfoxide and in dichloromethane as well as that of $Pt(C_3S_5)(Et\text{-}pa)$ in dimethyl sulfoxide. The intense band at 530 nm observed for the selenium complex in dimethyl sulfoxide is ascribed to the π–π^* transition of the C_3Se_5 ligand [8]. The corresponding band due to the $C_3S_5^{2-}$ ligand is observed at 480 nm. The band observed at a longer wavelength for the C_3Se_5 complex corresponds to the raised Pt—Se bond order compared with the Pt–S bond order; an appreciable lowering of the π^* energy level of the selenium ligand in comparison with the sulfur ligand causes an easier backdonation from the metal ions to the selenium ligand. The band observed at 645 nm in dichloromethane may be ascribed to an intramolecular ligand-to-ligand charge-transfer transition, as described for the corresponding NiN_2S_2 and PtN_2S_2 complexes [1, 2, 16–19], or a metal-to-ligand charge transfer d–π^* (diselenolate) transition suggested by a recent study on luminescences of PtN_2S_2 complexes [20]. The band occurs at 600 nm in dimethyl sulfoxide. The negative solvatochroism suggests the polar electronic structure of the complex in the ground state. The Pr^i-pa analog has also shown quite similar spectral behavior. On the other hand, $Pt(C_3S_5)(Pr^i\text{-}pa)$ indicates a much larger energy shift of this band (660 nm in dichloromethane and 550 nm in dimethyl sulfoxide) [1]. Thus, $Pt(C_3Se_5)(R\text{-}pa)$ (R = Et and Pr^i) complexes are less polar than the C_3S_5 analogs.

Oxidation of $Pt(C_3Se_5)(L)$ complexes

Cyclic voltammograms of $Pt(C_3Se_5)(Et\text{-}pa)$ and $Pt(C_3S_5)(Et\text{-}pa)$ measured in *N,N*-dimethylformamide are illustrated in Fig. 2. The former

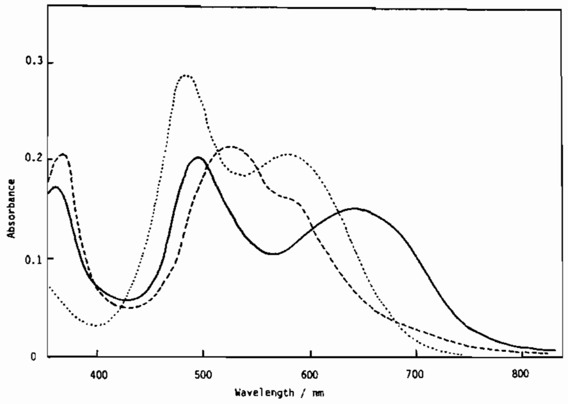


Fig. 1. Electronic absorption spectra of $Pt(C_3Se_5)(Et\text{-}pa)$ in dichloromethane (——) and in dimethyl sulfoxide (– – –) and of $Pt(C_3S_5)(Et\text{-}pa)$ in dimethyl sulfoxide (· · ·); 2.6×10^{-5} mol dm^{-3}.

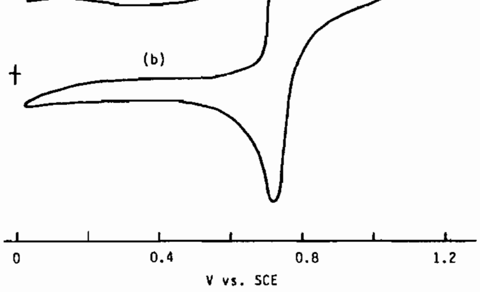


Fig. 2. Cyclic voltammograms of (a) $Pt(C_3Se_5)(Et\text{-}pa)$ (sweep rate, 100 mV s^{-1}) and (b) $Pt(C_3S_5)(Et\text{-}pa)$ (sweep rate, 50 mV s^{-1}) in *N,N*-dimethylformamide at room temperature; 1.0×10^{-4} mol dm^{-3}, $[NBu^n_4][ClO_4]$ 0.1 mol dm^{-3}.

complex shows an irreversible oxidation wave ($E_{p,a} = 0.68$ V versus SCE), while the latter undergoes a reversible oxidation process ($E_{a,p} = 0.78$ V versus SCE). Pt(C_3Se_5)(Pr^i-pa) and Pt(C_3Se_5)(bpy) also give irreversible oxidation waves: $E_{a,p} = 0.60$ and 0.59 V versus SCE, respectively. These C_3Se_5 complexes are oxidized at somewhat lower potentials than the C_3S_5 complexes. This behavior is similar to the observation that the oxidation potentials of $[M(C_3Se_5)_2]^{n-}/[M(C_3Se_5)_2]^{(n-1)-}$ are 0.06–0.39 V lower than those of $[M(C_3S_5)_2]^{n-}/[M(C_3S_5)_2]^{(n-1)-}$ (M = Ni^{II}, Pd^{II} [15] or Cu^{II} [14], $n = 2$; Au^{III}, $n = 1$ [5]).

Finely powdered Pt(C_3Se_5)(L) (L = bpy, Et-pa and Pr^i-pa) complexes suspended in hexane reacted with excess amounts of iodine to afford Pt(C_3Se_5)(L)·I_x ($x = 5.4$–6.8) containing excess amounts of iodine, while reactions of Pt(C_3Se_5)(L) (L = Et-pa and Pr^i-pa) dissolved in *N,N*-dimethylformamide with iodine gave PtI_2(C_3Se_5)(L).

Binding energies of Pt 4f electrons determined from X-ray photoelectron spectra are summarized in Table 3. The iodine-doped complexes and PtI_2(C_3Se_5)(L) (L = Et-pa and Pr^i-pa) have 1.1–1.5 eV higher binding energies compared with Pt(C_3Se_5)(L). Furthermore, these iodine-doped complexes have shown no ESR signals. Thus, they seem to be in the Pt(IV) state. This is greatly different from the C_3S_5-centered oxidation observed for Pt(C_3S_5)(L)·I_x ($x = 1.7$–2.2) complexes which are essentially in the Pt(II) oxidation state and exhibit intense ESR signals due to the oxidized C_3S_5 moiety [1, 2]. The metal-centered oxidation of the present PtSe_2N_2 complexes is consistent with somewhat increased electron density around the metal caused by the higher Pt–Se bond order compared with the corresponding PtS_2N_2 complexes as described above.

Although the iodine-doped complexes contain excess amounts of iodine as pointed out above, the I_3^- [21] and I_5^- ions [22] were not detected by Raman spectra. The Pt(II) ion is oxidized by iodine to the Pt(IV) state bound with the I^- ions.

TABLE 3. Binding energies of Pt 4f electrons of Pt(C_3Se_5)(L) complexes and the iodine-doped species

Complex	Binding energy (eV)	
	Pt $4f_{7/2}$	Pt $4f_{5/2}$
Pt(C_3Se_5)(Et-pa)	72.1	75.3
Pt(C_3Se_5)(Pr^i-pa)	72.6	75.8
Pt(C_3Se_5)(bpy)	72.6	75.8
Pt(C_3Se_5)(Et-pa)·$I_{5.4}$	73.9	77.1
Pt(C_3Se_5)(Pr^i-pa)·$I_{6.8}$	73.9	77.2
Pt(C_3Se_5)(bpy)·$I_{6.4}$	74.1	77.3
PtI_2(C_3Se_5)(Et-pa)	73.9	76.9
PtI_2(C_3Se_5)(Pr^i-pa)	73.6	76.9

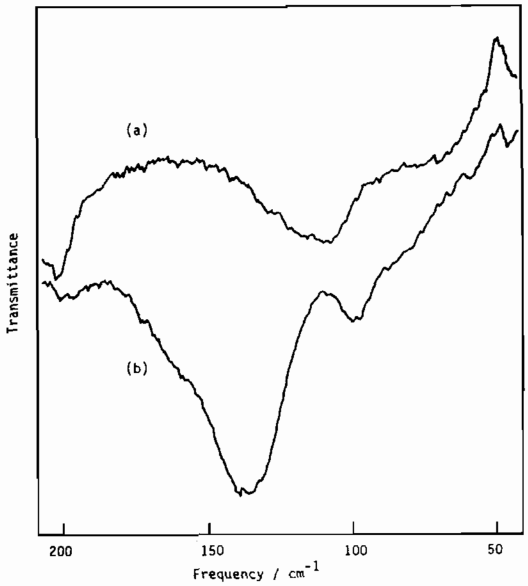


Fig. 3. Far-IR spectra of (a) Pt(C_3Se_5)(Et-pa) and (b) Pt(C_3Se_5)(Et-pa)·$I_{5.4}$ in Nujol mulls.

Far-IR spectra of Pt(C_3Se_5)(Et-pa) and Pt(C_3Se_5)(Et-pa)$I_{5.4}$ are illustrated in Fig. 3. The strong absorption band at 140 cm^{-1} and the weak band at 100 cm^{-1} observed for the latter complex are assigned to asymmetric and symmetric Pt–I stretching, respectively [23], indicating a *trans* conformation of the Pt–I bonds.

Electrical conductivities of the complexes measured for the compacted pellets at room temperature are summarized in Table 4. Pt(C_3Se_5)(L) (L = Et-pa, Pr^i-pa, and bpy) behave essentially as an insulator with very small conductivities. On the other hand, the iodine-doped complexes exhibit somewhat higher conductivities, in the order of 10^2–10^3, than the original species. This is very close to the Pt(C_3S_5)(L) complexes reported previously [1, 2].

Since selenium has more diffuse, expanded p and d orbitals than sulfur and some $[M(C_3Se_5)_2]^{n-}$ (M = Ni, $n = 1$; M = Cu, $n = 2$ [15]; M = Au, $n = 1$ [5]) complexes exhibit many intermolecular

TABLE 4. Electrical conductivities (σ) of Pt(C_3Se_5)(L) and their iodine-doped complexes[a]

Complex	$\sigma_{r.t.}$ (S cm^{-1})
Pt(C_3Se_5)(Et-pa)	2.8×10^{-9}
Pt(C_3Se_5)(Pr^i-pa)	5.4×10^{-9}
Pt(C_3Se_5)(bpy)	7.6×10^{-10}
Pt(C_3Se_5)(Et-pa)·$I_{5.4}$	2.5×10^{-6}
Pt(C_3Se_5)(Pr^i-pa)·$I_{6.8}$	1.3×10^{-6}
Pt(C_3Se_5)(bpy)·$I_{6.4}$	6.0×10^{-7}
PtI_2(C_3Se_5)(Et-pa)	9.4×10^{-7}
PtI_2(C_3Se_5)(Pr^i-pa)	1.3×10^{-7}

[a] Measured for compacted pellets.

non-bonded Se–Se contacts in the solid state, the oxidized $PtSe_2N_2$ complexes would have been expected to have higher conductivities. In the reactions of PtN_2Se_2 complexes with iodine, however, the metal-centered oxidation occurs with the formation of Pt–I bonds, leading to no Pt--Pt contacts. Moreover, effective Se--Se contacts are likely to be formed among the oxidized C_3Se_5 moieties. Thus, the oxidized C_3Se_5–Pt complexes construct no effective conduction pathways in the solid state and exhibit insufficient increase in conductivity.

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