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Properties of Pt(II) complexes with a sulfur-rich dithiolate ligand having alkyl chains and of their oxidized species. The X-ray crystal structure of $[NBu^n_4]_2[Pt\{C_6S_8(C_{10}H_{21})_2\}_2]$

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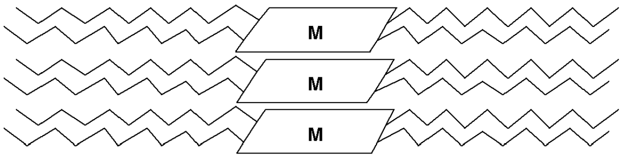
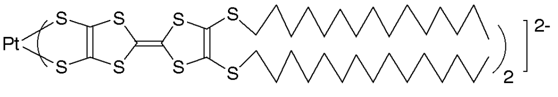
Reactions of $[NBu^n_4]_2[PtCl_4]$ with $Na_2[C_6S_8R_2]$ [$C_6S_8R_2^{2-}$ = 2-{bis(alkylthio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate(2−); R = $C_{10}H_{21}$, $C_{14}H_{29}$ or $C_{18}H_{37}$] in methanol afforded $[NBu^n_4]_2[Pt(C_6S_8R_2)_2]$. The crystal structure of $[NBu^n_4]_2[Pt\{C_6S_8(C_{10}H_{21})_2\}_2]$ was determined by X-ray analysis. The crystal packing structure consists of columns of anion units assembled through the association of alkyl chains, where the metal-center units are separated by the bulky cations. These complexes exhibit oxidation potentials of −0.25 to +0.35 V *vs.* SCE. They were oxidized by bromine or iodine to yield essentially two-electron oxidized species $[Pt(C_6S_8R_2)_2]^0$, with ligand-centered oxidation. The oxidized complexes (R = $C_{10}H_{21}$ and $C_{14}H_{29}$) exhibit electrical conductivities (σ) of 1.4×10^{-2} to 4.9×10^{-2} S cm^{-1} measured for compacted pellets at room temperature, while the oxidized species with R = $C_{18}H_{37}$ behaves as an insulator ($\sigma < 10^{-8}$ S cm^{-1}). Electronic states and molecular interactions of the complexes in the solid state are discussed based on EPR, XPS, electronic absorption and reflectance spectra.

Organic–inorganic composite materials and supermolecular assemblies having unique structures and functions, such as optical, electrical and magnetic properties, have been extensively designed and prepared.[1–6] Lamellar solids constructed with alternately arranged metal complex units and organic domains attract much attention from the standpoint of their unique structures and properties.[1,7,8] Such organic–inorganic molecular composites with layered structures may be formed by metal complexes with sulfur-rich dithiolate ligands having long alkyl chains (**A**), since long alkyl chains often associate to form a layered structure,[3,4,9–12] and metal complexes with sulfur-rich dithiolate ligands exhibit molecular interactions through several S···S non-bonded contacts in the solid state.[13–17] Planar platinum(II) complexes can also form one-dimensional molecular columns through metal–metal interactions, and the oxidized species may become electrical conductors.[18–20]



A

We have designed planar platinum(II) complexes with a sulfur-rich dithiolate ligand constructed with a C_6S_8 skeleton having long alkyl chains: (**B**; R = $C_{10}H_{21}$, $C_{14}H_{29}$, $C_{18}H_{37}$) which are expected to form columnar and/or layered structures with both association of the long alkyl chains and of bis(sulfur-rich dithiolato)platinum(II) units. In this work, these platinum(II) complexes and their oxidized species have been prepared. Their spectroscopic and electrochemical properties and electrical conductivities of the oxidized species, together with the X-ray crystal structure of $[NBu^n_4]_2[Pt\{C_6S_8(C_{10}H_{21})_2\}_2]$, are described.



B

Experimental

Preparation of pro-ligand compounds, $(C_2H_5OCOC_2H_4)_2C_6S_8R_2$ [R = $C_{10}H_{21}$ 1, $C_{14}H_{29}$ 2 and $C_{18}H_{37}$ 3]

An acetonitrile (350 cm^3) solution containing $[NBu^n_4]_2[Zn(C_3S_5)_2]$[21] (19.3 g, 20.5 mmol) and $C_{10}H_{21}Br$ (25.0 g, 113 mmol) was refluxed for 3 h under an argon atmosphere. After the solution was dried under reduced pressure, the solids obtained were dissolved in dichloromethane, washed with water several times, and the solution was dried with anhydrous $MgSO_4$. The resulting solid was recrystallized from hot ethanol to give $C_3S_5(C_{10}H_{21})_2$ (50% yield). By a similar procedure, $C_3S_5(C_2H_4COOEt)_2$ was obtained by the reaction of $[NBu^n_4]_2[Zn(C_3S_5)_2]$ (26.2 g, 27.8 mmol) with $EtOCOC_2H_4Br$ (27.2 g, 150 mmol) (85% yield).

$C_3S_5(C_2H_4COOEt)_2$ (16.6 g, 41.6 mmol) and $Hg(OCOMe)_2$ (35.4 g, 111 mmol) were dissolved in a mixture of chloroform–acetic acid (3 : 1 v/v, 360 cm^3) and the solution was stirred for 20 h at room temperature. After filtration through Celite, the solution was washed with an $NaHCO_3$ aqueous solution, dried with anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to afford $C_3S_4O(C_2H_4COOEt)_2$ (80% yield).

$C_3S_5(C_{10}H_{21})_2$ (16.0 g, 33.3 mmol) and $C_3S_4O(C_2H_4COOEt)_2$ (12.7 g, 33.3 mmol) were dissolved in triethyl phosphite (240 cm^3) and the solution was refluxed for 5 h. To the resulting solution was added methanol (200 cm^3) to afford solid compound **1**, which was recrystallized from hot methanol (38% yield). Anal. Found: C, 53.15; H, 7.75. Calc. for $C_{30}H_{60}O_4S_8$: C, 53.05; H, 7.45%.

By a similar procedure to that described above, $C_3S_5(C_{14}H_{29})_2$ and $C_3S_5(C_{18}H_{37})_2$ were prepared by the reaction of $[NBu^n_4]_2[Zn(C_3S_5)_2]$ with $C_{14}H_{29}Br$ and $C_{18}H_{37}Br$, respectively, in acetonitrile (94 and 91% yields). By a similar procedure to that described for **1**, compounds **2** and **3** were prepared by the reaction of $C_3S_4O(C_2H_4COOEt)_2$ with $C_3S_5(C_{14}H_{29})_2$ and $C_3S_5(C_{18}H_{37})_2$, respectively, in triethyl phosphite (32 and 61% yields). Anal. Found: C, 57.1; H, 8.25. Calc. for $C_{44}H_{76}O_4S_8$ **2**: C, 57.1; H, 8.3%. Found: C, 60.8; H, 8.8. Calc. for $C_{52}H_{92}O_4S_8$ **3**: C, 60.2; H, 8.95%.

^{1}H NMR (in $CDCl_3$): **1**: δ 0.81 (6H, t, CH_3), 2.60 (4H, t, CH_2), 2.75 (4H, t, CH_2), 3.00 (4H, t, CH_2), 4.09 (4H, m, CH_2). **2**: δ 0.88 (6H, t, CH_3), 2.68 (4H, t, CH_2), 3.07 (4H, t, CH_2), 4.17 (4H, q, CH_2). **3**: δ 0.88 (6H, t, CH_3), 2.67 (4H, t, CH_2), 2.79 (4H, t, CH_2), 3.07 (4H, t, CH_2), 4.17 (4H, m, CH_2).

The preparation route is illustrated in Scheme 1.

Preparation of Pt(II) complexes, $[NBu^n_4]_2[Pt\{C_6S_8R_2\}_2]$ $[R = C_{10}H_{21}$ **4**, $C_{14}H_{29}$ **5** and $C_{18}H_{37}$ **6**$]$

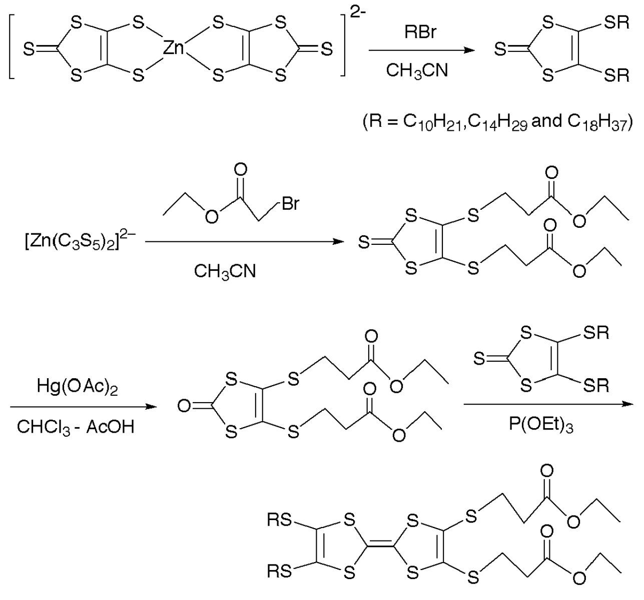
All the following reactions were performed under an argon atmosphere. Compound **1** (490 mg, 0.60 mmol) was dissolved in an ethanol (20 cm^3) solution containing sodium metal (60 mg, 2.6 mmol). The resulting solution of $Na_2[C_6S_8(C_{10}H_{21})_2]$ was added to an ethanol (10 cm^3) solution of $[NBu^n_4]_2[PtCl_4]$ (250 mg, 0.30 mmol) and the solution was stirred for 2 h at room temperature. The precipitate of complex **4** obtained was collected by filtration, washed with ethanol, and dried *in vacuo* (83% yield). Anal. Found: C, 52.9; H, 8.3; N, 1.5. Calc. for $C_{84}H_{156}N_2PtS_{16}$: C, 53.05; H, 8.3; N, 1.45%.

By a similar procedure to that described above, complexes **5** and **6** were prepared by the reaction of $[NBu^n_4]_2[PtCl_4]$ with compounds **2** and **3** in ethanol (65 and 75% yields, respectively). Anal. Found: C, 56.0; H, 8.7; N, 1.4. Calc. for $C_{100}H_{188}N_2PtS_{16}$ **5**: C, 56.5; H, 8.9; N, 1.3%. Found: C, 59.65; H, 9.55; N, 0.9. Calc. for $C_{116}H_{220}N_2PtS_{16}$ **6**: C, 59.25; H, 9.45; N, 1.2%.

^{1}H NMR (in $CDCl_3$): **4**: δ 0.88 (12H, t, CH_3), 2.78 (8H, t, CH_2), 3.41 (16H, m, CH_2). **5**: δ 0.88 (12H, t, CH_3), 2.79 (8H, m, CH_2), 3.35 (16H, m, CH_2).

Preparation of oxidized Pt(II) complexes, $[Pt(C_6S_8R_2)_2]$ $[R = C_{10}H_{21}$ **7**, $C_{14}H_{29}$ **8** and $C_{18}H_{37}$ **9**$]$

To a diethyl ether (10 cm^3) solution of complex **4** (150 mg, 0.077 mmol) was added with stirring a diethyl ether (5 cm^3) solution of bromine (0.015 mg, 0.020 mmol) to afford immediately a black precipitate of complex **7**, which was collected by filtration, washed with acetone, and dried *in vacuo* (75% yield). Anal. Found: C, 42.7; H, 5.65. Calc. for $C_{52}H_{84}PtS_{16}$: C, 44.05; H, 5.95%. Oxidation of **4** using iodine, $[Fe(C_5H_5)_2][PF_6]$ or $[TTF]_3[BF_4]_2$ ($TTF^{\cdot+}$ = tetrathiafulvalenium radical cation) as the oxidant also afforded **7** (two-electron oxidized species).



Scheme 1

By a similar method to that described for **7** using bromine as the oxidant, two-electron oxidized species **8** and **9** were obtained from complexes **5** and **6**, respectively. Anal. Found: C, 48.7; H, 6.95. Calc. for $C_{68}H_{116}PtS_{16}$ **8**: C, 49.75; H, 7.1%. Found: C, 53.2; H, 8.0. Calc. for $C_{84}H_{148}PtS_{16}$ **9**: C, 54.05; H, 8.0%

Physical measurements

Electron absorption spectra were recorded on a JASCO V-570 UV/VIS/NIR spectrophotometer and powder reflectance spectra with a 60ϕ integrating sphere unit. EPR spectra[22] were recorded as described previously. ^{1}H NMR spectra were recorded at 270 MHz using a JEOL EX-270 spectrometer at the Graduate School of Science, Osaka University, the chemical shifts being measured relative to tetramethylsilane (TMS) as the internal standard in chloroform-d$_1$. X-Ray photoelectron spectra were obtained by irradiating the complexes with Mg-Kα X-rays (300 W) at 298 K using an ULVAC-PHI ESCA 5700 photoelectron spectrometer, Osaka Municipal Technical Research Institute, and were calibrated with the carbon 1s$_{1/2}$ photoelectron peak (285 eV). Cyclic voltammograms of complexes **4–6** in dichloromethane or tetrahydrofuran were measured using $[NBu^n_4][ClO_4]$ as the supporting electrolyte, as described previously.[17] Electrical resistivities of the complexes were measured at room temperature for compacted pellets by the conventional two-probe method.[23]

Crystal structure determination of $[NBu^n_4]_2[Pt\{C_6S_8(C_{10}H_{21})_2\}_2]$ **4**

Diffraction data were collected on a Rigaku AFC-7R four-circle diffractometer with graphite-monochromated Mo-Kα radiation. Crystallographic data are summarized in Table 1. Reflection data were corrected for Lorentz and polarization effects, together with absorption[24] and decay.

The structure was solved by direct methods (SHELX-86)[25] and refined on *F* by the full-matrix least-squares technique. All the non-hydrogen atoms were refined anisotrophically and the hydrogen atoms fixed at geometrically calculated positions. C(42) and C(43) atoms of one butyl group of the tetrabutylammonium cation were disordered, having an occupancy factor of 0.5. Calculations were performed with the TEXSAN

Table 1 Experimental crystallographic data for $[NBu^n_4]_2$-$[Pt\{C_6S_8(C_{10}H_{21})_2\}_2]$ **4**

Formula	$C_{84}H_{156}N_2PtS_{16}$
M	1902.32
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a/Å	12.416(2)
b/Å	22.881(4)
c/Å	9.315(2)
α/°	99.93
β/°	101.19(2)
γ/°	83.39(1)
V/Å^3	2548.0(7)
Z	1
D_{calc}/g cm^{-3}	1.240
Crystal size/nm	$0.30 \times 0.10 \times 0.50$
F(000)	1008
μ(Mo-Kα)/mm^{-1}	1.74
T/°C	23
Measured 2θ range/°	6–55
No. of reflections collected	11662
No. of reflections with $I > 3\sigma(I)$	6598
R^a	0.039
$R_w{}^b$	0.043

$^a R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. $^b R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|]^{1/2}$, $w^{-1} = \sigma^2(F_0) + 0.0001F_0{}^2$.

structure analysis package[26] on an SGI-02 workstation at the Graduate School of Science, Osaka University. Atomic scattering factors were taken from the usual sources.[27] Fig. 1 and 2 were drawn with a local version of ORTEP II.[28]

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Mater. Chem.*, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/172. See http: //www.rsc.org/suppdata/cc/1999/2413/ for crystallographic files in .cif format.

Results and discussion

Crystal structure of $[\mathrm{NBu^n}_4]_2[\mathrm{Pt}\{\mathrm{C_6S_8(C_{10}H_{21})_2}\}_2]$ 4

The molecular structure of the anion of complex **4** is shown in Fig. 1, together with the atom-labelling scheme. Selected bond distances and angles of the anion moiety are listed in Table 2. The platinum atom is located on the centre of symmetry. Two dithiolate ligands coordinate to the platinum(II) ion to form an almost regular square-planar geometry around the metal atom with an S(1)–Pt–S(2) angle of 89.45(5)°. Pt–S distances [2.310(1), 2.310(2) Å] are close to those of other bis(dithiolato)platinum(II) anion complexes; $[\mathrm{NBu^n}_4]_2[\mathrm{Pt(mnt)_2}]$ (mnt^{2-} = maleonitrile-2,3-dithiolate) [2.279(2), 2.287(2) Å],[29] $[\mathrm{TDAE}][\mathrm{Pt(mnt)_2}]$ (TDAE^{2+} = tetrakis(dimethylamino)ethene dication) [2.278(4), 2.300(4) Å],[30] $[\mathrm{NBu^n}_4][\mathrm{Pt(C_3S_5)_2}]$ ($\mathrm{C_3S_5}^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-thionate) [2.275(2), 2.276(1) Å],[31] and $[\mathrm{NEt_4}][\mathrm{Pt(dddt)_2}]$ (dddt^{2-} = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) [2.269(3), 2.270(6) Å].[32] The C=C bond distances of the $\mathrm{C_6S_8}$ skeleton [1.336(7)–1.348(7) Å] are close to those of the $\mathrm{C_3S_5}$ [1.348(7) Å] and dddt ligands [1.34(3) Å] of the abovementioned complexes. The S(3), S(4), S(5), S(6), C(3) and C(4) atoms of the $\mathrm{C_6S_8}$ skeleton are nearly coplanar (±0.03 Å), and the other sulfur atoms deviate to the same side of the best plane by 0.49–0.68 Å. This is similar to the case of $\mathrm{C_8H_4S_8(CH_2CH_2CN)_2}$.[16] The S-alkyl groups greatly deviate from this plane with C(5)–S(7)–C(7) and C(6)–S(8)–C(17) angles of 101.9(3) and 101.7(3)°, respectively. This deviation of the S-alkyl groups is also similar to that of the abovementioned $\mathrm{C_8H_4S_8}$ compound and $[\mathrm{Ni(C_6S_8Et_2)_2}]$.[33]

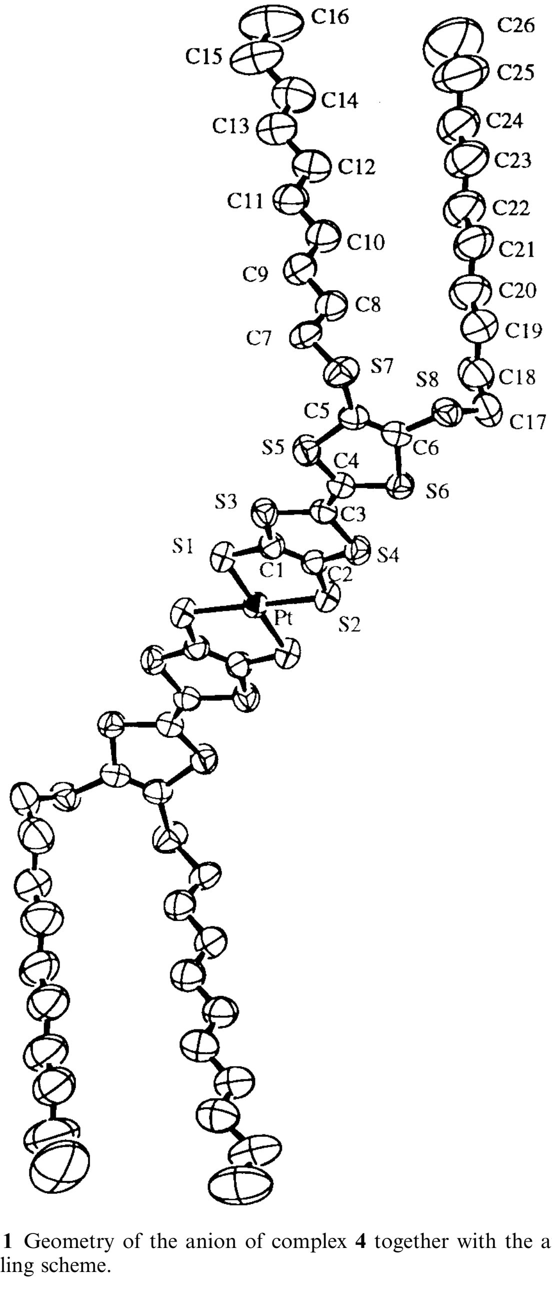


Fig. 1 Geometry of the anion of complex **4** together with the atom-labelling scheme.

Table 2 Selected bond lengths (Å) and angles (°) for $[\mathrm{Nbu^n}_4]_2[\mathrm{Pt}\{\mathrm{C_6S_8(C_{10}H_{21})_2}\}_2]$ **4** with estimated standard deviations in parentheses

Pt–S(1)	2.310(2)	Pt–S(2)	2.310(1)
S(1)–C(1)	1.755(5)	S(2)–C(2)	1.744(6)
S(3)–C(1)	1.751(6)	S(3)–C(3)	1.758(5)
S(4)–C(2)	1.767(5)	S(4)–C(3)	1.751(6)
S(5)–C(4)	1.756(6)	S(5)–C(5)	1.768(6)
S(6)–C(4)	1.763(5)	S(6)–C(6)	1.745(6)
S(7)–C(5)	1.736(6)	S(7)–C(7)	1.804(7)
S(8)–C(6)	1.757(6)	S(8)–C(17)	1.809(7)
C(1)–C(2)	1.345(7)	C(3)–C(4)	1.336(7)
C(5)–C(6)	1.348(7)		
S(1)–Pt–S(2)	89.45(5)	Pt–S(1)–C(1)	101.0(2)
Pt–S(2)–C(2)	101.1(2)	C(1)–S(3)–C(3)	95.4(3)
C(2)–S(4)–C(3)	95.4(3)	C(4)–S(5)–C(5)	94.8(3)
C(4)–S(6)–C(6)	95.0(3)	C(5)–S(7)–C(7)	101.9(3)
C(6)–S(8)–C(17)	101.7(3)	S(1)–C(1)–C(2)	123.3(5)
S(3)–C(1)–C(2)	117.5(4)	S(2)–C(2)–C(1)	123.9(4)
S(4)–C(2)–C(1)	116.3(4)	S(3)–C(3)–S(4)	113.7(3)
S(3)–C(3)–C(4)	123.2(5)	S(5)–C(4)–S(6)	112.6(3)
S(5)–C(4)–C(3)	123.4(4)	S(5)–C(6)–C(5)	117.3(4)
S(8)–C(6)–C(5)	123.0(5)		

In the crystal phase, the anion moieties are arranged through association of the long alkyl chains to form a layered structure, as shown in Fig. 2. There are no significant interactions between the bis(dithiolato)platinum(II) centre units even though S···S contacts, which is due to the presence of the bulky tetrabutylammonium ion. However, in the oxidized species some S···S interactions may occur between the bis(dithiolato)platinum(II) units owing to the absence of the bulky cation moieties, as described below.

Electrochemical and spectroscopic properties of complexes 4–6

A cyclic voltammogram of complex **4** measured in dichloromethane exhibited a pseudo-reversible wave corresponding to the redox process $[\mathrm{Pt}\{\mathrm{C_6S_8(C_{10}H_{21})_2}\}_2]^{2-/-}$ at $E_{1/2}{}^{\circ} = -0.03$ V (*vs.* saturated calomel electrode, SCE; $\Delta E = E_{\mathrm{pc}} - E_{\mathrm{pa}} = 150$ mV). The $[\mathrm{Pt}\{\mathrm{C_6S_8(C_{10}H_{21})_2}\}_2]^-$ anion was further oxidized at +0.38 V (*vs.* SCE). A large adsorption wave is observed in the reduction process of the two-electron oxidized species. The oxidation potentials are similar to those of the $[\mathrm{Pt(C_3S_5)_2}]^{2-}$ anion (−0.08 and +0.11 V *vs.* SCE)[34] and higher than those of the $[\mathrm{Pt(C_8H_4S_8)_2}]^{2-}$ anion [$\mathrm{C_8H_4S_8}^{2-}$ = 2-{(4,5-ethylenedithio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate] (−0.47 and −0.26 V *vs.* SCE).[15] Similarly, cyclic voltammograms of **5** and **6** measured in tetrahydrofuran exhibited oxidation potentials at −0.25, +0.25 and −0.25, +0.05 V (*vs.* SCE) for the $[\mathrm{Pt(C_6S_8R_2)_2}]^{2-}$ and $[\mathrm{Pt(C_6S_8R_2)_2}]^-$ species, respectively.

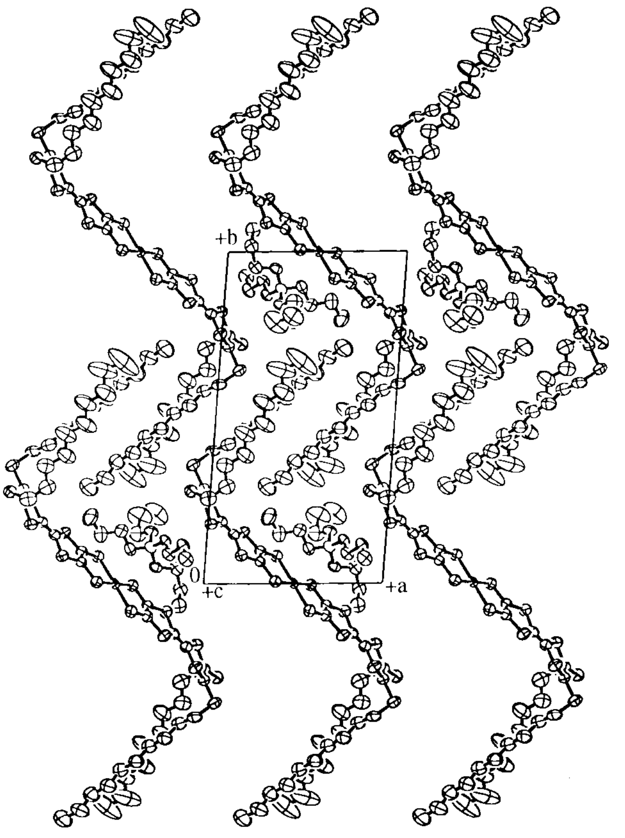


Fig. 2 Packing diagram of complex **4**.

Electronic absorption spectra of complex **4** in dichloromethane in the presence of varying amounts of $[Fe(C_5H_5)_2][PF_6]$ as an oxidizing agent are illustrated in Fig. 3. With the addition of the oxidizing agent to the solution of **4** in increasing amounts, the spectrum of **4** changed with the generation of isosbestic points, resulting in the spectrum of the two-electron oxidized $[Pt(C_6S_8R_2)_2]^0$ species. The band at 1500 nm for **4** is ascribed to the dithiolate ligand-to-platinum(II) ion charge transfer transition, as the bands observed at the near-infrared region for some metal–dithiolate complexes.[35] As the amount of the oxidized species is increased, the band diminishes in intensity, leading to the higher energy shift of the band occurring at 1100 nm.

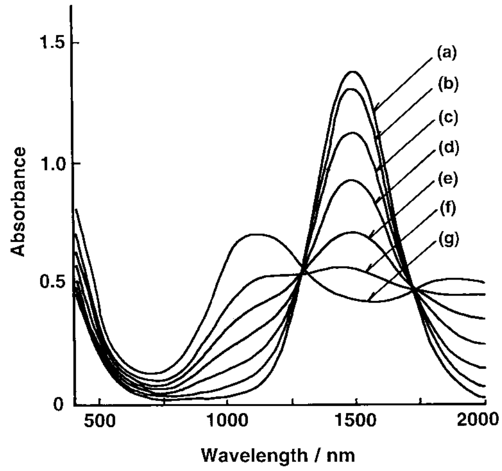


Fig. 3 Electronic absorption spectra of complex **4** (6.0×10^{-5} mol dm^{-3}) in dichloromethane in the presence of $[Fe(C_5H_5)_2][PF_6]$: (a) 0, (b) 1.2×10^{-5}, (c) 2.4×10^{-5}, (d) 3.6×10^{-5}, (e) 4.8×10^{-5}, (f) 6.0×10^{-5}, (g) 1.2×10^{-4} mol dm^{-3}.

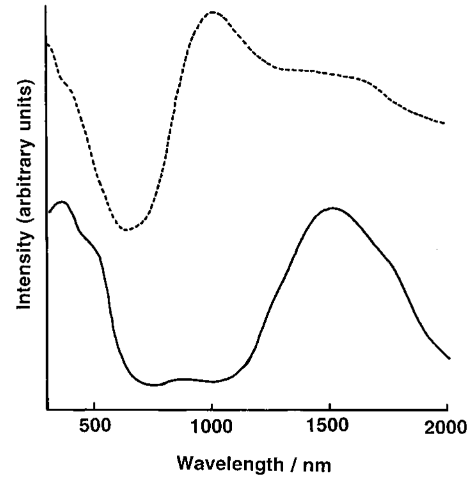


Fig. 4 Powder reflectance spectra of complexes **4** (—) and **7** (- - -).

Properties of the oxidized complexes

Complexes **4**–**6** have been oxidized by the $[Fe(C_5H_5)_2]^+$ cation, iodine and bromine to afford essentially two-electron oxidized species **7**–**9**. Fig. 4 shows powder reflectance spectra of complex **4** and its oxidized species **7**. Complex **4** has a band at 1500 nm, as observed at 1300 nm in the absorption spectrum in dichloromethane, and **7** exhibits a band at 1000 nm which corresponds to the band at 1100 nm observed in the absorption spectrum in solution, as shown in Fig. 3. This higher energy shift upon oxidization of the complex was also seen for the π–π^* transition bands of the dithiolate ligand of some C_3S_5–metal complexes[22,36,37] and of $C_8H_4S_8$–metal complexes.[16,38] Furthermore, broad bands appear in the longer wavelength region, which are likely to come from the molecular interactions of the oxidized species through S···S non-bonded contacts in the solid phase. Complexes **8** and **9** also exhibit similar reflectance spectra.

The oxidized species 7–9 exhibit essentially an isotropic, sharp EPR signal at $g = 2.01$ (peak-to-peak linewidth, 2.3–2.5 mT). The complexes are almost two-electron oxidized species containing a small amount of the paramagnetic $[Pt(C_6S_8R_2)_2]^-$ anion. The anion moieties are surrounded by diamagnetic $[Pt(C_6S_8R_2)_2]^0$ species, affording a sharp signal. Similar sharp EPR signals were also observed at $g = 2.01$ for $[NBu^n{}_4]_x[Pt(C_8H_4S_8)_2]$ ($x = 0.05$, 0.1 and 0.4).[16] These EPR signals observed at $g = 2.01$ are ascribed to the radical species of the one-electron oxidized dithiolate ligand, as reported for partially oxidized C_3S_5–[22,36,37,39] and $C_8H_4S_8$–metal complexes.[16,17] Thus, $C_6S_8R_2$ ligand-centered oxidation is suggested to occur for the present oxidized complexes. In accordance with this, the binding energies of platinum $4f_{7/2}$ and $4f_{5/2}$ electrons, determined by XPS, for the oxidized species **7**–**9** are 72.3 and 75.6, 72.5, and 72.8 and 76.1 eV, respectively. These values are essentially the same as those of the unoxidized species; 72.3 and 75.5 for **4**, 72.3 and 75.6 for **5**, and 72.8 and 76.0 eV for **6**. This finding supports the proposal of ligand-centered oxidation.

Electrical conductivities of complexes **4**–**6** measured for compacted pellets at room temperature are $< 10^{-8}$ S cm^{-1}. Although they are essentially insulators, their oxidized complexes **7** and **8** show high electrical conductivities of 4.9×10^{-2} and 2.5×10^{-2} S cm^{-1}, respectively. In complex **4**, the $[Pt\{C_6S_8(C_{10}H_{21})_2\}_2]^{2-}$ moieties are separated from each other by the bulky tetrabutylammonium cation, as shown in Fig. 2. However, oxidation is likely to result in effective packing of the $[Pt(C_6S_8)_2]$ moieties suitable for the formation of an electron-conduction pathway in the solid phase. The molecular interactions are confirmed by the broad bands at longer wavelengths in the reflectance spectrum of the oxidized species (Fig. 4). This may be caused by S···S non-bonded contacts, as observed in the crystal structures of one-electron oxidized $[M(C_3S_5)_3]^-$ (M = Mo and W) complexes.[22] In the oxidized species **8** similar molecular interactions may occur in the solid state, resulting in the high electrical conductivity. On the other hand, the oxidized complex **9** shows very low conductivity ($<10^{-8}$ S cm^{-1}), behaving as an insulator. This complex seems to have a molecular packing which is unsuitable for the formation of an electron-conduction pathway.

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