Preparation, Spectroscopy and Oxidation of $[Re(C_3S_5)_3]^-$ and $[ReO(C_3S_5)_2]^-$ Complexes and Crystal Structure of $[PPh_4][ReO(C_3S_5)_2]$†

Gen-etsu Matsubayashi,* Takashi Maikawa and Motohiro Nakano
Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan

---

Reaction of $ReCl_5$ with $Na_2[C_3S_5]$ [$C_3S_5^{2-}$ = 4,5-dimercapto-1,3-dithiole-2-thionate(2−)] in ethanol in the presence of $[PPh_4]Br$ gave $[PPh_4][ReO(C_3S_5)_2]$ **1**. The salt $[NBu^n_4][Re(C_3S_5)_3]$ **2** was obtained by reaction of $ReCl_5$ with $[NBu^n_4]_2[Zn(C_3S_5)_2]$ in acetonitrile. Oxidation reactions of **2** with iodine or $[Fe(C_5H_5)_2][PF_6]$ in dichloromethane afforded $[Re(C_3S_5)_3]$ (contaminated with 5 or 10% of **2**). These oxidized complexes have electrical conductivities of 2.2×10^{-2} and 4.6×10^{-3} S cm^{-1} at room temperature for compacted pellets. Cyclic voltammetry and electronic absorption spectra of **1** and **2**, together with IR, ESR and X-ray photoelectron spectra of the oxidized species of **2** are discussed. X-Ray structure analysis of **1** reveals that the anions having a square-pyramidal geometry around the Re^V are separately arranged in the crystal: monoclinic, space group $P2_1/n$, $a = 12.437(8)$, $b = 25.56(4)$, $c = 11.137(8)$ Å, $\beta = 105.58(6)°$ and $Z = 4$. Block-diagonal least-squares refinement based on 4591 reflections with $|F_o| > 3\sigma(F)$ converged at $R = 0.052$.

Planar metal complexes with the sulfur-rich ligand $C_3S_5^{2-}$ [4,5-dimercapto-1,3-dithiole-2-thionate(2−)] have been extensively studied because of their electrical conductivities.[1-3] On the other hand, non-planar bulky metal complexes with this ligand have been little noticed as electrical conductors, since they seem intuitively to be rather unfavourable for molecular packings in the solid state. Bulky C_3S_5–metal complexes, however, may preferably yield new structural arrangements having effective conduction pathways through non-bonded sulfur–sulfur contacts. Several partially oxidized $[V(C_3S_5)_3]^{n-}$,[4-7] $[M(C_3S_5)_3]^{n-}$ (M = Mo or W),[8,9] and $[Cu_4(C_3S_5)_3]^{n-}$ ($n < 2$) anionic complexes[10,11] were reported to behave as electrical conductors.

Six- and five-co-ordinate rhenium complexes with sulfur-rich dithiolene ligands, in which the metal ion can exhibit stable oxidation states,[12] are of much interest as new electrical conductors having multi-dimensional sulfur–sulfur contacts. Previously, six-co-ordinate rhenium–dithiolene complexes, $[Re(S_2C_2R_2)_3]$ (R = H or Me), were reported to become semi-conductors having electrical conductivities of 10^{-3}–10^{-5} S cm^{-1}.[13] This paper reports the preparation and spectroscopic properties of $[ReO(C_3S_5)_2]^-$ and $[Re(C_3S_5)_3]^-$ complexes and the conductivities of oxidized $[Re(C_3S_5)_3]$ species. The crystal structure of $[PPh_4][ReO(C_3S_5)_2]$ is also described.

Experimental

Preparations.—$[PPh_4][ReO(C_3S_5)_2]$ **1**. All the following reactions were performed under a nitrogen atmosphere. An ethanol (15 cm^3) solution of $ReCl_5$ (270 mg, 740 μmol) was added to an ethanol (15 cm^3) solution containing 4,5-bis(benzoylthio)-1,3-dithiole-2-thione[14] (610 mg, 1.5 mmol), sodium metal (240 mg, 10.4 mmol) and $[PPh_4]Br$ (630 mg, 1.5 mmol), and the solution was stirred for 15 min then allowed to stand for 1 h at room temperature. The precipitate obtained was recrystallized from ethanol–dichloromethane (1 : 1, v/v) to afford dark red columns of complex **1** (30% yield) (Found: C, 38.2; H, 2.2. Calc. for $C_{30}H_{20}OPReS_{10}$: C, 38.55; H, 2.15%). The Re=O bond formation, as apparent from the structure, seems to come from a slight amount of water contained in the solvent.

$[NBu^n_4][Re(C_3S_5)_3]$ **2**. An acetonitrile (20 cm^3) solution containing $[NBu^n_4]_2[Zn(C_3S_5)_2]$[14] (430 mg, 460 μmol) and $ReCl_5$ (84 mg, 230 μmol) was allowed to stand for 15 h at room temperature. The precipitate obtained was dissolved in dichloromethane (10 cm^3) and filtered off. To the filtrate was added diethyl ether (10 cm^3) to afford a black precipitate of complex **2**, which was collected by centrifugation, washed with diethyl ether, and dried *in vacuo* (6% yield) (Found: C, 29.0; H, 3.25; N, 1.4. Calc. for $C_{25}H_{36}NReS_{15}$: C, 29.5; H, 3.55; N, 1.4%).

Oxidized $[Re(C_3S_5)_3]$ *complexes obtained by reactions with oxidants.* To a dichloromethane (10 cm^3) solution of complex **2** (14 mg, 14 μmol) was added with stirring a dichloromethane (10 cm^3) solution of iodine (18 mg, 70 μmol). Immediately black solids of $[Re(C_3S_5)_3]$ **3** (contaminated with approximately 5% of **2**) precipitated, which were collected by centrifugation, washed with dichloromethane and diethyl ether, and dried *in vacuo* (74% yield) (Found: C, 15.0; H, 0.6; N, < 0.3. Calc. for C_9ReS_{15}: C, 13.95%). To a dichloromethane (10 cm^3) solution of **2** (20 mg, 20 μmol) was added with stirring a dichloromethane (5 cm^3) solution of $[Fe(C_5H_5)_2][PF_6]$[5] (20 mg, 60 μmol). Immediately black solids of $[Re(C_3S_5)_3]$ **4** (contaminated with approximately 10% of **2**) precipitated, which were collected by centrifugation, washed with dichloromethane, methanol and diethyl ether, and dried *in vacuo* (79% yield) (Found: C, 15.5; H, 0.45; N, < 0.3%). The discrepancy between the experimental and calculated figures and the presence of a small amount of N in these compounds indicate contamination by a small amount of **2** which could not be removed.

Physical Measurements.—Infrared spectra were measured for KBr disks using a Perkin Elmer 983G spectrophotometer, electronic absorption (200–900 nm), powder reflectance,[15] ESR and X-ray photoelectron spectra[16] as described previously. Electronic absorption spectra (800–1600 nm) were measured using a JASCO UVIDEC-590 spectrophotometer, ^{13}C NMR spectra at 100.4 MHz using a JEOL JNM-GSX-400 spectrometer at the Faculty of Engineering, Osaka University; chemical shifts were measured relative to tetramethylsilane as internal standard in $[^2H_2]$dichloromethane. Cyclic voltam-

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

mograms were recorded for complexes dissolved in dichloromethane solution as described previously.[17] Electrical conductivities of the complexes were measured for compacted pellets at room temperature by the conventional two-probe method.[18]

Crystal Structure Determination of $[PPh_4][ReO(C_3S_5)_2]$ **1**.—Accurate unit-cell parameters were obtained from a least-squares fit based on the setting angles of 25 reflections with 2θ values from 22 to 31°, measured with a Rigaku four-circle diffractometer at the Research Centre for Protein Engineering, Institute for Protein Research, Osaka University.

Crystal data. $C_{30}H_{20}OPReS_{10}$, $M = 934.3$, monoclinic, space group $P2_1/n$, $a = 12.437(8)$, $b = 25.56(4)$, $c = 11.137(8)$ Å, $\beta = 105.58(6)°$, $U = 3410(6)$ Å^3, $Z = 4$, $D_c = 1.820(3)$ g cm^{-3}, $F(000) = 1832.0$ and μ(Mo-Kα) = 44.3 cm^{-1}.

Intensities were collected in the range $3.4 < 2\theta < 50°$ for a crystal with approximate dimensions 0.13 × 0.17 × 0.38 mm, using graphite-monochromatized Mo-Kα ($\lambda = 0.710\,69$ Å) radiation and the ω–2θ scan technique at a 2θ scan rate of 8° min^{-1} and scan width 2θ of $(1.0 + 0.35 \tan\theta)°$. Three check reflections were monitored after every 100. No significant variation in their intensities was observed throughout the data collection. Lorentz and polarization factors were applied and absorption correction was made.[19] Maximum and minimum transmission coefficients were 1.00 and 0.82, respectively. A total of 6450 unique reflections were measured, of which 4591 with $|F_o| > 3\sigma(F)$ were used for the structure determination.

The structure was solved according to the Patterson method. Subsequent Fourier maps showed the positions of all the non-hydrogen atoms, which were refined anisotropically by the block-diagonal least-squares procedure. No attempt was made to refine hydrogen atoms. The final refinement with anisotropic thermal parameters for the non-hydrogen atoms converged at $R = 0.052$ and $R' = 0.068$, using the weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0005F_o^2$. Atomic scattering factors used in the refinement were taken from ref. 20. Atomic positional parameters are shown in Table 1.

Crystallographic calculations were performed using the programs of Professor K. Nakatsu, Kwansei Gakuin University, on an ACOS S-930 computer at the Research Centre of Protein Engineering, Institute for Protein Research, Osaka University. Fig. 1 was drawn with a local version of ORTEP II.[21]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Crystal Structure and Properties of $[PPh_4][ReO(C_3S_5)_2]$ **1**.—The crystal structure consists of discrete anions and cations with no significant close atom–atom contacts among them. A perspective view of the anion moiety is given in Fig. 1 and selected bond lengths and angles are summarized in Table 2. The oxorhenium(V) group is co-ordinated by four sulfur atoms, the geometry around the metal atom being square pyramidal. Atoms S(1), S(5), S(6) and S(10) form a square-basal plane (±0.034 Å) and the rhenium atom is displaced from the best plane by 0.729 Å toward the apical oxygen atom. This geometry is very close to those of $[MoO(C_3S_5)_2]^{2-}$ (ref. 22) and oxorhenium(V) complexes with the $ReOS_4$ core.[23–25] Structural data for reported complexes having the MOS_4 core are listed in Table 3. Both the C_3S_5 ligands of **1** form least-squares planes with maximum deviations of ±0.08 Å for S(1)–S(5) and C(1)–C(3) and of ±0.04 Å for S(6)–S(10) and C(4)–C(6). The rhenium atom deviates by 0.100 Å from the former best plane and 0.359 Å from the latter. The dihedral angle between these two planes is 32.3°, somewhat larger than that (26.3°) of $[NBu^n{}_4]_2[MoO(C_3S_5)_2]$.[22] The Re–S bond distances of **1** are very close to those of reported $[ReOS_4]^-$ type complexes. The Re–O bond distance is somewhat longer than that of $Cs[ReO(S_2C_2O_2)_2]$, consistent with the fact that the ν(Re=O) stretching IR band of the former is observed at lower wavenumber (960 cm^{-1}) than that of the latter (995 cm^{-1}).[23]

Complex **1** shows ^{13}C NMR signals of the C_3S_5 ligand at δ 149.4 (C=C) and 221.3 (C=S) in [$^2H_2$]dichloromethane,

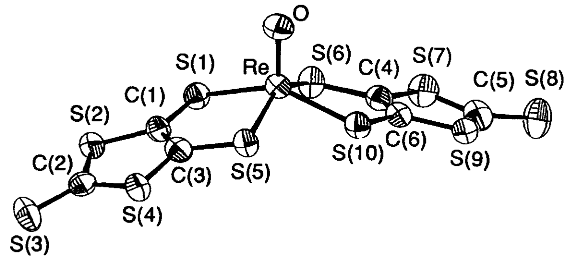

Fig. 1 Perspective view of the anion of $[PPh_4][ReO(C_3S_5)_2]$ **1**, together with the atom labelling scheme

Table 1 Atomic coordinates for $[PPh_4][ReO(C_3S_5)_2]$ **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Re	0.454 27(4)	0.699 12(2)	0.434 24(5)
S(1)	0.437 1(3)	0.719 6(2)	0.225 5(3)
S(2)	0.523 3(3)	0.669 4(2)	0.023 1(3)
S(3)	0.673 1(4)	0.598 8(2)	−0.069 7(4)
S(4)	0.661 8(3)	0.595 8(2)	0.193 5(4)
S(5)	0.589 5(3)	0.638 7(2)	0.416 7(3)
S(6)	0.411 1(3)	0.787 5(2)	0.438 6(3)
S(7)	0.441 2(3)	0.866 2(2)	0.652 5(4)
S(8)	0.531 7(5)	0.901 6(2)	0.914 6(5)
S(9)	0.583 4(4)	0.796 0(2)	0.829 6(4)
S(10)	0.571 6(3)	0.711 2(2)	0.633 0(3)
P	0.804 0(3)	0.399 5(2)	0.175 8(3)
O	0.341 2(7)	0.664 9(4)	0.444 7(8)
C(1)	0.514 8(11)	0.671 1(6)	0.175 4(12)
C(2)	0.622 3(12)	0.620 0(6)	0.042 3(13)
C(3)	0.578 8(11)	0.636 7(5)	0.258 8(11)
C(4)	0.464 7(11)	0.805 0(6)	0.597 2(12)
C(5)	0.519 7(12)	0.857 8(7)	0.800 8(14)
C(6)	0.532 0(11)	0.773 6(6)	0.675 4(11)
C(7)	0.744 3(11)	0.437 4(6)	0.278 7(11)
C(8)	0.804 3(13)	0.478 6(5)	0.346 4(12)
C(9)	0.757 6(17)	0.506 2(7)	0.430 3(16)
C(10)	0.654 3(15)	0.492 1(7)	0.440 8(14)
C(11)	0.594 6(13)	0.450 5(7)	0.369 2(15)
C(12)	0.637 8(11)	0.421 9(6)	0.290 4(14)
C(13)	0.742 8(11)	0.420 3(5)	0.018 2(11)
C(14)	0.650 1(12)	0.452 7(5)	−0.012 4(13)
C(15)	0.598 9(14)	0.464 0(6)	−0.136 8(14)
C(16)	0.646 7(15)	0.444 6(6)	−0.230 3(13)
C(17)	0.740 5(14)	0.413 3(7)	−0.199 6(14)
C(18)	0.789 5(12)	0.400 5(6)	−0.076 6(12)
C(19)	0.774 3(10)	0.331 6(5)	0.192 8(11)
C(20)	0.751 6(10)	0.298 2(6)	0.090 4(12)
C(21)	0.726 4(13)	0.245 8(6)	0.103 6(14)
C(22)	0.725 0(12)	0.226 8(6)	0.221 3(15)
C(23)	0.749 7(12)	0.260 4(6)	0.325 4(14)
C(24)	0.773 2(12)	0.313 5(6)	0.313 3(13)
C(25)	0.952 4(11)	0.410 9(6)	0.211 6(12)
C(26)	1.023 3(13)	0.374 6(7)	0.286 5(17)
C(27)	1.141 5(13)	0.385 7(8)	0.317 4(16)
C(28)	1.179 7(14)	0.429 0(9)	0.271 8(15)
C(29)	1.108 4(17)	0.464 3(9)	0.201 8(22)
C(30)	0.988 1(14)	0.457 6(8)	0.167 6(18)

consistent with a diamagnetic rhenium(v) species in the d^2 state. The absorption spectrum measured in dichloromethane exhibits an intense band at 438 nm, which is ascribed to a π–π^* transition of the C_3S_5 ligand. This band appears at a shorter wavelength than that of the complex $[MoO(C_3S_5)_2]^{2-}$ (485 nm in dichloromethane),[22] which suggests greater stabilization of the occupied π level of the ligand by the rhenium(v) ion than by the molybdenum(IV) ion. In accordance with this, as is shown by the cyclic voltammogram in Fig. 2, the oxidation of **1** occurs at a higher potential [1.10 V *vs.* saturated calomel electrode (SCE) in dichloromethane] than that of the complex $[MoO(C_3S_5)_2]^{2-}$ (a reversible redox process, $E_{\frac{1}{2}}^{0} = 0.15$ V *vs.* SCE in dichloromethane).[22] The oxidation potential of **1** is considerably lower compared with that of $[ReO(mnt)_2]^-$ [mnt = 1,2-dicyanoethylene-1,2-dithiolate(2−)] (+1.76 V *vs.* SCE).[26]

Spectroscopic and Electrochemical Properties of Complex **2**.—Complex **2** exhibits ^{13}C NMR signals due to the C_3S_5 ligand at δ 163.0 (C=C) and 219.1 (C=S) in CD_2Cl_2, indicating a diamagnetic rhenium(v) species in the d^2 state. The cyclic voltammogram of **2** measured in dichloromethane is also illustrated in Fig. 2. The $[Re(C_3S_5)_3]^-$ anion is oxidized to $[Re(C_3S_5)_3]$ at 0.76 V (*vs.* SCE), and cathodic peak potentials occur at −0.63 and −1.28 V corresponding to the $[Re(C_3S_5)_3]^-$–$[Re(C_3S_5)_3]^{2-}$ and $[Re(C_3S_5)_3]^{2-}$–$[Re(C_3S_5)_3]^{3-}$ processes, respectively. The oxidation potential of $[Re(C_3S_5)_3]^-$ is appreciably higher than those of $[Mo(C_3S_5)_3]^{2-}$ and $[W(C_3S_5)_3]^{2-}$ (0.21 and 0.18 V *vs.* SCE, respectively, in dimethylformamide).[8,9] This is also due to greater stabilization of the occupied π level of the present complex compared with those of Mo^{IV} and W^{IV}, as described for $[ReO(C_3S_5)_2]^-$ above.

The electronic absorption spectrum of complex **2** is shown in Fig. 3, together with the spectral change in the presence of $[Fe(C_5H_5)_2][PF_6]$. The bands at 370 and 470 nm of **2** are ascribed to π–π^* transitions of the C_3S_5 ligand. The latter band corresponds to characteristic intense bands observed for $Na_2[C_3S_5]$ (515 nm in methanol), $[Zn^{II}(C_3S_5)_2]^{2-}$ (530 nm in acetonitrile) and $[Cu^{II}(C_3S_5)_2]^{2-}$ (540 nm in acetonitrile).[27] However, the position of the band maximum occurs at somewhat higher energy than those and rather close to those of the complexes $[Au^{III}(C_3S_5)_2]^-$ (468 nm in acetonitrile),[28] $[Mo^{IV}(C_3S_5)_3]^{2-}$ (490 nm in acetonitrile)[8] and $[Cu^I{}_4(C_3S_5)_3]^{2-}$ (458 nm in acetonitrile).[10] In complex **2** and these anionic complexes, charges of +1.7 and +1.3 from the metal centres participate formally in the bonding to each C_3S_5 ligand, while a charge of +1.0 is involved with the complexes of Na^I, Zn^{II} and Cu^{II}. Since the positive charges of the metal ions can

Table 2 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for $[PPh_4][ReO(C_3S_5)_2]$ **1**

Re–S(1)	2.336(4)	S(5)–C(3)	1.729(13)
Re–S(5)	2.329(4)	S(6)–C(4)	1.769(13)
Re–S(6)	2.326(5)	S(7)–C(4)	1.735(16)
Re–S(10)	2.322(4)	S(7)–C(5)	1.691(15)
Re–O	1.687(10)	S(8)–C(5)	1.666(17)
S(1)–C(1)	1.751(16)	S(9)–C(5)	1.759(17)
S(2)–C(1)	1.728(15)	S(9)–C(6)	1.760(13)
S(2)–C(2)	1.735(15)	S(10)–C(6)	1.770(15)
S(3)–C(2)	1.635(17)	C(1)–C(3)	1.369(18)
S(4)–C(2)	1.736(14)	C(4)–C(6)	1.309(18)
S(4)–C(3)	1.758(15)		
P–C(7,13,19,25)	1.795–1.804 (average 1.800)		
C–C(7–30)	1.355–1.452 (average 1.399)		
S(1)–Re–S(5)	86.5(1)	C(5)–S(9)–C(6)	95.0(7)
S(1)–Re–S(6)	81.0(1)	Re–S(10)–C(6)	103.0(4)
S(5)–Re–S(10)	83.4(1)	S(1)–C(1)–C(3)	120.6(11)
S(6)–Re–S(10)	86.6(1)	S(2)–C(1)–C(3)	118.1(11)
S(1)–Re–O	109.3(3)	S(2)–C(2)–S(3)	123.6(8)
S(5)–Re–O	107.2(4)	S(2)–C(2)–S(4)	112.6(9)
S(6)–Re–O	107.5(4)	S(4)–C(3)–C(1)	113.6(10)
S(10)–Re–O	109.0(3)	S(5)–C(3)–C(1)	122.9(11)
Re–S(1)–C(1)	104.4(5)	S(6)–C(4)–C(6)	120.8(12)
C(1)–S(2)–C(2)	97.3(7)	S(7)–C(4)–C(6)	117.1(10)
C(2)–S(4)–C(3)	98.3(7)	S(7)–C(5)–S(9)	113.9(9)
Re–S(5)–C(3)	104.2(5)	S(7)–C(5)–S(8)	124.6(10)
Re–S(6)–C(4)	103.8(5)	S(9)–C(6)–C(4)	116.7(11)
C(4)–S(7)–C(5)	97.2(7)	S(10)–C(6)–C(4)	123.3(10)

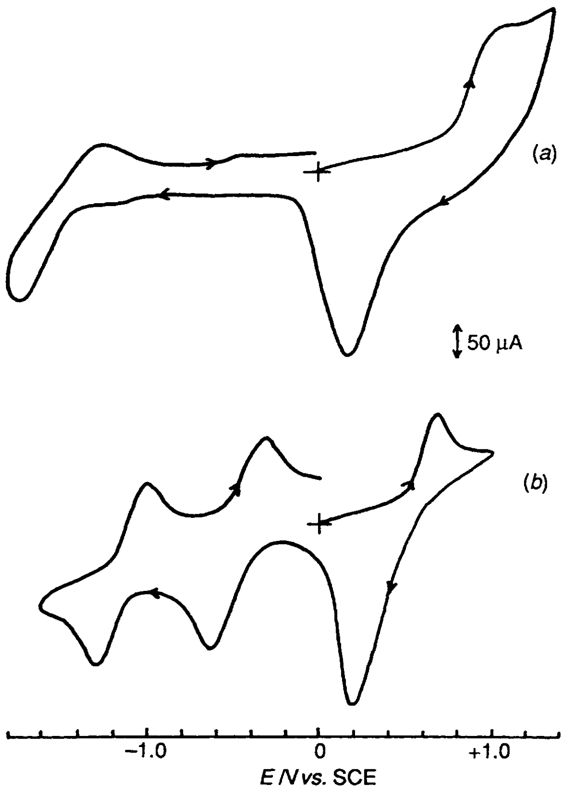

Fig. 2 Cyclic voltammograms of $[PPh_4][ReO(C_3S_5)_2]$ **1** (*a*) and $[NBu^n{}_4][Re(C_3S_5)_3]$ **2** (1.0 × 10^{-3} mol dm^{-3}) in dichloromethane (*b*). Supporting electrolyte: 0.1 mol dm^{-3} $[NBu^n{}_4][ClO_4]$. Sweep rate: 1 V s^{-1}

Table 3 Structural data for MOS_4 cores

	Complex				
	a	*b*[23]	*c*[24]	*d*[25]	*e*[22]
M–O/Å	1.687(10)	1.674(7)	1.689(9)	1.70(2)	1.65(2)
M–S/Å	2.322–2.336(4)	2.323–2.337(3)	2.341(4)	2.33–2.38(1)	2.39–2.41(1)
O–M–S/°	107.2–109.3(4)	108.8(2)	106.9–110.3(4)	103.1–113.3(4)	105–108(1)
S–M–S/°	81.0–86.6(1)	80.5–87.6(1)	83.3–86.5(1)	83.4–86.3(4)	84.4–85.2(4)
M ⋯ S_4/Å	0.729	0.752	0.731	0.71	0.718

[a] $[PPh_4][ReO(C_3S_5)_2]$, this work. [b] $Cs[ReO(S_2C_2O_2)_2]$. [c] $[AsPh_4][ReO(SPh)_4]\cdot MeCN$. [d] $[NHEt_3][ReO(SC_6H_2Me_3\text{-}2,4,6)_4]$. [e] $[NBu^n{}_4]_2[MoO(C_3S_5)_2]$.

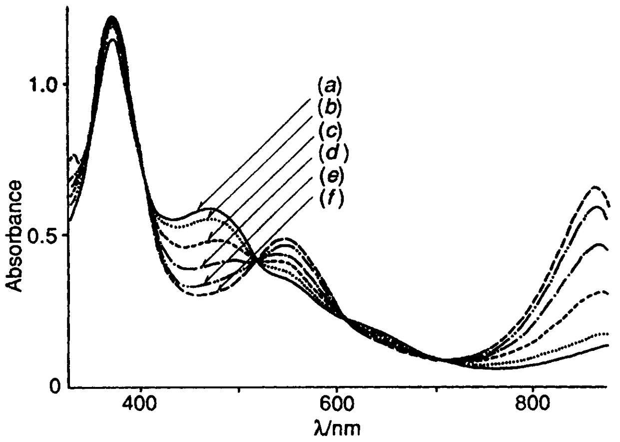

Fig. 3 Electronic absorption spectra of complex **2** (4.9×10^{-5} mol dm^{-3}) in dichloromethane in the presence of $[Fe(C_5H_5)_2][PF_6]$: (*a*) 0, (*b*) 0.98×10^{-5}, (*c*) 1.95×10^{-5}, (*d*) 2.95×10^{-5}, (*e*) 3.9×10^{-5}, (*f*) 4.9×10^{-5} mol dm^{-3}

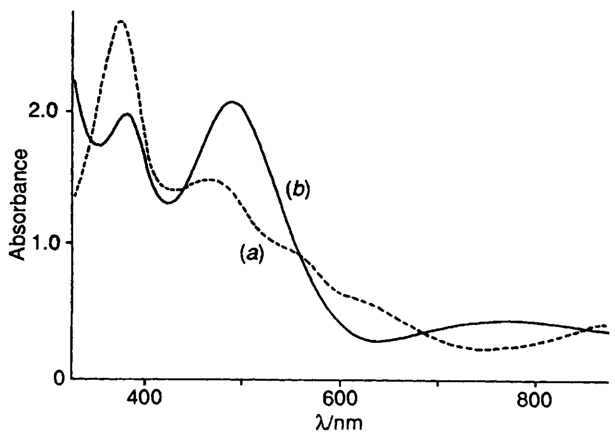

Fig. 4 Electronic absorption spectra of complex **2** (9.8×10^{-5} mol dm^{-3}) in dichloromethane (*a*) and in the presence of $[NBu^n_4][BH_4]$ (9.8×10^{-4} mol dm^{-3}) (*b*)

stabilize the ground state of the C_3S_5 ligand, the latter complexes and **2** are likely to give higher-energy π–π* transitions. Furthermore, complex **2** shows a broad band at 940 nm, which can be assigned to a metal-to-ligand charge-transfer transition, as previously reported for $[Re(S_2C_2Ph_2)_3]$.[29]

By adding $[Fe(C_5H_5)_2][PF_6]$ as an oxidizing agent to a solution of complex **2** the spectrum is changed to one with isosbestic points, the final spectrum being that of the one-electron oxidized complex $[Re(C_3S_5)_3]$. The π–π* transition band at 468 nm is remarkably shifted to longer wavelength (550 nm). Furthermore, an intensified metal-to-ligand charge-transfer band occurs at 850 nm. These spectral behaviours are similar to those of $[Mo(C_3S_5)_3]$ and $[W(C_3S_5)_3]$.[8,9]

Addition of an excess amount of $[NBu^n_4][BH_4]$ as a reducing agent to a dichloromethane solution of complex **2** yields the one-electron reduced species $[Re(C_3S_5)_3]^{2-}$, the spectrum of which is shown in Fig. 4. The band due to the π–π* transition at 490 nm is somewhat intensified compared with that of $[Re(C_3S_5)_3]^-$ and the metal-to-ligand charge-transfer band occurs at considerably shorter wavelength (780 nm) than that of **1**. Isolation of the reduced species as a solid has been unsuccessful because of its extreme instability.

Spectroscopic and Electrical Properties of Oxidized $[Re(C_3S_5)_3]$ *Complexes*.—Reactions of complex **2** with excess amounts of the $[Fe(C_5H_5)_2]^+$ cation or iodine have afforded the essentially one-electron oxidized species $[Re(C_3S_5)_3]$ **3** and **4** containing slight amounts of the tetrabutylammonium cation. The binding energies of Re $4f_{7/2}$ electrons for these species determined by X-ray photoelectron spectroscopy (41.3 and 41.7 eV for **3** and **4**, respectively) are essentially the same as that of **2** (41.6 eV). This indicates the rhenium(V) state and ligand-centred oxidations for **3** and **4**, as observed for $[V(C_3S_5)_3]^{n-}$,[4,5] $[Cu_4(C_3S_5)_3]^{n-}$ ($n < 2$),[11] and $[Au(C_3S_5)_2]^{m-}$ ($m < 1$).[27] In accordance with this, the ν(C=C) stretching IR band of the ligand of the oxidized species (1340 cm^{-1}) occurs at a lower wavenumber compared with complex **2** (1390 cm^{-1}). Furthermore, **3** and **4** show a rather sharp, approximately isotropic powder ESR signal ($g = 2.013$; peak-to-peak linewidth, 7.4 mT) at 77 K, similar to those of oxidized C_3S_5–metal complexes with ligand-centred oxidation, $[V(C_3S_5)_3]^-$ ($g = 2.01$),[5] $[Au(C_3S_5)_2]$ ($g = 2.010$)[28] and $[Mo(C_3S_5)_3]^{n-}$ ($n = 0.05$ or 0.3, $g = 2.008$ or 2.007).[8]

The electrical conductivity of complex **2** measured for a compacted pellet at room temperature is 1.8×10^{-8} S cm^{-1}. Although it is essentially an insulator, the oxidized species show high conductivities (2.2×10^{-2} and 4.6×10^{-3} S cm^{-1} for **3** and **4**, respectively). In complex **2** the bulky $[Re(C_3S_5)_3]^-$ moieties seem to be separated from each other by the bulky tetrabutylammonium cation, as observed for $[NBu^n_4]_2[M(C_3S_5)_3]$ (M = Mo or W).[8,9] However, oxidation is likely to lead to an effective packing of the $[Re(C_3S_5)_3]$ moieties suitable for the formation of an electron-conduction pathway in the solid state. The existence of molecular interactions may be confirmed by a broad band in the near-infrared region observed in the powder reflectance spectra of these oxidized species. This can be caused by sulfur–sulfur non-bonded contacts owing to the absence of a bulky cation and decreased repulsions among $[Re(C_3S_5)_3]$ moieties, as observed in the crystal structures of one-electron oxidized $[V(C_3S_5)_3]^-$,[4] $[Mo(C_3S_5)_3]^-$ and $[W(C_3S_5)_3]^-$ complexes.[9]

Acknowledgements

We thank Professor K. Nakatsu of Kwansei Gakuin University, Nishinomiya, for use of the programs for the X-ray analysis, and Mr. I. Kawafune of Osaka Municipal Technical Research Institute for the measurement of X-ray photoelectron spectra.

References

1 P. Cassoux and L. V. Interrante, *Comments Inorg. Chem.*, 1991, **12**, 47.
2 G. Matsubayashi, *Rev. Heteroatom Chem.*, 1991, **4**, 171.
3 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115.
4 G. Matsubayashi, K. Akiba and T. Tanaka, *Inorg. Chem.*, 1988, **27**, 4744.
5 K. Akiba, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, 1989, **165**, 245.
6 W. E. Broderick, E. M. McGhee, M. R. Godfrey, B. M. Hoffman and J. A. Ibers, *Inorg. Chem.*, 1989, **28**, 2902.
7 J. D. Martin, E. Canadell and P. Batail, *Inorg. Chem.*, 1992, **31**, 3176.
8 G. Matsubayashi, K. Douki and H. Tamura, *Chem. Lett.*, 1992, 1251.
9 K. Douki, G. Matsubayashi, H. Tamura, M. Nakano and W. Mori, unpublished work.
10 G. Matsubayashi and A. Yokozawa, *J. Chem. Soc., Chem. Commun.*, 1991, 68.
11 A. Yokozawa and G. Matsubayashi, *Inorg. Chim. Acta*, 1991, **186**, 165.
12 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 1988.
13 E. J. Rosa and G. N. Schrauzer, *J. Phys. Chem.*, 1969, **73**, 3132.
14 L. Valade, J.-P. Legros, M. Bousseau, P. Cassoux, M. Barbauskas and L. V. Interrante, *J. Chem. Soc., Dalton Trans.*, 1985, 783.
15 G. Matsubayashi, S. Tanaka and A. Yokozawa, *J. Chem. Soc., Dalton Trans.*, 1992, 1827.
16 T. Nojo, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, 1989, **159**, 49.
17 S. Tanaka and G. Matsubayashi, *J. Chem. Soc., Dalton Trans.*, 1992, 2837.
18 K. Ueyama, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, 1984, **87**, 143.

19 A. C. T. North, D. C. Phillips and F. C. Mathews, *Acta Crystallogr., Sect. A*, 1968, **4**, 351.

20 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

21 C. K. Johnson, ORTEP II, Report ORNL 5183, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

22 G. Matsubayashi, T. Nojo and T. Tanaka, *Inorg. Chim. Acta*, 1988, **154**, 133.

23 R. Mattes and H. Weber, *Z. Anorg. Allg. Chem.*, 1981, **474**, 216.

24 A. C. McDonell, T. W. Hambley, M. R. Snow and A. G. Wedd, *Aust. J. Chem.*, 1983, **36**, 253.

25 P. J. Blower, J. R. Dilworth, J. Hutchinson, T. Nicholson and J. Zubieta, *Inorg. Chim. Acta*, 1984, **90**, L27.

26 A. Davison, C. Orvig, H. S. Trop, M. Sohn, B. V. DePamphilis and A. G. Jones, *Inorg. Chem.*, 1980, **19**, 1988.

27 G. Matsubayashi, K. Takahashi and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1988, 967.

28 G. Matsubayashi and A. Yokozawa, *J. Chem. Soc., Dalton Trans.*, 1990, 3535.

29 G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1966, **88**, 3235.

Received 15*th April* 1993; *Paper* 3/02162I