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Isolation, structure and spectroscopic properties of $[Re_2(C_3S_5)_5]^{2-}$ complexes and electrical conductivities of their oxidized species†

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Salts of the dianion $[Re_2(C_3S_5)_5]^{2-}$ [$C_3S_5{}^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-thionate(2−)] with $PPh_4{}^+$ **1**, $NEt_4{}^+$ **2** and $NBu^n{}_4{}^+$ **3** were prepared. A single-crystal X-ray analysis of **1** revealed that the dinuclear anion containing a Re–Re single bond and two Re–S–Re bridges involving the C_3S_5 ligands contains distorted-octahedral co-ordination geometries around both metal atoms and that the anions are associated into a dimeric form through sulfur–sulfur contacts, being further arranged into a chain through other such contacts. Redox potentials of the $[Re_2(C_3S_5)_5]^{2-}$ anion were determined by cyclic voltammetry. Complexes **1** and **2** were oxidized by iodine, $[Fe(C_5H_5)_2][PF_6]$, and $[ttf]_3[BF_4]_2$ ($ttf^{\bullet+}$ = the tetrathiafulvalenium radical cation) or current-controlled electrolysis to yield species $[ttf][Re_2(C_3S_5)_5]$, $[PPh_4]_x$- and $[NEt_4]_y$-$[Re_2(C_3S_5)_5]$ (x,y = 0.1–0.65). They behave as semiconductors with electrical conductivities of 2.0×10^{-3}–4.9×10^{-2} S cm^{-1} for compacted pellets at room temperature. The electronic states of the oxidized complexes are discussed on the basis of electronic absorption, IR, ESR as well as X-ray photoelectron spectra.

Oxidized planar metal complexes of $C_3S_5{}^{2-}$ [4,5-disulfanyl-1,3-dithiole-2-thionate(2−)] are known to become good electrical conductors,[1–3] and some nickel(II) and palladium(II) complexes exhibit superconductivity at low temperature.[4,5] They have effective electron-conduction pathways *via* molecular interactions through sulfur–sulfur non-bonded contacts in the solid state. Non-planar bulky metal complexes with this sulfur-rich ligand are expected to have new types of molecular packing with sulfur–sulfur interactions which lead to two- or three-dimensional electron-conduction pathways in their oxidized species. Several electrically conducting complexes of C_3S_5 (M = V, Mo, W or Cu) with bulky geometries have been studied.[6–13] Recently we reported electrical conductors made from oxidized $[Re(C_3S_5)_3]$ anion complexes.[14]

In this paper we report the preparation, electrochemical and spectroscopic properties of bulky dinuclear $[Re_2(C_3S_5)_5]^{2-}$ anion complexes and the electrical conductivities of their oxidized species, as well as a single-crystal X-ray analysis of $[PPh_4]_2[Re_2(C_3S_5)_5]$.

Experimental

Preparations

$[PPh_4]_2[Re_2(C_3S_5)_5]$ 1, $[NEt_4]_2[Re_2(C_3S_5)_5]$ 2 and $[NBu^n{}_4]_2$-$[Re_2(C_3S_5)_5]$ 3. All the following reactions were performed under a nitrogen atmosphere. The salt $[NBu^n{}_4]_2[Re_2Cl_8]$[15] (100 mg, 88 μmol) was suspended in a methanol (50 cm^3) solution containing 4,5-bis(benzoyl)-1,3-dithiole-2-thione[16] (210 mg, 530 μmol) and sodium metal (36 mg, 1.6 mmol). The reaction mixture was stirred for 10 min at 60 °C, then filtered, and a methanol (10 cm^3) solution of $[PPh_4]Br$ (500 mg, 1.2 mmol) added to the filtrate. Dark green solids precipitated immediately, which were filtered off and recrystallized from dichloromethane–ethanol (1 : 1 v/v) to yield dark green crystals of complex **1** (55% yield) (Found: C, 37.1; H, 2.0. Calc. for $C_{63}H_{40}P_2Re_2S_{25}$: C, 37.2; H, 2.0%). A similar reaction of $[NBu^n{}_4]_2[Re_2Cl_8]$ (100 mg, 88 μmol) with $Na_2[C_3S_5]$ (36 mg, 1.6 mmol) dissolved in methanol (60 cm^3), followed by addition of a methanol (10 cm^3) solution of $[NEt_4]Br$ (400 mg, 1.9 mmol) or $[NBu^n{}_4]Br$ (500 mg, 1.55 mmol), afforded dark green solids. They were filtered off and recrystallized from acetone–ethanol (1 : 1 v/v) to give dark green microcrystals of **2** and **3** (54 and 39% yields, respectively) (Found: C, 23.4; H, 2.55; N, 1.85. Calc. for $C_{63}H_{40}N_2Re_2S_{25}$ **2**: C, 23.05; H, 2.5; N, 1.75. Found: C, 31.0; H, 3.95; N, 1.65. Calc. for $C_{47}H_{72}N_2Re_2S_{25}$ **3**: C, 30.7; H, 3.95; N, 1.5%).

$[PPh_4]_{0.1}[Re_2(C_3S_5)_5]$ 4 and $[PPh_4]_{0.2}[Re_2(C_3S_5)_5]$ 5. A dichloromethane (5 cm^3) solution of iodine (33 mg, 130 μmol) was added with stirring to a dichloromethane (15 cm^3) solution of complex **1** (35 mg, 17 μmol). A black solid **4** precipitated, and was collected by centrifugation, washed with dichloromethane and diethyl ether and dried *in vacuo* (96% yield) (Found: C, 15.4; H, 0.3. Calc. for $C_{17.4}H_{2.0}P_{0.1}Re_2S_{25}$: C, 15.05; H, 0.15%). Similarly, complex **1** (30 mg, 15 μmol) was treated with $[Fe(C_5H_5)_2][PF_6]$[7] (26 mg, 74 μmol) in dichloromethane (30 cm^3) to afford **5** (85% yield) (Found: C, 16.2; H, 0.5. Calc. for $C_{19.8}H_{4.0}P_{0.2}Re_2S_{25}$: C, 16.7; H, 0.3%).

$[NEt_4]_{0.3}[Re_2(C_3S_5)_5]$ 6 and $[NEt_4]_{0.5}[Re_2(C_3S_5)_5]$ 7. To an acetone (40 cm^3) solution of complex **2** (50 mg, 31 μmol) was added with stirring an acetone (10 cm^3) solution of iodine (40 mg, 160 μmol). A black solid **6** obtained immediately was collected by centrifugation, washed with acetone and diethyl ether, and dried *in vacuo* (88% yield) (Found: C, 14.95; H, 0.55; N, 0.35. Calc. for $C_{17.4}H_{6.0}N_{0.3}Re_2S_{25}$: C, 15.0; H, 0.45; N, 0.3%). A similar reaction of **2** (30 mg, 19 μmol) with $[Fe(C_5H_5)_2][PF_6]$ (30 mg, 90 μmol) in acetonitrile (40 cm^3) gave **7** (91% yield) (Found: C, 16.1; H, 0.8; N, 0.25. Calc. for $C_{19.0}H_{10.0}N_{0.5}Re_2S_{25}$: C, 16.1; H, 0.7; N, 0.50%).

$[ttf][Re_2(C_3S_5)_5]$ 8. An acetonitrile (40 cm^3) solution of $[ttf]_3[BF_4]_2$[17] [ttf = tetrathiafulvalene, *i.e.* 2-(1,3-dithiol-2-ylidene)-1,3-dithiole] (36 mg, 46 μmol) was added with stirring to an acetonitrile (30 cm^3) solution of complex **2** (40 mg, 31 μmol). A black solid **8** precipitated, which was collected by centrifugation, washed with acetonitrile and diethyl ether, and

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

dried *in vacuo* (97% yield) (Found: C, 16.25; H, 0.4. Calc. for $C_{21}H_4Re_2S_{29}$: C, 16.2; H, 0.25%).

$[NEt_4]_{0.65}[Re_2(C_3S_5)_5]$ 9 by electrocrystallization. An acetonitrile (50 cm^3) solution containing complex **2** (20 mg, 12 µmol) and $[NEt_4][ClO_4]$ (570 mg, 2.5 mmol) was subjected to a controlled-current (1 mA) electrolysis in a cell consisting of platinum wires (anode and cathode) for 1 h. Black microcrystals of **9** obtained on the anode were collected by centrifugation, washed with acetonitrile and diethyl ether, and dried *in vacuo* (10 mg yield) (Found: C, 16.95; H, 0.95; N, 0.65. Calc. for $C_{20.2}H_{13.0}N_{0.65}Re_2S_{25}$: C, 16.85; H, 0.9; N, 0.65%).

Measurements

Electronic absorption,[18] IR, ESR,[13] and X-ray photoelectron (XPS) spectra[19] were recorded as described previously. The ^{13}C NMR spectra were recorded at 100.4 MHz using a JEOL JNM-GSX-400 spectrometer at the Faculty of Engineering, Osaka University, the chemical shifts being measured relative to tetramethylsilane as an internal standard in CD_2Cl_2. The electrospray ionization (ESI) mass spectrum was obtained by a sector-type JEOL-D300 mass spectrometer equipped with a laboratory-made ESI interface. For the measurement of the negative-ion mass spectrum, an acetonitrile solution of complex **2** (1.0×10^{-4} mol dm^{-3}) was electrosprayed at the tip of a needle supplied with a negative high voltage. No acids or salts were added to the solution to promote the ionization. The cyclic voltammogram of **1** was measured in dichloromethane using $[NBu^n_4][ClO_4]$ as an electrolyte, as described previously.[20] Specific resistivities of the complexes were measured for compacted pellets by the conventional two-probe method.[21]

Crystallography

Accurate unit-cell parameters for $[PPh_4]_2[Re_2(C_3S_5)_5]$ **1** were determined from a least-squares fit based on 25 reflections with 2θ values from 27.3 to 27.5°, measured with a Rigaku AFC-5R four-circle diffractometer at the Faculty of Engineering, Osaka University, using graphite-monochromated Mo-Kα (λ = 0.710 69 Å) radiation. Crystallographic data for complex **1** are summarized in Table 1. The intensities were corrected for Lorentz and polarization effects, together with absorption[22] and decay (maximum 1.99%).

The structure was solved by direct methods[23] and refined anisotropically on *F* by a full-matrix least-squares procedure for the non-hydrogen atoms. The calculations were performed with the TEXSAN package[24] on an IRIS/Indigo workstation at the Faculty of Engineering, Osaka University. Atomic scattering factors were taken from ref. 25. The final positional parameters for non-hydrogen atoms with standard deviations are given in Table 2. Figs. 1 and 2 were drawn with a local version of ORTEP II.[26]

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Crystal structure of complex 1

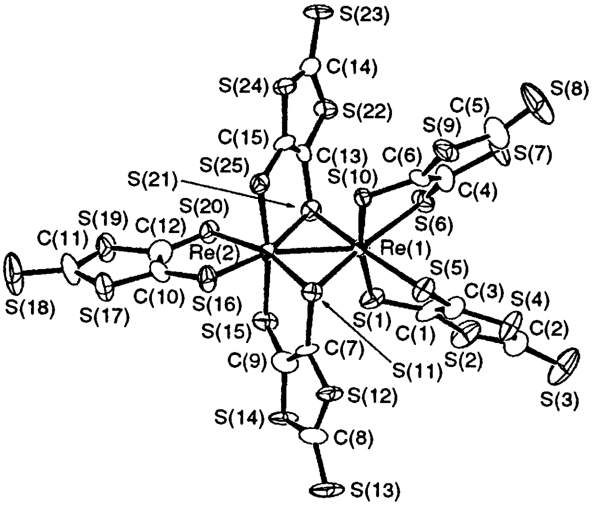


Fig. 1 Geometry of the dinuclear anion of complex **1** together with the atom-labelling scheme

Table 1 Crystallographic data for $[PPh_4]_2[Re_2(C_3S_5)_5]$ **1**

Formula	$C_{63}H_{40}P_2Re_2S_{25}$
M	2032.87
Crystal size/mm	0.30 × 0.10 × 0.60
Crystal description	Black, prisms
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	16.051(4)
b/Å	17.571(4)
c/Å	15.731(4)
α/°	113.86(2)
β/°	93.99(3)
γ/°	69.41(3)
U/Å^3	3784(2)
Z	2
D_c/g cm^{-3}	1.784
F(000)	1996
µ/ cm^{-1}	39.8
T/°C	23
Measured 2θ range/°	6–55
No. reflections collected	17 380
No. of reflections with $I > 3\sigma(I)$	8807
R^a	0.075
R'^b	0.075
Transmission factors	0.575–1.000

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/\sigma^2(F)$.

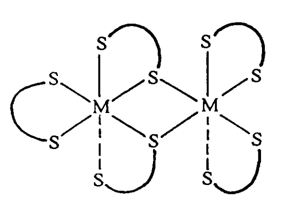
A perspective view of the anion of complex **1** is illustrated in Fig. 1 together with atom labelling scheme. Selected bond distances and angles of the anion relevant to the Re_2S_{10} core are summarized in Table 3. The $[Re_2(C_3S_5)_5]^{2-}$ anion is regarded as an $[Re(C_3S_5)_2]^0$ unit co-ordinated *via* sulfur atoms in the *cis* positions by an octahedral $[Re(C_3S_5)_3]^{2-}$ species and a metal–metal bond. The Re_2S_{10} core has approximate C_2 symmetry with respect to the Re(1)–Re(2) axis. Similar dinuclear geometries containing sulfur bridges involving dithiolate ligands were found for the α-$[Ru_2(S_2CNPr^i_2)_5]^+$,[27] $[Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2]^+$ [28] and $[Co_2(S_2CNEt_2)_5]^+$ complexes,[29] although the dicobalt complex has no Co–Co bond. The geometry around each Re atom is a distorted tris-chelated octahedron, having the same chirality (Δ,Δ or Λ,Λ). This is the same as that of the above osmium complex, while the other two complexes possess two distorted tris-chelated octahedra with opposite chiralities (Δ,Λ). The Re(1)–Re(2) distance [2.721(1) Å] is similar to that of rhenium metal (2.746 Å)[30] and corresponds to a Re–Re single bond, and is also similar to the M–M distances observed for $[Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]^-$ [2.783(1) Å],[31] $[Re_2(NNPh)_2(SPh)_7]^-$ [2.747(2) Å],[32] α-$[Ru_2(S_2CNPr^i_2)_5]^+$ [2.789(4) Å][27] and $[Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2]^+$ [2.791(2) Å].[28] The Re–S distances [2.324(3)–2.431(4) Å] agree closely with those for $[Re(S_2C_2Ph_2)_3]$ [2.30(1)–2.33(1) Å],[33] $[Re_2O_3(S_2CNEt_2)_4]$ [2.410(3)–2.468(3) Å],[34] $[ReN(S_2CNEt_2)_2]$ [2.381(2)–2.391(2) Å],[35] $[Re(S_2CNEt_2)_3(CO)]$ [2.433(2)–2.518(2) Å][36] and $[ReO(C_3S_5)_2]^-$ [2.322(4)–2.336(4) Å].[14]

Table 2 Atomic coordinates for the non-hydrogen atoms of $[PPh_4]_2[Re_2(C_3S_5)_5]$ **1** with estimated standard deviations in parentheses

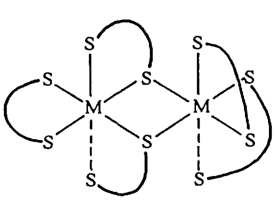
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	0.202 00(5)	−0.080 22(5)	−0.127 61(5)	C(18)	0.471(3)	0.206(2)	0.453(2)
Re(2)	0.052 49(5)	−0.069 70(5)	−0.221 88(5)	C(19)	0.528(3)	0.226(3)	0.417(3)
S(1)	0.290 5(3)	−0.224 3(3)	−0.234 0(3)	C(20)	0.584(2)	0.259(2)	0.475(2)
S(2)	0.477 5(4)	−0.336 1(4)	−0.213 7(4)	C(21)	0.578(2)	0.281(3)	0.569(2)
S(3)	0.623 9(5)	−0.402 3(5)	−0.106 3(6)	C(22)	0.436(1)	0.405(1)	0.797(1)
S(4)	0.454 2(4)	−0.253 4(4)	−0.013 5(4)	C(23)	0.434(1)	0.441(2)	0.891(2)
S(5)	0.266 5(3)	−0.132 4(3)	−0.008 8(3)	C(24)	0.385(2)	0.534(2)	0.944(2)
S(6)	0.332 3(3)	−0.038 3(3)	−0.117 0(4)	C(25)	0.336(2)	0.588(2)	0.899(2)
S(7)	0.393 2(4)	−0.081 4(5)	−0.053 5(4)	C(26)	0.335(2)	0.549(2)	0.799(3)
S(8)	0.363 1(6)	0.227 8(7)	0.243 6(5)	C(27)	0.383(2)	0.455(2)	0.744(2)
S(9)	0.219 2(4)	0.164 6(4)	0.153 7(3)	C(28)	0.466(2)	0.218(2)	0.758(2)
S(10)	0.137 6(3)	0.061 1(3)	−0.009 8(3)	C(29)	0.404(2)	0.250(2)	0.832(2)
S(11)	0.069 9(3)	−0.099 4(3)	−0.087 5(3)	C(30)	0.379(3)	0.195(3)	0.857(3)
S(12)	0.089 1(4)	−0.266 7(3)	−0.058 3(3)	C(31)	0.422(2)	0.105(3)	0.804(3)
S(13)	0.119 4(5)	−0.459 7(4)	−0.124 4(4)	C(32)	0.482(2)	0.064(2)	0.724(3)
S(14)	0.103 4(4)	−0.373 7(3)	−0.255 5(3)	C(33)	0.508(2)	0.129(2)	0.704(2)
S(15)	0.097 3(4)	−0.225 7(3)	−0.309 6(3)	C(34)	0.617(1)	0.281(2)	0.775(1)
S(16)	−0.099 3(3)	−0.059 0(4)	−0.197 3(3)	C(35)	0.648(2)	0.356(2)	0.796(2)
S(17)	−0.250 9(3)	−0.062 8(4)	−0.320 0(4)	C(36)	0.731(1)	0.349(2)	0.831(2)
S(18)	−0.340 7(5)	−0.067 6(6)	−0.493 9(5)	C(37)	0.781(1)	0.268(2)	0.837(2)
S(19)	−0.154 0(4)	−0.075 6(4)	−0.474 2(3)	C(38)	0.756(2)	0.199(2)	0.815(2)
S(20)	0.010 6(3)	−0.069 0(3)	−0.372 3(3)	C(39)	0.671(1)	0.205(2)	0.788(2)
S(21)	0.178 0(3)	−0.052 7(3)	−0.268 5(3)	C(40)	0.891(1)	0.304(1)	0.616(1)
S(22)	0.211 2(3)	0.107 8(4)	−0.266 0(4)	C(41)	0.816(2)	0.278(2)	0.581(2)
S(23)	0.165 6(5)	0.302 0(4)	−0.212 7(5)	C(42)	0.813(2)	0.195(2)	0.573(2)
S(24)	0.049 9(4)	0.232 5(3)	−0.148 5(4)	C(43)	0.890(2)	0.136(2)	0.598(2)
S(25)	−0.010 5(3)	0.088 2(3)	−0.145 6(3)	C(44)	0.963(2)	0.162(2)	0.627(1)
P(1)	0.506 5(4)	0.292 6(4)	0.733 3(4)	C(45)	0.968(1)	0.241(1)	0.630(1)
P(2)	0.894 5(4)	0.408 6(4)	0.630 6(3)	C(46)	0.798(1)	0.461(1)	0.579(1)
C(1)	0.375(1)	−0.250(1)	−0.168(1)	C(47)	0.800(2)	0.442(2)	0.490(2)
C(2)	0.524(1)	−0.334(1)	−0.110(2)	C(48)	0.716(3)	0.475(3)	0.453(2)
C(3)	0.365(1)	−0.212(1)	−0.067(1)	C(49)	0.647(2)	0.531(2)	0.505(2)
C(4)	0.312(1)	−0.040(1)	−0.006(1)	C(50)	0.645(2)	0.553(3)	0.588(2)
C(5)	0.327(1)	−0.162(2)	0.156(2)	C(51)	0.720(2)	0.511(2)	0.631(2)
C(6)	0.230(1)	0.081(1)	0.043(1)	C(52)	0.885(1)	0.480(2)	0.753(1)
C(7)	0.085(1)	−0.215(1)	−0.132(1)	C(53)	0.871(2)	0.573(2)	0.784(2)
C(8)	0.103(1)	−0.369(1)	−0.142(1)	C(54)	0.866(2)	0.625(2)	0.883(2)
C(9)	0.091(1)	−0.266(1)	−0.226(1)	C(55)	0.877(2)	0.589(2)	0.945(2)
C(10)	−0.142(1)	−0.066(1)	−0.302(1)	C(56)	0.895(2)	0.497(2)	0.914(2)
C(11)	−0.255(1)	−0.067(2)	−0.432(1)	C(57)	0.902(2)	0.439(2)	0.816(1)
C(12)	−0.096(1)	−0.071(1)	−0.376(1)	C(58)	1.000(1)	0.386(1)	0.570(2)
C(13)	0.142(1)	0.064(1)	−0.234(1)	C(59)	1.023(2)	0.332(2)	0.484(2)
C(14)	0.144(1)	0.218(1)	−0.209(1)	C(60)	1.101(2)	0.313(2)	0.438(2)
C(15)	0.068(1)	0.121(1)	−0.182(1)	C(61)	1.167(2)	0.338(2)	0.484(2)
C(16)	0.518(2)	0.263(2)	0.607(1)	C(62)	1.150(2)	0.380(2)	0.575(3)
C(17)	0.455(2)	0.230(2)	0.552(2)	C(63)	1.061(2)	0.414(2)	0.625(2)

Table 3 Selected bond lengths (Å) and angles (°) of $[PPh_4]_2$-$[Re_2(C_3S_5)_5]$ **1**

Re(1)–Re(2)	2.721(1)	Re(2)–S(11)	2.351(4)
Re(1)–S(1)	2.365(5)	Re(2)–S(15)	2.372(5)
Re(1)–S(5)	2.418(5)	Re(2)–S(16)	2.422(5)
Re(1)–S(6)	2.426(5)	Re(2)–S(20)	2.418(4)
Re(1)–S(10)	2.324(5)	Re(2)–S(21)	2.344(5)
Re(1)–S(11)	2.422(5)	Re(2)–S(25)	2.379(5)
Re(1)–S(21)	2.431(4)		
S(1)–Re(1)–S(5)	84.9(2)	S(16)–Re(2)–S(20)	85.4(2)
S(6)–Re(1)–S(10)	84.3(2)	S(21)–Re(2)–S(25)	87.7(2)
S(11)–Re(1)–S(21)	107.8(2)	Re(1)–S(11)–Re(2)	69.5(1)
S(11)–Re(2)–S(15)	87.1(2)	Re(1)–S(21)–Re(2)	69.5(1)
S(11)–Re(2)–S(21)	113.2(2)		



(Δ, Δ)



(Δ, Λ)

Although atoms Re(1), S(11), Re(2) and S(21) are coplanar, S(5), S(6), S(16) and S(20) deviate considerably from this plane. The transoid S–Re–S angles are 162.6–172.0°, indicating distorted octahedral geometries around Re(1) and Re(2). Particularly, S(5)–Re(1)–S(21), S(6)–Re(1)–S(11), S(11)–Re(2)–S(20), and S(16)–Re(2)–S(21) angles (162.6–164.2°) deviate greatly from a linear arrangement. This is different from the almost trigonal prism of $[Re(S_2C_2Ph_2)_3]$[33] and $[W(C_3S_5)_3]^-$,[13] and the distorted trigonal prism of $[M(C_3S_5)_3]^{2-}$,[13] $[M\{S_2C_2(CN)_2\}_3]^{2-}$ (M = Mo or W)[37] and $[W(S_2C_2S_2CO)_3]^{2-}$.[38]

The packing diagram of the $[Re_2(C_3S_5)_5]^{2-}$ anion of complex **2** is shown in Fig. 2. Several S ··· S contacts within the sum of the van der Waals radii (3.7 Å) are observed between the anion moieties: S(9) ··· S(16′) 3.369(8), S(10) ··· S(11′) 3.492(6), S(10) ··· S(16′) 3.375(6), S(11) ··· S(11′) 3.519(9) and S(12) ··· S(25′), 3.370(7) Å. Thus, the anion moieties related centrosymmetrically form a dimeric association, which further interacts through the S(7) ··· S(7″) contact [3.57(1) Å] to form a chain of molecular interaction along the *a* axis in the crystal phase. Similar S ··· S molecular interactions in bulky metal complexes of C_3S_5 were observed for $[mphenz]_2[V(C_3S_5)_3]$ (mphenz = *N*-methylphenazinium),[6] $[Fe(C_5Me_5)_2][W(C_3S_5)_3]$[13] and $[EtNC_5H_5]_2[Cu_4(C_3S_5)_3]$.[8] The oxidized $[Re_2$-

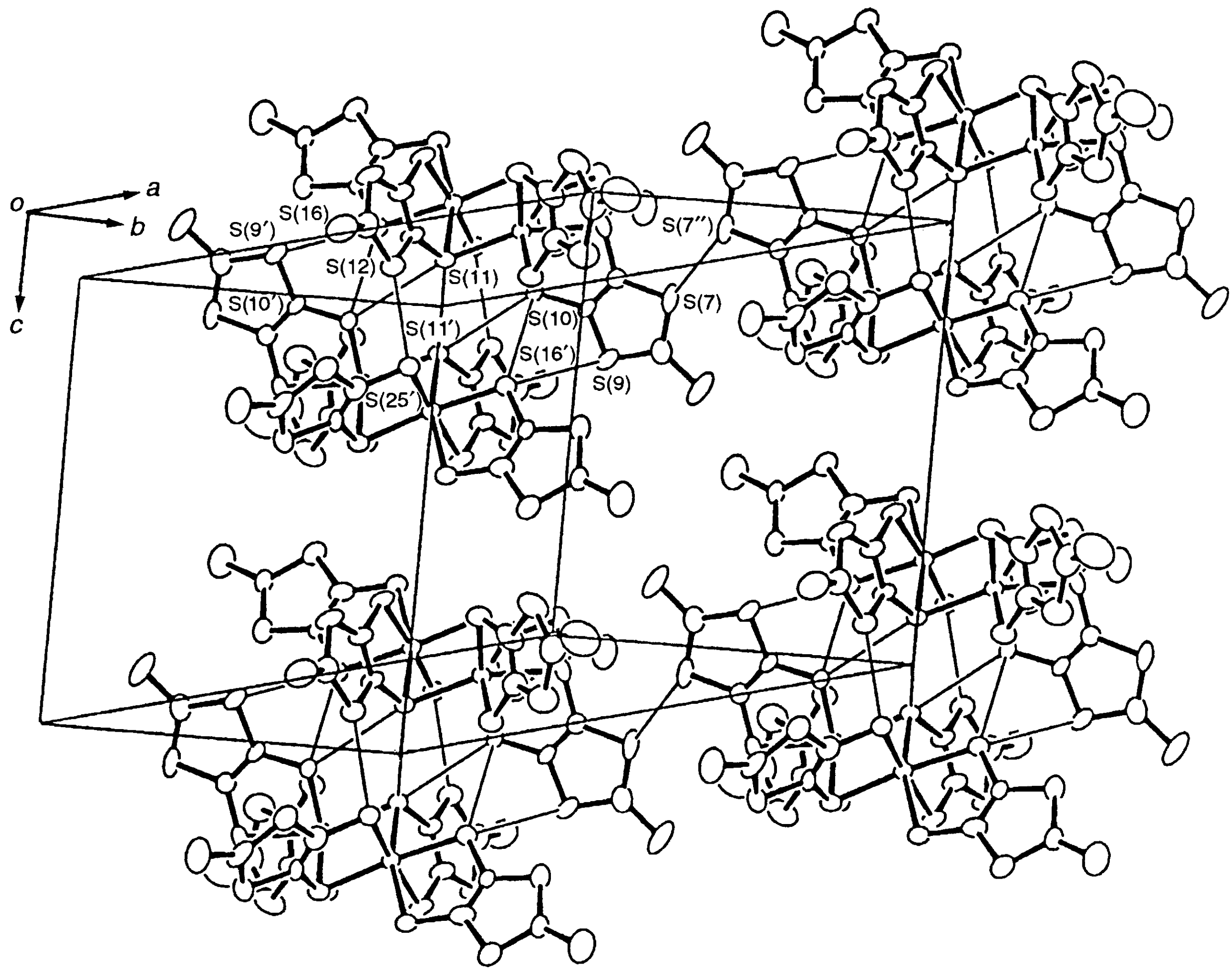


Fig. 2 Packing diagram of the $[Re_2(C_3S_5)_5]^{2-}$ anions of complex **1**. Fine lines represent S $\cdots$ S non-bonded contacts less than 3.7 Å

$(C_3S_5)_5]$ anion species are expected to have further S $\cdots$ S molecular interactions owing to decreased repulsions among them. As described below, the oxidized species of **1** and **2** exhibit appreciably increased electrical conductivities which are due to the formation of electron-conduction pathways through more extended S $\cdots$ S molecular contacts.

Electrochemical and spectroscopic properties of the $[Re_2(C_3S_5)_5]^{2-}$ anion

The electrospray ionization mass spectrum of complex **2** dissolved in acetonitrile exhibited a single peak at *m*/*z* 677 ($z = -2$), as shown in Fig. 3, which indicates the presence of the dinuclear form of the anion in solution. The ^{13}C NMR spectrum of **3** dissolved in CD_2Cl_2 showed three C=S signals at δ 217.0, 219.5 and 220.2 in 2:1:2 ratio, and five C=C signals at δ 146.7, 161.4, 167.1, 168.5 and 172.8 with almost equal intensities. The appearance of these signals indicates the existence of the dinuclear geometry for the anion in solution, as found in the solid state for **1**. The terminal C_3S_5 group linked to Re(2) gives a C=C signal and both the bridging C_3S_5 ligands and terminal C_3S_5 groups linked to Re(1) exhibit two signals, respectively, due to their non-equivalent C=C carbons.

A cyclic voltammogram of complex **1** measured in dichloromethane is illustrated in Fig. 4. The $[Re_2(C_3S_5)_5]^{2-/3-}$ and $[Re_2(C_3S_5)_5]^{3-/4-}$ couples occur at $E_{\frac{1}{2}}° = -0.38$ and -0.72 V (*vs.* saturated calomel electrode, SCE), respectively. The intense reduction wave which appears at 0.2 V is due to an appreciable adsorption of the oxidized species on the electrode. The $[Re_2(C_3S_5)_5]^{2-}$ anion is successively oxidized at +0.36 and +0.43 V (*vs.* SCE). The first oxidation peak potential of this anion is considerably lower than that of the $[Re(C_3S_5)_3]^-$ complex (0.76 V *vs.* SCE in dichloromethane).[14]

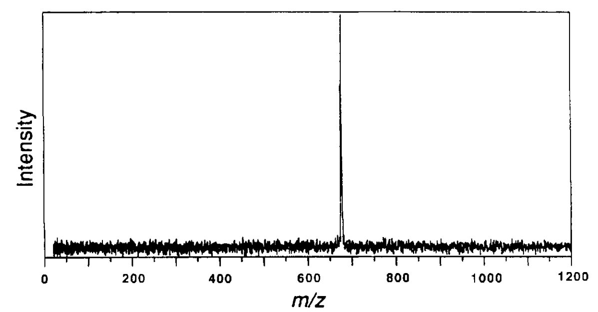


Fig. 3 Negative-ion ESI mass spectrum of complex **2** in acetonitrile

As shown in Fig. 5, the electronic absorption spectrum of complex **1** exhibits bands ascribed to the π–π* transitions of the C_3S_5 ligand in the region 400–510 nm, as observed for other metal complexes of C_3S_5.[39,40] The band observed at 650 nm can be assigned to a metal–ligand charge-transfer transition.[41] It appears at a longer wavelength upon oxidation of this anion, as described below. Such bands were also observed for $[Re(C_3S_5)_3]^-$ [14] and $[M(C_3S_5)_3]^-$ (M = Mo or W) complexes.[11,13]

Complexes **1** and **2** have two rhenium atoms with different surroundings. However, they exhibit an XPS band due to rhenium $4f_{\frac{7}{2}}$ electrons at 41.2 eV. Although they formally contain three kinds of C_3S_5 ligand, the IR C=C stretching band occurs at 1340 cm^{-1}. These findings suggest the delocalization of electrons through the dinuclear anion, resulting in almost equivalent metals and ligand as regards their electronic states.

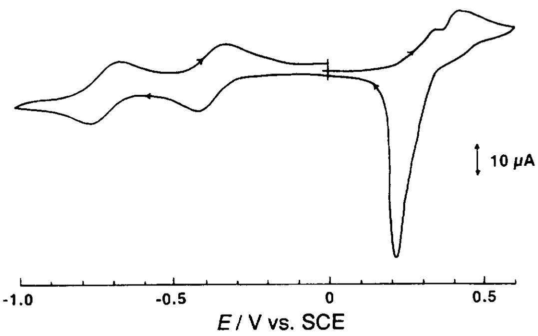


Fig. 4 Cyclic voltammogram of complex **1** (1.0×10^{-3} mol dm^{-3}) in dichloromethane at room temperature. Supporting electrolyte: 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$. Sweep rate: 0.01 V s^{-1}

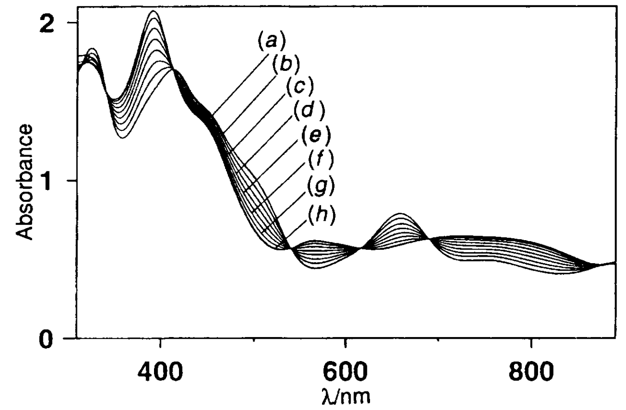


Fig. 5 Electronic absorption spectra of complex **1** (3.7×10^{-5} mol dm^{-3} in dichloromethane in the presence of $[Fe(C_5H_5)_2][PF_6]$: (*a*) 0, (*b*) 0.74×10^{-5}, (*c*) 1.5×10^{-5}, (*d*) 2.2×10^{-5}, (*e*) 3.0×10^{-5}, (*f*) 3.7×10^{-5}, (*g*) 4.4×10^{-5}, (*h*) 5.2×10^{-5} and (*i*) 7.4×10^{-5} mol dm^{-3}

Spectroscopic properties and electrical conductivities of the oxidized species

Fig. 5 also shows the spectral changes for complex **1** on adding various amounts of $[Fe(C_5H_5)_2][PF_6]$ as oxidant. Addition of excess amounts of the oxidant gives the final spectrum of the $[Re_2(C_3S_5)_5]$ species. Similar spectral changes have been observed for an acetonitrile solution of **1** upon controlled-potential electrolysis at 0.50 V *vs.* SCE, and also for the $[Re(C_3S_5)_3]^-$ complex in the presence of the oxidant.[14] Since the first and second oxidation potentials of the present complex are very similar, separate spectra due to the one- and two-electron oxidized species are not observed, in contrast to those for $[M(C_3S_5)_3]^{2-}$ (M = Mo or W).[11,13]

Reactions of complexes **1** and **2** with some oxidants as well as the electrochemical oxidation of **2** have afforded oxidized species **4**–**9**. Complexes **4**–**7** and **9** exhibit a C=C stretching frequency of 1270 cm^{-1}. This low-frequency shift from the value (1340 cm^{-1}) observed for **1** and **2** indicates that they undergo essentially two-electron ligand-centred oxidation.[42] Complex **8** gives a band at 1300 cm^{-1}, which corresponds to that of a one-electron oxidized species. Similar low-frequency shifts of the C=C stretching band were observed for other metal complexes of C_3S_5.[7,14,42] The oxidized species **4**–**7** and **9** give rather sharp ESR signals at $g = 2.01$ (peak-to-peak linewidth = 7 mT), as illustrated for **6** in Fig. 6. These complexes are almost two-electron-oxidized species containing a small amount of the paramagnetic $[Re_2(C_3S_5)_5]^-$ anion. The anions are surrounded by diamagnetic $[Re_2(C_3S_5)_5]$ moieties. Thus, the ESR signals are sharp, in contrast to the broad signal (linewidth = 90 mT) of the paramagnetic $[W(C_3S_5)_3]^-$ anion in the solid state.[13] Signals similar to that of **6** were observed for partially oxidized complexes of Cu^I, Au^{III}, Mo^{IV} and W^{IV} with C_3S_5 upon ligand-centred oxidation.[9,13,40] Complex **8** exhibits signals due to the one-electron-oxidized anion and the ttf$^{\bullet +}$ radical cation ($g = 2.01$), in accord with the salts $[ttf]_2[V(C_3S_5)_3]$,[6] $[ttf]$-$[Au(C_3S_5)_2]$,[40] and $[ttf]_{0.7}[Ni(C_3S_5)(C_3Se_5)]$.[18] The binding energies of the rhenium $4f_{\frac{7}{2}}$ electrons for the oxidized species determined by XPS (41.6 and 41.5 eV for **6** and **8**, respectively) are essentially the same as that of **2** (41.2 eV). These findings are consistent with ligand-centred oxidation.

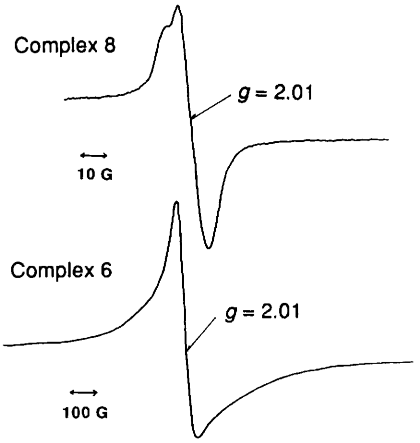


Fig. 6 Powder ESR spectra of complex **6** at 77 K and of **8** at room temperature. G = 10^{-4} T

Table 4 Electrical conductivities (σ_{rt})*

Complex	$\sigma_{r.t.}$/S cm^{-1}	Complex	$\sigma_{r.t.}$/S cm^{-1}
1	7.1×10^{-9}	**6**	1.2×10^{-2}
2	2.9×10^{-8}	**7**	8.0×10^{-3}
4	2.0×10^{-3}	**8**	4.9×10^{-2}
5	6.2×10^{-3}	**9**	8.2×10^{-3}

* Measured at room temperature for compacted pellets.

Table 4 lists the electrical conductivities of the complexes measured at room temperature for compacted pellets. Complexes **1** and **2** exhibit very low conductivites. On the other hand, the oxidized species **3**–**9** behave as semiconductors with high conductivities. The oxidized species have effective electron-conduction pathways constructed through extended S···S contacts which are caused by the ligand-centred oxidation. Although bulkiness of the anions seems to be unfavourable for the molecular packing in the solid state, the low concentration of the cation moieties and decreased repulsions of the anion moieties upon oxidation lead to effective packings of the anions through S···S interactions, as for oxidized bulky $[M(C_3S_5)_3]$ (M = Re, Mo or W) anion complexes.[13,14]

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References

1 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115.
2 G. Matsubayashi, *Review on Heteroatom Chemistry*, Myu, Tokyo, 1991, vol. 4, p. 171.
3 R.-M. Olk, B. Olk, W. Dietzsch, R. Kirmse and W. Hoyer, *Coord. Chem. Rev.*, 1992, **117**, 99.
4 L. Brossard, M. Ribault, L. Valade and P. Cassoux, *Physica B&C (Amsterdam)*, 1986, **143**, 378.

5 H. Tajima, M. Inokuchi, A. Kobayashi, T. Ohta, R. Kato, H. Kobayashi and H. Kuroda, *Chem. Lett.*, 1993, 1235.
6 G. Matsubayashi, K. Akiba and T. Tanaka, *Inorg. Chem.*, 1988, **27**, 4744.
7 K. Akiba, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, 1989, **165**, 245.
8 G. Matsubayashi and A. Yokozawa, *J. Chem. Soc., Chem. Commun.*, 1991, 68.
9 A. Yokozawa and G. Matsubayashi, *Inorg. Chim. Acta*, 1991, **186**, 165.
10 W. E. Broderick, E. M. McGhee, M. R. Godfrey, B. M. Hoffman and J. A. Ibers, *Inorg. Chem.*, 1989, **28**, 2902.
11 G. Matsubayashi, K. Douki and H. Tamura, *Chem. Lett.*, 1992, 1251.
12 J. D. Martin, E. Canadell and P. Batail, *Inorg. Chem.*, 1992, **31**, 3176.
13 G. Matsubayashi, K. Douki, H. Tamura, M. Nakano and W. Mori, *Inorg. Chem.*, 1993, **32**, 5990.
14 G. Matsubayashi, T. Maikawa and M. Nakano, *J. Chem. Soc., Dalton Trans.*, 1993, 2995.
15 A. B. Brignole and F. A. Cotton, *Inorg. Synth.*, 1972, **13**, 82.
16 L. Valade, J.-P. Legros, M. Bousseau, P. Cassoux, M. Garbauskas and M. Interrante, *J. Chem. Soc., Dalton Trans.*, 1985, 783.
17 F. Wudl, *J. Am. Chem. Soc.*, 1975, **79**, 1962.
18 G. Matsubayashi, S. Tanaka and A. Yokozawa, *J. Chem. Soc., Dalton Trans.*, 1992, 1827.
19 T. Nojo, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, 1989, **159**, 49.
20 S. Tanaka and G. Matsubayashi, *J. Chem. Soc., Dalton Trans.*, 1992, 2837.
21 K. Ueyama, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, 1984, **87**, 143.
22 A. C. T. North, D. C. Phillips and F. C. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
23 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF Program System: direct methods for difference structures, an automatic procedure for phase extension and refinement of difference structure factors, Technical Report 1984/1, Crystallography Laboratory, Toernooiveld, Nijmegen, 1984; G. M. Sheldrick, SHELXS 86, a Computer Program for the Solution of Crystal Structures, University of Göttingen, 1985.
24 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Woodlands, TX, 1992.
25 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
26 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
27 C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1975, 2410.
28 L. J. Maheu and L. H. Pignolet, *Inorg. Chem.*, 1979, **18**, 3626.
29 A. R. Hendrickson, R. L. Martin and D. Taylor, *J. Chem. Soc., Dalton Trans.*, 1975, 2182.
30 A. R. C. L. Mooney, *Phys. Rev.*, 1947, **72**, 1269; *Acta Crystallogr.*, 1948, **1**, 161.
31 P. J. Blower, J. R. Dilworth, J. P. Hutchinson and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1985, 1533.
32 T. Nicholson and J. Zubieta, *Inorg. Chim. Acta*, 1985, **100**, L35.
33 R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1966, **5**, 411.
34 S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1972, 1073.
35 S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1972, 1079.
36 S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1974, 486.
37 G. Brown and E. I. Stiefel, *Inorg. Chem.*, 1973, **12**, 2140.
38 X. Yang, G. K. W. Freeman, T. B. Rauchfuss and S. R. Wilson, *Inorg. Chem.*, 1991, **30**, 3034.
39 G. Matsubayashi, K. Takahashi and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1988, 967.
40 G. Matsubayashi and A. Yokozawa, *J. Chem. Soc., Dalton Trans.*, 1990, 3535.
41 G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1966, **88**, 3235.
42 Y. Sakamoto, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, 1986, **113**, 137.

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