Crystal structures of [Rh(η^5-C$_5$H$_5$)(C$_3$S$_5$)] and [Rh(η^5-C$_5$Me$_5$)(C$_3$S$_5$)]$_2$ and properties of their oxidized species

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Abstract

[Rh(η^5-C$_5$H$_5$)(C$_3$S$_5$)] and [Rh(η^5-C$_5$Me$_5$)(C$_3$S$_5$)]$_2$ [C$_3$S$_5^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-thionate(2-)] were prepared by reactions of [NMe$_4$]$_2$[C$_3$S$_5$] with [Rh(η^5-C$_5$H$_5$)Cl$_2$]$_2$ and [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$, respectively. Their X-ray crystal structural analyses revealed a monomeric form for the former complex and a dimeric geometry containing bridging S–Rh–S bonds for the latter in the solid state. They were reacted with bromine to afford [RhBr(L)(C$_3$S$_5$)] (L = η^5-C$_5$H$_5$ and η^5-C$_5$Me$_5$) with the Rh–Br bond and one electron-oxidation on the C$_3$S$_5$ ligand. ESR spectra and spin densities for these oxidized species are discussed.
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1. Introduction

Many metal complexes with the sulfur-rich dithiolate ligand, C$_3$S$_5^{2-}$ [4,5-disulfanyl-1,3-dithiole-2-thionate(2-)], have been extensively studied, since their oxidized species behave often as good electrical conductors and superconductors [1–3]. They construct effective electron-conduction pathways through sulfur–sulfur non-bonded contacts in the solid state. Although planar C$_3$S$_5$–metal complexes are effective for such molecular packings in the solid state, non-planar C$_3$S$_5$–metal complexes may exhibit unique molecular packings through the sulfur-sulfur contacts leading to new physical properties. Cyclopentadienyl- and pentamethylcyclopentadienyl–metal complexes with the C$_3$S$_5$-ligand are of much interest on their oxidation. Although several metal complexes of these types have been studied and their structures clarified [4–17], there are few reports on their oxidation [14,16,17]. Upon oxidation of these complexes, the C$_3$S$_5$ ligand-centered oxidation is expected to occur, as observed for other oxidized C$_3$S$_5$–metal complexes [17–20]. Such oxidized species may behave as unique electrical

conductors through efficient non-bonded S–S contacts in the solid state.

This paper reports preparations of [Rh(η^5-C$_5$H$_5$)-(C$_3$S$_5$)] and [Rh(η^5-C$_5$Me$_5$)(C$_3$S$_5$)]$_2$ and their X-ray crystal structures. Furthermore, geometries and electronic states of their oxidized species [RhBr(L)(C$_3$S$_5$)] (L = η^5-C$_5$H$_5$ and η^5-C$_5$Me$_5$) obtained by reactions of the above complexes with bromine are discussed based on ESR spectra and calculated spin densities.

2. Experimental

2.1. Materials

[Rh(η^5-C$_5$H$_5$)Cl$_2$]$_2$ [21], [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$ [21,22] and 4,5-bis(cyanoethylthio)-1,3-dithiole-2-thione, C$_3$S$_5$-(CH$_2$CH$_2$CN)$_2$, as a pro-ligand compound of the C$_3$S$_5^{2-}$ dithiolate [23], were prepared according to the literatures.

2.2. Preparation of [Rh(η^5-C$_5$H$_5$)(C$_3$S$_5$)] (1) and [Rh(η^5-C$_5$Me$_5$)(C$_3$S$_5$)]$_2$ (2)

All the following reactions were performed under an argon atmosphere. To an ethanol (30 cm^3) solution of C$_3$S$_5$(CH$_2$CH$_2$CN)$_2$ (280 mg, 0.90 mmol) was added with

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vigorous stirring a methanol (45 cm^3) solution containing NMe$_4$OH (900 mg, 9.8 mmol) and the solution was stirred for 15 min. The resulting red brown solids of [NMe$_4$]$_2$[C$_3$S$_5$] were filtered, and dissolved in ethanol (30 cm^3). To the solution was added with stirring an acetonitrile (100 cm^3) solution of [Rh(η^5-C$_5$H$_5$)Cl$_2$]$_2$ (100 mg, 0.21 mmol) and the solution was stirred for 10 min at room temperature. The resulting crude black solids of **1** were dissolved in chloroform (100 cm^3) and the solution was filtered through silica gel. The concentrated filtrate solution was followed by addition of hexane (500 cm^3) to afford a black precipitate of **1**, which was washed with hexane and dried in vacuo (44% yield). *Anal.* Found: C, 26.38; H, 1.40. Calc. for C$_8$H$_5$RhS$_5$: C, 26.37; H, 1.38%. ^{1}H NMR (in DMSO-d$_6$): δ 6.12 (5H, s).

Similarly, black solids of complex **2** were also prepared by the reaction of an ethanol solution of [NMe$_4$]$_2$[C$_3$S$_5$] with a dichloromethane solution of [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$ (73% yield). *Anal.* Found: C, 35.81; H, 3.65. Calc. for C$_{13}$H$_{15}$RhS$_5$: C, 35.94; H, 3.48%. ^{1}H NMR (in CDCl$_3$): δ 2.02 (15H, s).

The dimeric molecular geometry of **2** in the solid state has been clarified by the X-ray crystal structure analysis, as described below.

2.3. Preparation of oxidized species [RhBr(η^5-C$_5$H$_5$) (C$_3$S$_5$)] (3) and [RhBr(η^5-C$_5$Me$_5$)(C$_3$S$_5$)] (4)

To a dichloromethane (400 cm^3) solution of **1** (73 mg, 0.20 mmol) was added with stirring a dichloromethane (1.0 cm^3) solution containing bromine [5.2 mm^3 (d = 3.1 g cm^{-3}), 0.10 mmol]. The volume of the solution was reduced to 100 cm^3 under reduced pressure and to the solution was added hexane (500 cm^3) to afford black solids of **3**. They were collected by filtration and dried in vacuo (48% yield). *Anal.* Found: C, 21.93; H, 1.37. Calc. for C$_8$H$_5$BrRhS$_5$: C, 21.63; H, 1.13%.

Similarly, black solids of **4** were also obtained by the reaction of **2** with a half molar amount of bromine in dichloromethane, followed by addition of hexane (40% yield). *Anal.* Found: C, 30.28; H, 3.04. Calc. for C$_{13}$H$_{15}$BrRhS$_5$: C, 30.36; H, 2.94%.

2.4. Physical measurements

IR, electronic absorption, ESR [23] and powder reflectance spectra [24] were recorded as described previously. ^{1}H NMR spectra were also measured as previously [25]. Cyclic voltammograms of the complexes in dichloromethane were measured using [NBu$_4$][ClO$_4$] as an electrolyte [26]. Electrospray ionization (ESI) mass spectra were obtained as described previously [20], using the spectrometer, Kansai University. Electrical resistivities of the oxidized complexes were measured at room temperature for compacted pellets by the conventional two-probe method [26].

2.5. Theoretical calculation of Mulliken spin density distribution for the [RhBr(η^5-C$_5$Me$_5$)(C$_3$S$_5$)] radical species

In order to elucidate the spin density distribution for the oxidized radical species **4**, Mulliken spin densities have been evaluated by a hybrid DFT calculation (UB3PW91/LANL2DZ level, GAUSSIAN98 [27]), based on the atomic coordinates of the analogous complex [CoBr(η^5-C$_5$Me$_5$)(C$_3$S$_5$)] [16] with the replace of the cobalt atom by the rhodium atom.

2.6. Crystal structure determinations of [Rh(η^5-C$_5$H$_5$) (C$_3$S$_5$)] (1) and [Rh(η^5-C$_5$Me$_5$)(C$_3$S$_5$)]$_2$ (2)

Intensity data were collected up to $2\theta = 60°$ on a Rigaku AFC5R diffractometer at room temperature for **1** and on a Rigaku RAXIS-RAPID imaging plate diffractometer at −40 °C for **2** at the Graduate School of Science, Osaka University, with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Crystal data and details of measurements for both the complexes are summarized in Table 1. The intensity data were processed using the PROCESS-AUTO program and corrected for absorption by North-Phillips method [28] (transmission factors 0.706–0.782) but not for decay for **1**, and by Higashi method [29] (transmission factors 0.529–0.781) for **2**. Cell constants were obtained by least-squares refinement of the setting angles of 24 reflections (25.0° < 2θ < 29.8°) for **1** and of 18 280 reflections (4.8° < 2θ < 60.0°) for **2**.

Table 1
Crystallographic data for [Rh(η^5-C$_5$H$_5$)(C$_3$S$_5$)] (**1**) and [Rh(η^5-C$_5$Me$_5$)(C$_3$S$_5$)]$_2$ (**2**)

	1	2
Empirical formula	C$_8$H$_5$RhS$_5$	C$_{26}$H$_{30}$Rh$_2$S$_{10}$
M	364.38	869.02
Crystal system	monoclinic	monoclinic
Space group	$P2_1c$	$C2/c$
Unit cell dimensions		
a (Å)	5.946(2)	13.2299(2)
b (Å)	7.891(3)	15.0643(4)
c (Å)	23.736(2)	16.5624(6)
β (°)	96.60(1)	92.674 (1)
V (Å^3)	1106.3(5)	3297.3(2)
Z	4	4
D_{calc} (g cm^{-3})	2.188	1.751
T (K)	296	233
μ (Mo Kα) (mm^{-1})	2.439	1.652
Reflection collected	3516	17 860
Independent reflections	3291	4650
R[a]	0.052	0.029
R_w[b] (all data)	0.169[c]	0.070[d]

[a] $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$.
[b] $R_w = \sum w(F_o^2 - F_c^2)^2$.
[c] $w^{-1} = \sigma^2(F_o^2) + (0.0607P)^2 + 5.6122P$.
[d] $w^{-1} = \sigma^2(F_o^2) + (0.0254P)^2 + 6.0878P$, where $P = (F_o^2 + 2F_c^2)/3$.

The structures were solved by the Patterson method using PATTY [30] for **1** and by the direct method using SIR92 [31] for **2** and both refined on F^2 by the full-matrix least-squares technique with SHELXL97 [32]. All the non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were geometrically calculated and refined with isotropic thermal parameters riding on those of the parent atoms.

Calculations were performed on SGI-O2 workstation at the Graduate School of Science, Osaka university. Atomic scattering factors were taken from the usual sources [33]. Figs. 1–3 were drawn using ORTEPII [34].

3. Results and discussion

3.1. Molecular and crystal structures of [Rh(η⁵-C₅H₅)(C₃S₅)] (1) and [Rh(η⁵-C₅Me₅)(C₃S₅)]₂(2)

The molecular structure of **1** is shown in Fig. 1, together with the atom-labeling scheme. Selected bond distances and angles relevant to the C_3S_5–Rh moiety of **1**, as well as those of **2** described below, are listed in Table 2. The rhodium atom is bonded to one η^5-C_5H_5 subunit with Rh-C distances of 2.127–2.186 Å and to the bidentate chelating dithiolate ligand [Rh-S(1) and -S(5), 2.241(2) and 2.242(2) Å] leading to a formally penta-coordinate geometry. This is also the same for the geometries of [Co(η^5-C_5H_5)(C_3S_5)] [35], [Ni(η^5-C_5H_5)(C_3S_5)] [36] and [Rh(η^5-C_5Me_5){$S_2C_2(CN)_2$}] [37]. The Rh-S distances are somewhat longer than those of related η^5-C_5Me_5-Rh(III) dithiolate complexes: [Rh(η^5-C_5Me_5)(C_3S_5)]₂(**2**) (2.3571, 2.3774 Å), [Rh(η^5-C_5Me_5){$S_2C_2(CN)_2$}](2.345, 2.346 Å) [37] and [Rh(η^5-C_5Me_5){$S_2C_2(CN)_2$}]₂(2.350, 2.351 Å) [38]. The C_3S_5 ligand including the metal atom is almost planar (±0.026 Å), and the dihedral angle between the C_3S_5-Rh plane and the η^5-C_5H_5 plane is 87.0(4). These findings are also very close to those of [Co(η^5-C_5H_5)(C_3S_5)] [35] and [Ni(η^5-C_5H_5)(C_3S_5)] [36].

The crystal structure of **1** reveals a one-dimensional array of the molecules through two short non-bonded
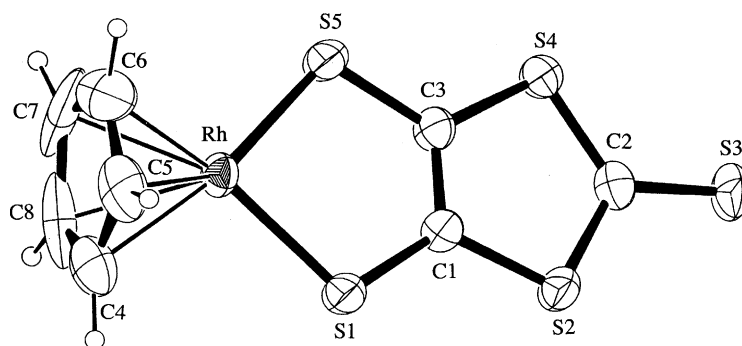

Fig. 1. Molecular geometry of **1** together with the atom-labeling scheme.
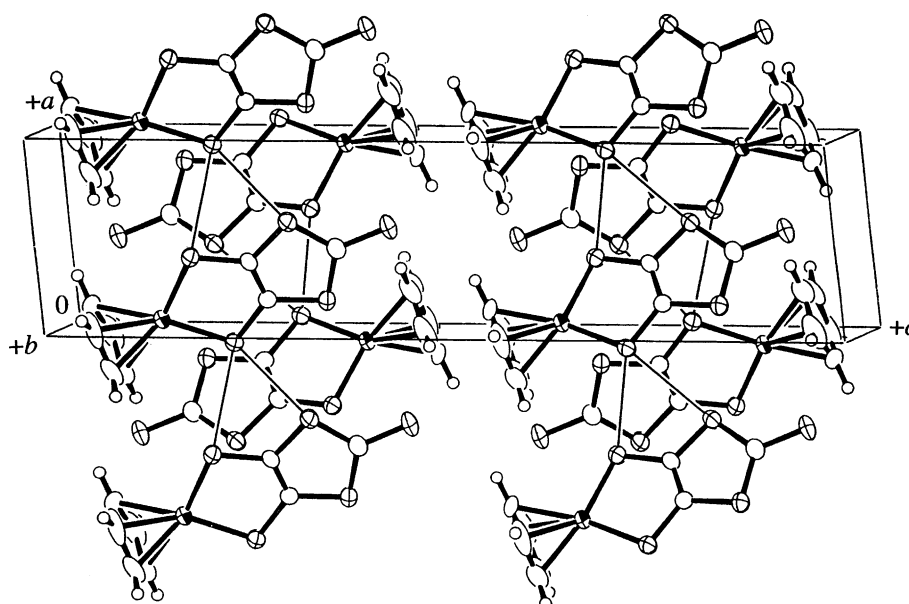

Fig. 2. Packing diagram of **1**. Fine lines represent S–S non-bonded contacts less than 3.7 Å.
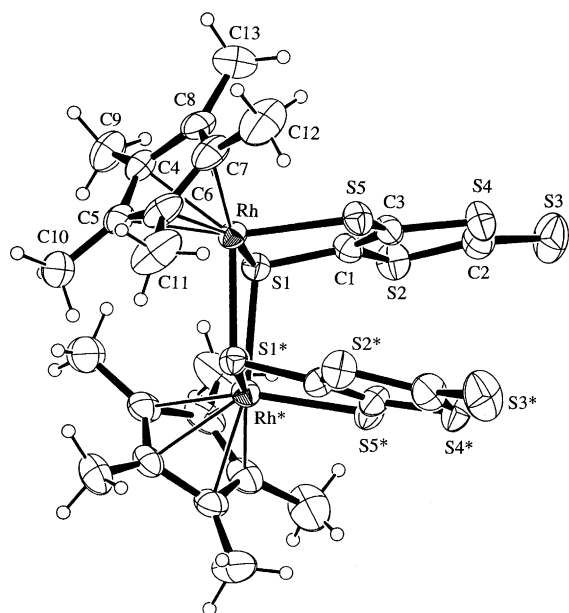
Fig. 3. Molecular geometry of **2** together with the atom-labeling scheme.

Table 2
Relevant bond distances (Å) and angles (°) for complexes **1** and **2**

	1	**2**
Rh–S(1)	2.241(2)	2.3774(5)
Rh–S(5)	2.242(2)	2.3571(6)
Rh–S(1*)		2.4083(6)
S(1)–C(1)	1.706(7)	1.754(2)
S(2)–C(1)	1.740(7)	1.737(2)
S(2)–C(2)	1.721(8)	1.721(3)
S(3)–C(2)	1.669(8)	1.645(3)
S(4)–C(2)	1.713(8)	1.733(3)
S(4)–C(3)	1.733(7)	1.746(2)
S(5)–C(3)	1.716(7)	1.726(2)
C(1)–C(3)	1.375(10)	1.346(3)
S(1)–Rh–S(5)	89.18(7)	88.55(2)
S(1)–Rh–S(1*)		82.63(2)
S(5)–Rh–S(1*)		95.89(2)
Rh–S(1)–C(1)	104.0(3)	101.06(7)
Rh–S(1)–Rh*		97.16(2)
C(1)–S(2)–C(2)	97.4(4)	97.7(1)
C(2)–S(4)–C(3)	97.2(4)	98.1(1)
Rh–S(5)–C(3)	104.4(2)	101.19(8)
S(1)–C(1)–C(3)	122.1(6)	122.6(2)
S(2)–C(1)–C(3)	115.1(5)	116.9(2)
S(2)–C(2)–S(4)	114.0(4)	112.3(1)
S(4)–C(3)–C(1)	116.3(6)	114.9(2)
S(5)–C(3)–C(1)	120.3(5)	125.8(2)

S–S contacts [S(1)–S(4) $(x − 1, y, z)$, 3.524(3) and S(1)–S(5) $(x − 1, y, z)$, 3.599(3) Å] along the a axis, as illustrated in Fig. 2.

The molecular geometry of **2** is displayed in Fig. 3, together with the atom-labeling scheme. Relevant bond distances and angles of **2** are also summarized in Table 2. Complex **2** is dimeric, consisting of two [Rh(η^5-C$_5$Me$_5$)(C$_3$S$_5$)] units which are related by a crystallo-

graphic two-fold axis at the midpoint between Rh and Rh* atoms, around which the atoms are related to those with asterisks. In the crystal structure there are no significant close atom-atom contacts among the dimeric molecular units. This dimerization is quite similar to that observed for [Rh(η^5-C$_5$Me$_5$){S$_2$C$_2$(CN)$_2$}]$_2$ [38]. Each rhodium atom is viewed as formally six-coordinate, assuming a three coordinate ligand for the η^5-C$_5$Me$_5$ group with R–C distances of 2.176–2.205 Å, and the complex belongs to the family of three-legged piano stool compounds. The rhodium atom is coordinated with S(1) and S(5) atoms [Rh–S(1), 2.3774(5) and Rh–S(5), 2.3571(6) Å], as well as the S(1*) atom bridging with the other rhodium atom [Rh–S(1*), 2.4083(6) Å]. The C$_3$S$_5$ ligand including the rhodium atom is almost planar (±0.050 Å). The dihedral angle between the C$_3$S$_5$-Rh plane and the η^5-C$_5$Me$_5$ plane is 52.20(4)° owing to the steric hindrance of the η^5-C$_5$Me$_5$ groups through the dimerization. The bridging Rh–S bond is rather weak, leading to a monomeric form in solution. This has been supported by the electrospray mass spectrum of **2** indicating the peak of the [Rh(η^5-C$_5$Me$_5$)(C$_3$S$_5$)]$^+$ species (m/z, 434) in dichloromethane, which has been formed by the oxidation of the neutral complex by electrolysis at the electrospray inlet, since it has a low oxidation potential, as described below.

3.2. Oxidation of 1 and 2

The cyclic voltammogram of **1** measured in dichloromethane has shown reversible oxidation waves; oxidation peak potentials, +0.45 and +0.73 V (vs. Ag/Ag$^+$), while complex **2** has exhibited the first and second peak potentials at +0.54 and +0.70 V in dichloromethane. The first oxidation potential of **1** is somewhat lower than that of **2**, which is the reverse tendency simply based on the more electron-releasing property of the η^5-C$_5$Me$_5$ group of **2**. Rather lower oxidation potentials were observed for [Co(L)(C$_3$S$_5$)] (L = η^5-C$_5$H$_5$ and η^5-C$_5$Me$_5$) (+0.388, +0.688 and +0.211, +0.605 V vs. Ag/Ag$^+$, respectively) [5].

Since the first oxidation potentials of **1** and **2** are somewhat high, they have not been oxidized by iodine. However, they are oxidized by bromine. Fig. 4 shows the electronic absorption spectra of **2** in the presence of various amounts of bromine in dichloromethane. Complex **2** exhibits intense bands at 430 and 600 nm, which are ascribed to the $\pi - \pi^*$ transition of the C$_3$S$_5$ ligand and an intramolecular charge transfer transition from the C$_5$Me$_5$ group to the Rh(III) ion/C$_3$S$_5$ ligand, respectively, as observed for the corresponding Co(III)-complex [17]. Reactions of **1** and **2** with bromine have afforded one-electron oxidized species **3** and **4**, respectively, as black solids.

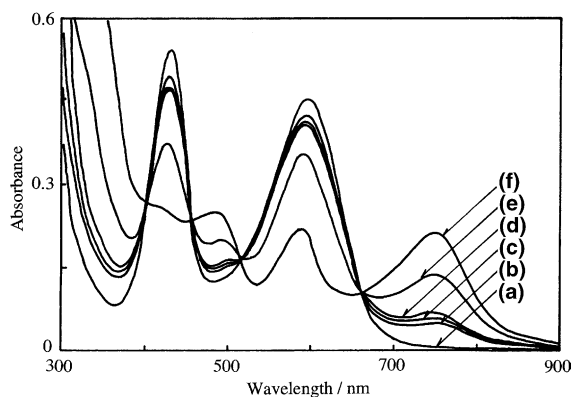These oxidized species dissolved in dichloromethane have exhibited ESR signals. Fig. 5 shows the observed

Fig. 4. Electronic absorption spectra of **2** (4.0×10^{-5} mol dm^{-3}) in dichloromethane in the presence of bromine. Concentration of bromine (mol dm^{-3}): (a) 0; (b) 0.8×10^{-5}; (c) 1.2×10^{-5}; (d) 2.0×10^{-5}; (e) 4.0×10^{-5}; (f) 1.4×10^{-4}.
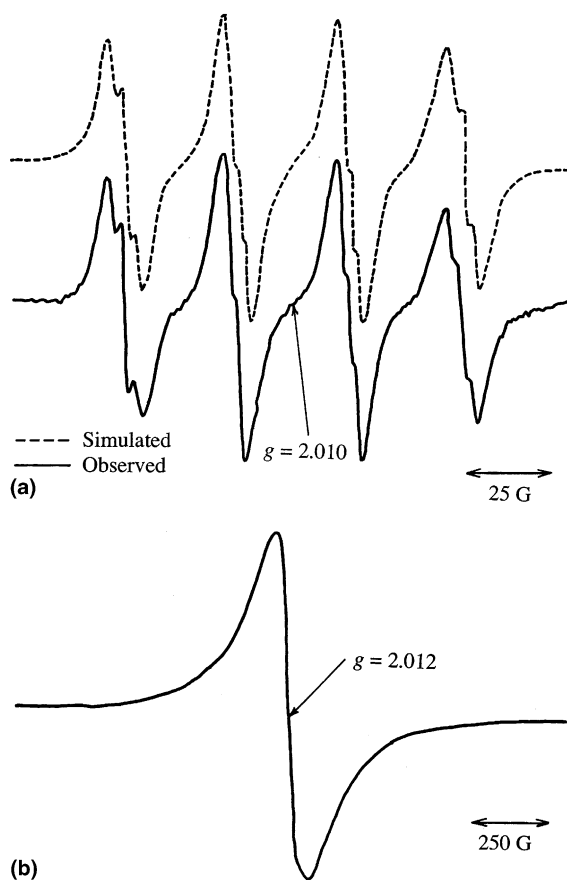

Fig. 5. ESR spectra of **2** (a) in dichloromethane (observed and simulated) and (b) in the solid state at room temperature.

coupling values indicate far less spin densities on the metal and bromine atoms, which is very similar to the case of [CoBr(η^5-C$_5$Me$_5$)(C$_3$S$_5$)] [16]. Mulliken spin densities have been evaluated by a DFT calculation [27] based on the assumed molecular structure for **2** using the geometry of [CoBr(η^5-C$_5$Me$_5$)(C$_3$S$_5$)] [16] having the rhodium atom in replace of the cobalt atom. The result shows the presence of 87% spins on the C$_3$S$_5$ ligand: Rh, 0.045; Br, 0.060; η^5-C$_5$Me$_5$, 0.035; S(1), S(5), 0.322; S(2), S(4), −0.010; S(3), 0.106; C(1),C(3), 0.076; C(2), −0.012. The solid state ESR spectrum of **2** shows a broad signal at $g = 2.012$ with the peak-to-peak linewidth of 9.7 mT (Fig. 5). These findings are consistent with the C$_3$S$_5$ ligand-centered oxidation, as observed for some oxidized C$_3$S$_5$–metal complexes [16,18–20].

Complex **1** has also shown an isotropic ESR signal at $g = 2.006$ (the ^{103}Rh and $^{79/81}$Br hyperfine couplings of 0.34×10^{-3} and 2.9×10^{-3} cm^{-1}, respectively) in dichloromethane similar to that of **2**. The almost isotropic broad signal in the solid state spectrum ($g = 2.007$, the peak-to-peak linewidth, 14 mT) has been similar to that of **2**.

The one electron-oxidized species **3** and **4** have exhibited no appreciable electrical conductivities: $< 10^{-7}$ S cm^{-1} for compacted pellets at room temperature. This is also the same for [CoBr(η^5-C$_5$Me$_5$)(C$_3$S$_5$)] [16]. Owing to the Rh–Br bond formation, as well as bulky η^5-C$_5$H$_5$ and η^5-C$_5$Me$_5$ groups, packing modes and molecular S–S interactions for these oxidized Rh(III)-species in the solid state may be ineffective for the electron conduction, although some related one electron-oxidized C$_8$H$_4$S$_8$–metal complexes, such as [Co(η^5-C$_5$H$_5$)(C$_8$H$_4$S$_8$)]$^+$ [17] and [Zr(η^5-C$_5$H$_5$)$_2$(C$_8$H$_4$S$_8$)]$^+$ complexes [39], behave as good electrical conductors.

Acknowledgements

and simulated spectra, together with that in the solid state. The isotropic spectrum observed at $g = 2.010$ consists of a doublet (^{103}Rh, $I = 1/2$) of quartet (^{79}Br (50.54%) and ^{81}Br (49.46%), $I = 3/2$); ^{103}Rh and $^{79/81}$Br hyperfine couplings are 0.47×10^{-3} and 3.0×10^{-3} cm^{-1}, respectively. This confirms the Rh–Br bond for the oxidized complex in solution. These small hyperfine

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