Transition Metal Complexes with Sulfur Ligands
XLVII*. S_2 Bridged Ruthenium Complexes with Sulfur Dominated Coordination Spheres and Highly Unusual Electronic Properties: $[\mu\text{-}S_2\{Ru(PPh_3)(\text{'}S_4\text{'})\}_2]$ and $[\mu\text{-}S_2\{Ru(PPh_3)(\text{'}^{bu}S_4\text{'})\}_2]$ ($\text{'}S_4\text{'}^{2-}$ = 1,2-Bis(2-mercaptophenylthio)ethane (2–); $\text{'}^{bu}S_4\text{'}^{2-}$ = 1,2-Bis(3,5-di(tertiarybutyl)-2-mercaptophenylthio)ethane (2–))

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Abstract

The ruthenium(II)-μ-disulfido complexes $[\mu\text{-}S_2\{Ru(PPh_3)(\text{'}S_4\text{'})\}_2]$ (1) and $[\mu\text{-}S_2\{Ru(PPh_3)(\text{'}^{bu}S_4\text{'})\}_2]$ (2) ($\text{'}S_4\text{'}^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane (2–); $\text{'}^{bu}S_4\text{'}^{2-}$ = 1,2-bis(3,5-di(tertiarybutyl)-2-mercaptophenylthio)ethane (2–)) form when $[Ru(Y)(PPh_3)(\text{'}L_4\text{'})]$ ($Y = PPh_3$, N_2H_4; $\text{'}L_4\text{'} = \text{'}S_4\text{'}^{2-}$, $\text{'}^{bu}S_4\text{'}^{2-}$) is reacted with elemental sulfur. 1 is also obtained from $[Ru(Y)(PPh_3)(\text{'}S_4\text{'})]$ and $(NBu_4)SH$ in the presence of oxygen. UV–Vis–NIR spectroscopic studies indicate that the intense blue green colour of 1 and 2 (λ_{max} = 640 (1) and 657 (2) nm) arises from transitions within the Ru_2S_2 core. Additionally, 1 and 2 show strong absorptions at 1049 and 1132 nm, respectively, which we assign to intervalence charge transfer (ICT) of a class II dimer with metal centers having sulfur dominated coordination spheres and an *even* number of electrons. The ICT is explained in terms of Ru^{II}/Ru^{III} and S_2^0/S_2^- transitions.

Introduction

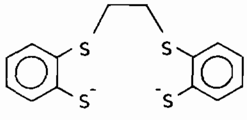
Transition metals in a coordination sphere dominated by sulfur donors are essential constituents of the active centers of electron transferases and oxidoreductases [2]. The elementary processes of the electron storage and transfer, however, remain largely unexplored. In many of these enzymes, iron sulfur clusters of the $[Fe_nS_n]$ type, n = *2*, *3*, *4*, are found [3, 4]. Synthetic analogues of these clusters have proved to uptake and release electrons reversibly without making or breaking chemical bonds [5], as was observed with more conventional metal sulfur complexes [6].

Transition metal complexes with sulfido ligands can be expected to undergo redox reactions also via the formation and cleavage of disulfido bonds according to eqn. (1).

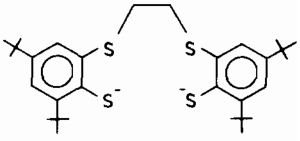
$$2[M\text{–}S] \rightleftharpoons [M\text{–}S\text{–}S\text{–}M]^{2+} + 2e^- \qquad (1)$$

In this respect, they should resemble the cystine–cysteine couple [7] and complexes with S_2 bridges become of considerable interest. In addition, such S_2 species are potential products of reactions between metal complexes and H_2S gas [8–10].

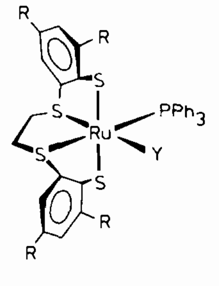
Bridging as well as terminal S_2 ligands are found in a number of complexes. A few examples are $[\mu\text{-}S_2\{Co(CN)_5\}_2]^{6-}$ [11], $[\mu\text{-}S_2\{Ru(NH_3)_5\}_2]^{4+}$ [12], $[\mu\text{-}S_2\{CpRu(PPh_3)_2\}_2]^{2+}$ [13], $[(\mu\text{-}S_2)(\mu\text{-}Cl_2)\{MoCl_3\}_2]^{2-}$ [14], $[\mu\text{-}S_2\{CpMn(CO)_2\}_2]$ [15], $[V(S_2)_2(terpy)]$ [16] or $[CpRe(CO)_2(S_2)]$ [17a].



$\text{'}S_4\text{'}^{2-}$



$\text{'}^{bu}S_4\text{'}^{2-}$



$Y = PPh_3, N_2H_4$

R = H : $\text{'}S_4\text{'}^{2-}$ R = ^tbu : $\text{'}^{bu}S_4\text{'}^{2-}$

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The field of disulfido complexes has recently been reviewed [17b], but in these species S_2 is the only sulfur ligand.

We have now found S_2 complexes with sulfur dominated metal fragments when we investigated the reactions of $[Ru(Y)(PPh_3)(\text{'}L_4\text{'})]$ ($Y = PPh_3$, N_2H_4; 'L$_4$' = 'S$_4$'$^{2-}$, '^{bu}S$_4$'$^{2-}$; 'S$_4$'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane (2−); '^{bu}S$_4$'$^{2-}$ = 1,2-bis(3,5-di(tertiarybutyl)-2-mercaptophenylthio)ethane (2−)) with H_2S, HS^- and elemental sulfur, respectively. These complexes show very unusual electronic properties and represent a new type of mixed valence compounds. Syntheses and properties of these complexes are reported here.

Experimental

General

All reactions were carried out under N_2 using standard Schlenk techniques. Solvents were dried and distilled under nitrogen before use. Spectra were recorded on the following instruments: Perkin-Elmer infrared spectrophotometer 983 G (KBr pellets), Jeol JNM-GX 270 FT NMR spectrometer, Shimadzu UV–Vis–NIR recording spectrophotometer UV-3100, Beckman DK 2A UV–Vis spectrophotometer and Varian MAT 212 mass spectrometer.

Magnetic measurements were carried out with a Johnson Matthey susceptibility balance at 295 K, cyclovoltammetric measurements with a PAR Model 264 A polarographic analyzer/stripping voltammeter (Ag/AgCl reference electrode, glassy carbon working and Pt counter electrode; 10^{-5} M solutions in CH_2Cl_2 containing 10^{-3} M $(NBu_4)ClO_4$ as conducting salt were degassed for 30 min with N_2 before measurement.

Starting materials [Ru(PPh$_3$)$_2$('S$_4$')], [Ru(N$_2$H$_4$)(PPh$_3$)('S$_4$')] [18] and [Ru(PPh$_3$)$_2$('^{bu}S$_4$')] [19] were prepared as described in the literature.

Syntheses

[μ-S$_2${Ru(PPh$_3$)('S$_4$')}$_2$] (1)

(a) From [Ru(PPh$_3$)$_2$('S$_4$')] and S$_8$. To a suspension of 934 mg (1 mmol) of [Ru(PPh$_3$)$_2$('S$_4$')] in 50 ml of THF is added 64.1 mg (2 mmol) of elemental sulfur. The mixture is stirred for 1 day under exclusion of light whereupon the colour changes from yellow to turquoise–blue. The precipitate is filtered off, washed with 15 ml of THF and dried in high vacuum for 1 day. The product is recrystallized from toluene (+20 → +5 °C) yielding microcrystalline blue–black **1**. Yield: 575 mg (82%). *Anal.* Calc. for $C_{64}H_{54}P_2Ru_2S_{10}$ (1407.8): C, 54.60; H, 3.87; S, 22.77. Found: C, 54.88; H, 3.77; S, 22.64%.

(b) From [Ru(N$_2$H$_4$)(PPh$_3$)('S$_4$')] and S$_8$. To the yellow solution of 430 mg (0.6 mmol) of [Ru(N$_2$H$_4$)(PPh$_3$)('S$_4$')] in 15 ml of THF is added 19 mg (0.6 mmol) of elemental sulfur. The mixture is stirred for 1 day under exclusion of light precipitating turquoise–blue **1** which is separated, washed with 15 ml of THF, dried in high vacuum for 1 day and characterized as above. Yield: 135 mg (32%).

(c) From [Ru(PPh$_3$)$_2$('S$_4$')] and (NBu$_4$)SH in the presence of air. To a yellow suspension of 934 mg (1 mmol) of [Ru(PPh$_3$)$_2$('S$_4$')] in 60 ml of THF is added dropwise a solution of 1.5 g (5.65 mmol) of (NBu$_4$)SH in 20 ml of THF. The suspension is stirred for 1 day under exclusion of light when a clear orange solution forms whose colour rapidly turns to blue–green when air is introduced. Precipitated turquoise–blue **1** is separated, washed with 15 ml of THF, dried in high vacuum for 1 day and characterized as above. Yield: 483 mg (62%).

(d) From [Ru(N$_2$H$_4$)(PPh$_3$)('S$_4$')] and (NBu$_4$)SH in the presence of air. To a yellow solution of 245 mg (0.35 mmol) of [Ru(N$_2$H$_4$)(PPh$_3$)('S$_4$')] in 15 ml of THF is added a solution of 620 mg (2.3 mmol) of (NBu$_4$)SH in 15 ml of THF. The mixture is heated to reflux for 3 h yielding a clear orange solution which is stirred under air. Precipitated **1** is filtered off, washed with 6 ml of THF, dried in high vacuum for 1 day and characterized as above. Yield: 105 mg (43%).

[μ-S$_2${Ru(PPh$_3$)('^{bu}S$_4$')}$_2$] (2)

A total of 28 mg (0.86 mmol) of elemental sulfur is added to a yellow suspension of 500 mg (0.43 mmol) of [Ru(PPh$_3$)$_2$('^{bu}S$_4$')] in 20 ml of THF. The mixture is stirred for 1 day under exclusion of light when the colour turns to turquoise–blue. Solid **2** is separated, washed with 15 ml of THF, dried in high vacuum for 1 day and recrystallized from toluene (+20 → +5 °C) to give blue–black microcrystals. Yield: 267 mg (67%). *Anal.* Calc. for $C_{96}H_{118}P_2Ru_2S_{10}$ (1856.7): C, 62.10; H, 6.41; S, 17.27. Found: C, 62.48; H, 6.02; S, 17.13%.

Results and Discussion

It was previously shown that one PPh_3 ligand of [Ru(PPh$_3$)$_2$('L$_4$')] ('L$_4$' = 'S$_4$'$^{2-}$, '^{bu}S$_4$'$^{2-}$) is labile towards substitution and [Ru(Y)(PPh$_3$)('L$_4$')] species with Y = CO, N_2H_4, NH_3 or HCl form under mild conditions [18–21]. A facile reaction also takes place with gaseous H_2S. In this case deep turquoise products were obtained. Their spectra and analyses indicated the formation of the binuclear disulfido complex [μ-S$_2${Ru(PPh$_3$)('S$_4$')}$_2$] (**1**). The reaction, however, was difficult to reproduce and the product could not be obtained in the pure state. Therefore we investigated alternative routes and found a preparative synthesis of **1** according to eqn. (2).

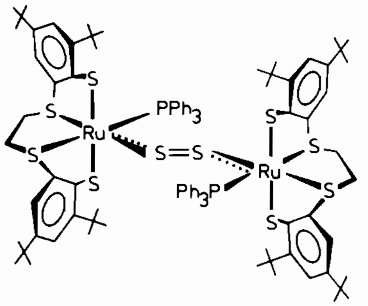
$$2[\mathrm{Ru(PPh_3)_2(`S_4')}] + \tfrac{1}{2}\mathrm{S_8} \xrightarrow[-2\mathrm{PPh_3S}]{\mathrm{THF/20\,^{\circ}C/1\ day}} [\mu\text{-}\mathrm{S_2\{Ru(PPh_3)(`S_4')\}_2}] \quad (2)$$

1

In the course of the reaction, the yellow suspension of [Ru(PPh$_3$)$_2$('S$_4$')] turned deep turquoise, and subsequently a black–blue microcrystalline product was isolated which analyzed for **1**. Additionally, PPh$_3$S was detected in solution by IR and ^{31}P NMR spectroscopy. **1** is sparingly soluble in CH_2Cl_2, THF and toluene, and insoluble in all other common solvents.

The binuclearity of **1** follows from its mass spectrum showing the molecular ion at $m/e = 1408$. KBr IR and ^{1}H NMR spectra allow no conclusion with respect to the structure of **1**. They only show signals of the [Ru(PPh$_3$)('S$_4$')] fragment (see Table 1). More conclusive is the ^{1}H NMR spectrum of [μ-S$_2${Ru(PPh$_3$)('^{bu}S$_4$')}$_2$] (**2**). **2** was prepared in order to obtain a better soluble and eventually better crystallizing derivative; it forms according to eqn. (3).

$$2[\mathrm{Ru(PPh_3)_2(`^{bu}S_4')}] + \tfrac{1}{2}\mathrm{S_8} \xrightarrow[-2\mathrm{PPh_3S}]{\mathrm{THF/20\,^{\circ}C/1\ day}}$$



(3)

2

As in the synthesis of **1**, the same colour change from yellow to deep turquoise was observed and **2** could be isolated as blue–black microcrystals. **2** is slightly more soluble than **1**, but so far no single crystals of **2** suited for X-ray structure determination could be obtained either.

The ^{1}H NMR spectrum of **2** in CD_2Cl_2 (Fig. 1) shows four sharp singlets in the t-butyl region. The number of signals indicates C_1 symmetry of the [Ru(PPh$_3$)('^{bu}S$_4$')] cores [19] and C_i or C_2 symmetry of the binuclear **2**. Since all complexes with the [Ru(PPh$_3$)('S$_4$')] or [Ru(PPh$_3$)('^{bu}S$_4$')] fragment, which were isolated so far, obey the 18 electron rule, **2** could have the structure which is schematically shown in eqn. (3): two [Ru(PPh$_3$)('^{bu}S$_4$')] cores of mirror symmetry are connected by a S_2 bridge. The mass spectrum of **2** shows no parent ion at $m/e = 1856$, but fragments at $m/e = 960$ and 928 which are assigned to [Ru(S$_2$)(PPh$_3$)('^{bu}S$_4$,)]$^+$ and [Ru(S)(PPh$_3$)('^{bu}S$_4$')]$^+$. The binuclearity of **2** could be substantiated by osmometric molecular mass determination in THF (poor solubility of **2** impeded the measurement but the value of $M = 1662 \pm 200$ is compatible only with a binuclear species).

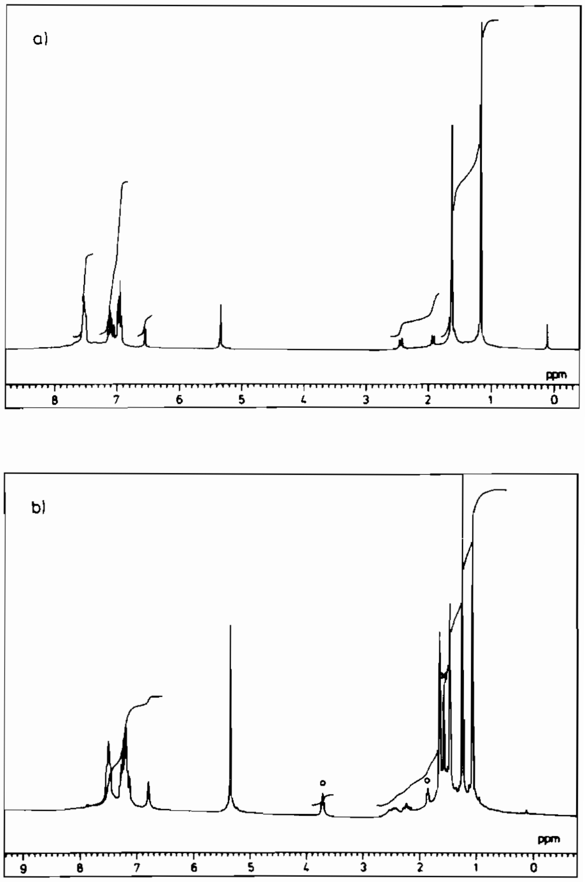


Fig. 1. ^{1}H NMR spectra in CD_2Cl_2 of (a) [Ru(PPh$_3$)$_2$('^{bu}S$_4$')] and (b) [μ-S$_2${Ru(PPh$_3$)('^{bu}S$_4$,)}$_2$] (**2**) (o = THF, x = traces of H_2O).

1 and **2** are surprisingly stable; with air no reaction occurs and when reacted with acids, e.g. HCl, no H_2S formation can be observed. **1** and **2** are also thermically relatively stable and can be heated in boiling toluene for 1 h; above 140 °C in DMF, rapid decomposition takes place.

1 also forms when the labile [Ru(N$_2$H$_4$)(PPh$_3$)('S$_4$')] is reacted with elemental sulfur according to eqn. (4).

$$2[\mathrm{Ru(N_2H_4)(PPh_3)(`S_4')}] + \tfrac{1}{4}\mathrm{S_8} \xrightarrow[-2\mathrm{N_2H_4}]{\mathrm{THF/20\,^{\circ}C/1\ day}} \mathbf{1} \quad (4)$$

Remarkable with respect to the formation of [M–S–S–M] from [M–S] bonds is the synthesis of **1** from [Ru(Y)(PPh$_3$)(‘S$_4$’)] (Y = PPh$_3$, N$_2$H$_4$) and SH$^-$ in the presence of air (eqn. (5)).

$$2\,[\mathrm{Ru(Y)(PPh_3)(‘S_4’)}] + 2(\mathrm{NBu_4})\mathrm{SH} \xrightarrow[-2\mathrm{Y}]{\mathrm{THF/+air}} \mathbf{1} + \text{other products} \qquad (5)$$

Y = PPh$_3$, N$_2$H$_4$

1 presumably forms via oxidation of the intermediate [Ru(SH)(PPh$_3$)(‘S$_4$’)]$^-$, which we have not been able to isolate so far. When we tried to precipitate the anion by addition of (NMe$_4$)Cl, the orange solution rapidly turned blue and subsequently **1** could be obtained. Obviously, [Ru(SH)(PPh$_3$)(‘S$_4$’)]$^-$ easily transforms into **1**, demonstrating the well-known high reactivity of SH complexes [10]; only a few complexes with SH and SH$_2$ ligands have been isolated so far [22, 8, 17a].

UV–Vis–NIR Spectroscopy

The most characteristic visible property of **1** and **2** is their deep turquoise colour being due to absorptions at 640 (**1**) and 657 (**2**) nm in the UV–Vis–NIR spectra of **1** and **2** (Fig. 2). It strongly contrasts with the yellow colour of the mononuclear [Ru(Y)(PPh$_3$)(‘L$_4$’)] complexes (Y = PPh$_3$, CO, N$_2$H$_4$ [18], NH$_3$ [20], HCl, SMe$_2$, SPh$_2$ [21]; ‘L$_4$’ = ‘S$_4$’$^{2-}$, ‘${}^{\mathrm{bu}}$S$_4$’$^{2-}$) which show no absorption in the respective region (Fig. 2). We assign these absorptions to π–π^* transitions in the Ru–S–S–Ru system. As in the deep green [μ-N$_2$H$_2${Ru(PPh$_3$)(‘S$_4$’)}$_2$] [23], which shows an intense absorption at 608 nm (additional to an absorption at 470 nm), the bridging ligands and the two Ru centers form a 4c–6e$^-$–π-system resulting in a strong chromophore.

Intense absorptions in the same range were observed in the related [μ-S$_2${CpRu(PPh$_3$)$_2$}$_2$]$^{2+}$ [13] and [μ-S$_2${Ru(NH$_3$)$_5$}$_2$]$^{4+}$ [12] ions.

Completely unexpected was the observation that **1** shows an additional intense band at 1049 nm (ϵ = 13661 l mol^{-1} cm^{-1}). For **2** this absorption appears at 1132 nm (ϵ = 10240 l mol^{-1} cm^{-1}). Both bands have shoulders at 820 and 870 nm (Fig. 2). This observation was unexpected since neither [Ru(Y)(PPh$_3$)(‘L$_4$’)] complexes nor the binuclear [μ-N$_2$H$_2${Ru(PPh$_3$)(‘S$_4$’)}$_2$] display bands in this region, in which usually the high intensity intervalence charge transfer (ICT) bands of mixed valence complexes appear. **1** and **2**, however, are formally not mixed valence complexes and in contrast to compounds such as the Creutz–Taube ion [μ-pyrazine{Ru(NH$_3$)$_5$}$_2$]$^{5+}$ [24] and related complexes [25], **1** and **2** possess an *even* number of electrons. We therefore made several attempts in order to determine the nature of the near infrared band of **1** and **2**.

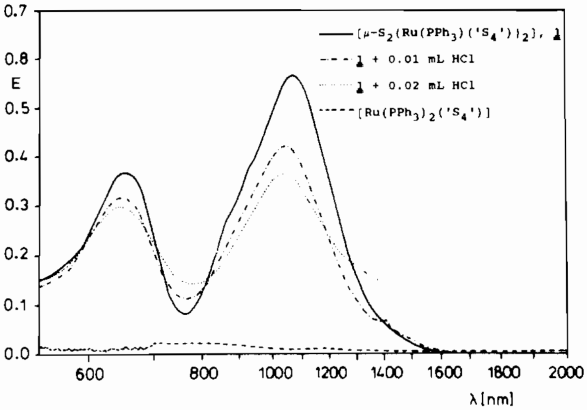
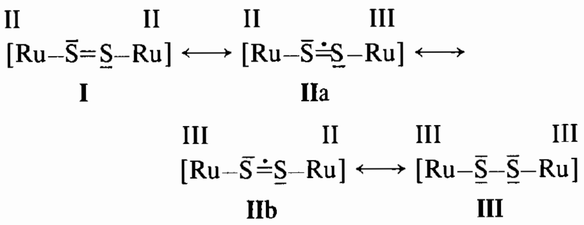


Fig. 2. UV–Vis–NIR spectrum of [μ-S$_2${Ru(PPh$_3$)(‘S$_4$’)}$_2$] (**1**) in CH$_2$Cl$_2$.

The following results indicate that the bands may indeed be due to ICT absorptions and in order to explain them, it is assumed that the RuSSRu cores of **1** and **2** are to be described in valence bond terms by the resonance structures **I**–**III** [26]:



$$\underset{\mathbf{I}}{[\overset{\mathrm{II}}{\mathrm{Ru}}-\bar{\mathrm{S}}=\underline{\mathrm{S}}-\overset{\mathrm{II}}{\mathrm{Ru}}]} \longleftrightarrow \underset{\mathbf{IIa}}{[\overset{\mathrm{II}}{\mathrm{Ru}}-\bar{\mathrm{S}}\overset{\bullet}{=}\underline{\mathrm{S}}-\overset{\mathrm{III}}{\mathrm{Ru}}]} \longleftrightarrow \underset{\mathbf{IIb}}{[\overset{\mathrm{III}}{\mathrm{Ru}}-\bar{\mathrm{S}}\overset{\bullet}{=}\underline{\mathrm{S}}-\overset{\mathrm{II}}{\mathrm{Ru}}]} \longleftrightarrow \underset{\mathbf{III}}{[\overset{\mathrm{III}}{\mathrm{Ru}}-\underline{\bar{\mathrm{S}}}-\underline{\bar{\mathrm{S}}}-\overset{\mathrm{III}}{\mathrm{Ru}}]}$$

The mixed valences of the Ru centers are generated by electron transfer from Ru to the bridging S$_2$ ligand which becomes a kind of superdisulfide [<S$\overset{\bullet}{=}$S>]$^-$ [27].

Vibrational spectroscopy could not differentiate between SS single or double bonds because the relevant IR region of 800–400 cm^{-1} [28, 29] is obscured by ‘S$_4$’$^{2-}$, ‘${}^{\mathrm{bu}}$S$_4$’$^{2-}$ and PPh$_3$ absorptions; Raman spectra could not be recorded because of fluorescence.

RuSSRu cores with electron configurations as shown by the resonance structures **IIa** and **IIb** were previously suggested for [μ-S$_2${Ru(NH$_3$)$_5$}$_2$]$^{4+}$ [26] in order to explain its residual paramagnetism of 0.45 μ_B/dimer [12]. For [μ-S$_2${Ru(NH$_3$)$_5$}$_2$]$^{4+}$, however, absorptions in the near infrared were not detected and the paramagnetism could be later traced back to small amounts of Ru(III)/Ru(IV) impurities [30], which originated from partial oxidation.

Partial oxidation or reduction of S$_2$ complexes is not uncommon and was also reported for [μ-S$_2${CpRu(PPh$_3$)$_2$}$_2$]$^{2+}$ [13]. Therefore we checked whether **1** or **2** contained paramagnetic oxidation or reduction products. When we measured the magnetic susceptibility of **1**, we indeed observed a paramagnetism of 0.34 μ_B/dimer (no diamagnetic correction applied). It led us to suspect that the 1049 nm band might be eventually due to an oxidized or reduced species, e.g. $[\mathbf{1}]^+$ or $[\mathbf{1}]^-$. Although the high intensity of the band made this suspicion not very likely, we tested whether the band was affected by treating solutions of **1** with either oxygen or hydrazine. No change could be observed and thus we assume that $[\mathbf{1}]^+$ or $[\mathbf{1}]^-$ are absent in the solutions of **1** which were used for recording the UV–Vis–NIR spectra.

Another alternative for explaining the 1049 nm band is n–π^* transitions. In the Ru–$\bar{\mathrm{S}}$=$\underline{\mathrm{S}}$–Ru system the sulfur atoms have lone pairs of electrons which principally can undergo n–π^* transitions. Such transitions are expected at longer wavelengths than π–π^* transitions, they are of lower intensity and should be pH dependent, because the lone pairs become bonding when protonated. When gaseous HCl is introduced into a CH_2Cl_2 solution of **1**, the 640 nm absorption does not change, but the shoulders at 820 and 870 nm disappear and the 1049 nm band is slightly shifted to 1031 nm and decreases in intensity. The same result is observed when a few drops of concentrated hydrochloric acid are added (Fig. 2).

We tentatively interpret these results by assuming that the shoulders at 820 and 870 nm are due to n–π^* transitions, since they disappear upon addition of acid.

When the lone pairs of the sulfur atoms in the RuSSRu core become protonated, a shift and decrease of intensity of the 1049 nm band is also to be expected if it is an ICT band.

Mixed valence complexes may be classified according to Robin and Day [31]. The most readily applicable diagnostic is the band width and solvent dependence of the ICT bands [32]. The NIR band of **1** was not shifted when the spectra were recorded in CH_2Cl_2 or THF. $\Delta\tilde{\nu}^{1/2}$ (in CH_2Cl_2) is 28 571 cm^{-1}; it is six times as large as $\Delta\tilde{\nu}^{1/2}$ obtained from Hush's correlation [33] ($\Delta\tilde{\nu}^{1/2} = (2310 \times \tilde{\nu}_{max})^{1/2}$ cm^{-1}) which is 4692 cm^{-1}. Both findings indicate that **1** must likely belong to class II compounds.

Table 1 summarizes selected spectroscopic data of **1** and **2**.

Cyclovoltammetry

Valence bond structures certainly describe the electronic structure of the RuSSRu core rather insufficiently, but they suggest redox activity of both **1** and **2**. Cyclovoltammetry indeed shows that many redox stages are accessible indicating the electronic flexibility of the RuSSRu core.

The mononuclear [Ru(Y)(PPh$_3$)('L$_4$')] complexes (Y = PPh$_3$, N$_2$H$_4$; 'L$_4$' = 'S$_4$'$^{2-}$, '^{bu}S$_4$'$^{2-}$) show only one irreversible reduction and two irreversible oxidation waves. **1** and **2**, on the other hand, show two reduction and four oxidation waves, the first reduction and first oxidation wave being quasireversible (Fig. 3, Table 2).

The reduction pattern may be explained by eqn. (6).

$$[\overset{\mathrm{II}}{\mathrm{Ru}}-\bar{\mathrm{S}}=\underline{\mathrm{S}}-\overset{\mathrm{II}}{\mathrm{Ru}}] \xrightarrow{+e^-} [\overset{\mathrm{II}}{\mathrm{Ru}}-\bar{\mathrm{S}}\dot{=}\underline{\mathrm{S}}-\overset{\mathrm{II}}{\mathrm{Ru}}]^- \xrightarrow{+e^-} [\overset{\mathrm{II}}{\mathrm{Ru}}-\underline{\bar{\mathrm{S}}}-\underline{\bar{\mathrm{S}}}-\overset{\mathrm{II}}{\mathrm{Ru}}]^{2-} \qquad (6)$$

The addition of a third electron is expected to lead to cleavage of the S–S bond.

Oxidation steps may involve, for example, species as shown in eqn. (7).

$$[\overset{\mathrm{II}}{\mathrm{Ru}}-\bar{\mathrm{S}}=\underline{\mathrm{S}}-\overset{\mathrm{II}}{\mathrm{Ru}}] \xrightarrow{-e^-} \{[\overset{\mathrm{II}}{\mathrm{Ru}}-\dot{\mathrm{S}}=\underline{\mathrm{S}}-\overset{\mathrm{II}}{\mathrm{Ru}}]^+ \longleftrightarrow [\overset{\mathrm{II}}{\mathrm{Ru}}-\bar{\mathrm{S}}=\underline{\mathrm{S}}-\overset{\mathrm{III}}{\mathrm{Ru}}]^+\} \xrightarrow{-e^-} \{[\overset{\mathrm{II}}{\mathrm{Ru}}-\dot{\mathrm{S}}=\underset{\cdot}{\mathrm{S}}-\overset{\mathrm{II}}{\mathrm{Ru}}]^{2+} \longleftrightarrow [\overset{\mathrm{III}}{\mathrm{Ru}}-\bar{\mathrm{S}}=\underline{\mathrm{S}}-\overset{\mathrm{III}}{\mathrm{Ru}}]^{2+}\} \qquad (7)$$

The capability of **1** and **2** to accept and release altogether at least six electrons is a property which

TABLE 1. Selected spectroscopic data of the S_2 complexes **1** and **2**

Compound	UV–Vis–NIR (nm) in CH_2Cl_2 [a]	^{1}H NMR (ppm) in CD_2Cl_2 [b]	^{31}P NMR (ppm) in CD_2Cl_2 [c]	FD-MS (*m/e*)
[μ-S$_2${Ru(PPh$_3$)('S$_4$')}$_2$] (**1**)	640 (ϵ = 8969)[d] 1049 (ϵ = 13661)	7.64–6.63(m) (46; C_6H_4, PPh_3) 3.97–2.14(m) (8; C_2H_4)	34.0	1408 $[M]^+$ 704 $[(M/2)]^+$
[μ-S$_2${Ru(PPh$_3$)('^{bu}S$_4$')}$_2$] (**2**)	657 (ϵ = 8230)[e] 1132 (ϵ = 10240)	7.52–6.80(m) (38; C_6H_2, PPh_3) 2.68–2.20(m) (8; C_2H_4) $\left.\begin{array}{l}1.62(s)\\1.47(s)\\1.23(s)\\1.06(s)\end{array}\right\}$ (72; $C(CH_3)_3$)	34.0	[f] 960 $[(M/2) + S]^+$ 928 $[(M/2)]^+$

[a] ϵ in l mol^{-1} cm^{-1}. [b] Relative to TMS. [c] Ref. to ext. $H_3\underline{P}O_4$. [d] Shimadzu UV-3100. [e] Beckman DK-2A. [f] No $[M]^+$ observed.

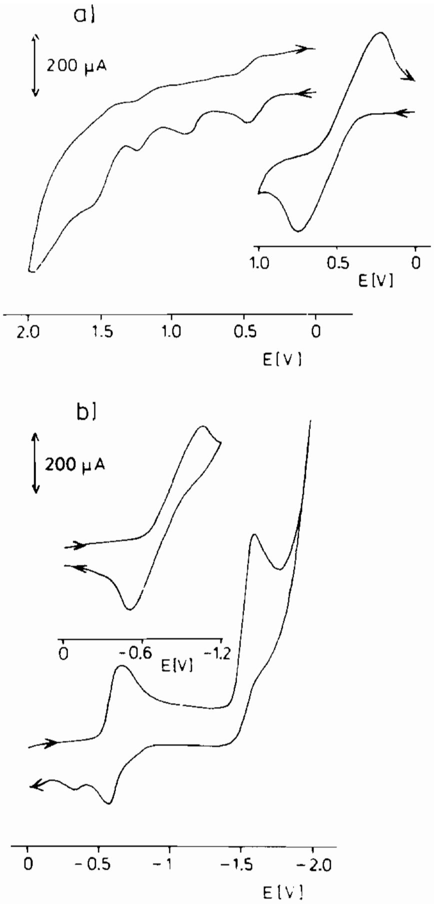


Fig. 3. Cyclic voltammogram for (a) oxidation and (b) reduction of 1 in CH_2Cl_2 (ν = 200 mV/s).

has not been found, as far as we are aware, for $[\mu\text{-}S_2\{Ru(NH_3)_5\}_2]^{4+}$ [34, 12, 13], or any other binuclear S_2 complexes and is principally observed in redoxactive biopolymers [35].

Conclusions

$[Ru(PPh_3)_2('S_4')]$ and $[Ru(PPh_3)_2('^{bu}S_4')]$ react with elemental sulfur in order to yield the binuclear S_2 complexes $[\mu\text{-}S_2\{Ru(PPh_3)('S_4')\}_2]$ (**1**) and $[\mu\text{-}S_2\{Ru(PPh_3)('^{bu}S_4')\}_2]$ (**2**). **1** is also obtained when $[Ru(Y)(PPh_3)('S_4')]$ (Y = PPh_3, N_2H_4) is reacted with SH^- and subsequently with oxygen. Probably $[Ru(SH)(PPh_3)('S_4')]^-$ forms as intermediate which is oxidized yielding **1** having a RuSSRu core: in this respect, the intermediate and **1** can serve as model of biological metal sulfido complexes which release electrons by forming disulfido bonds.

1 and **2** show characteristic π–π^* absorptions of the 4c–6e$^-$–π-system of the RuSSRu chromophore at 640 and 657 nm, respectively. Very unexpectedly, additional high intensity bands are observed at 1049 nm for **1** and 1132 nm for **2**. They are assigned to intervalence transitions of **1** and **2** which may be described as mixed valence complexes by the canonical structures

$$[\overset{\mathrm{II}}{\mathrm{Ru}}-\bar{\mathrm{S}}=\underline{\mathrm{S}}-\overset{\mathrm{II}}{\mathrm{Ru}}] \longleftrightarrow [\overset{\mathrm{II}}{\mathrm{Ru}}-\bar{\mathrm{S}}\dot{=}\underline{\mathrm{S}}-\overset{\mathrm{III}}{\mathrm{Ru}}] \longleftrightarrow$$

$$[\overset{\mathrm{III}}{\mathrm{Ru}}-\underline{\bar{\mathrm{S}}}-\underline{\bar{\mathrm{S}}}-\overset{\mathrm{III}}{\mathrm{Ru}}]$$

Solvent independence and $\Delta\nu^{1/2}$ of the NIR bands characterize **1** and **2** as class II mixed valence complexes.

The electronic flexibility of the RuSSRu core is also displayed by cyclovoltammetry: **1** and **2** show two reduction and four oxidation waves.

Thus, **1** and **2**, to our knowledge, are the first mixed valence complexes which have an even number of electrons and metal centers of identical oxidation state. They show that metal centers having sulfur dominated coordination spheres form species of

TABLE 2. Redox potentials E_p of **1** and **2** in CH_2Cl_2 (vs. NHE)

	C = 1		C = 2	
	$E_{p\,red}$ (V)	$E_{p\,ox}$ (V)	$E_{p\,red}$ (V)	$E_{p\,ox}$ (V)
Reduction				
$0 \rightleftharpoons [C]^-$	−0.56(q)	−0.47(q)	−0.58(q)	−0.44(q)
$[C]^- \rightleftharpoons [C]^{2-}$	−1.51(i)		−1.61(i)	
Oxidation				
$0 \rightleftharpoons [C]^+$	+0.23(q)	+0.37(q)	+0.25(q)	+0.33(q)
$[C]^+ \rightleftharpoons [C]^{2+}$		+0.80(i)		+0.97(i)
$[C]^{2+} \rightleftharpoons [C]^{3+}$		+1.14(i)		+1.30(i)
$[C]^{3+} \rightleftharpoons [C]^{4+}$		+1.43(i)		+1.56(i)

q = quasireversible, i = irreversible.

unusual electronic properties when they are connected via S_2 bridges.

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