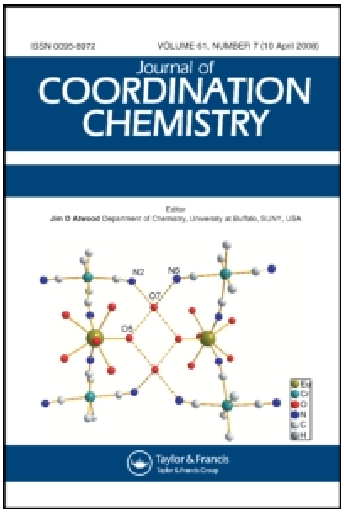

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Syntheses and molecular structures of ruthenium complexes with dithiophosphate ligands

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Syntheses and molecular structures of ruthenium complexes with dithiophosphate ligands

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Reactions of $[Ru(PPh_3)_3Cl_2]$ and $[RuHCl(CO)(PPh_3)_3]$ with $K[S_2P(OEt)_2]$ in THF afforded $[Ru\{S_2P(OEt)_2\}_2(PPh_3)_2]$ (**1**) and $[RuH(CO)\{S_2P(OEt)_2\}(PPh_3)_2]$ (**2**), respectively. The crystal structures of complexes **1** and **2** have been determined by X-ray crystallography. The ruthenium atom in both molecules of **1** and **2** adopt an octahedral configuration. The average Ru–P and Ru–S distances in **1** are 2.3324(10) and 2.4974(11) Å, respectively. The corresponding bond lengths for **2** are 2.3551(9) and 2.5474(11) Å.

Keywords: Ruthenium; Sulfur; Synthesis; Crystal structure; Dithiophosphate

1. Introduction

The chemistry of transition metal sulfur compounds has attracted much interest for their importance in the field of metalloenzymes, material precursor, and catalysts [1]. In recent years there has been an increased interest in ruthenium complexes with sulfur donor ligands, in part because of the high catalytic activity of RuS_2 in various hydrotreating processes [2]. As a part of this development, many examples of ruthenium thiolate complexes have been reported, however, the ruthenium complexes with dithio ligands are relatively rare [3]. Recently, we have reported a series of ruthenium complexes with the bis(dialkylthiophosphoryl)amides $N(SPR_2)_2$ which exhibit a high degree of geometric and electronic flexibility as they can deviate form planarity without substantial disruption in the P–S π bond [4]. In this connection, we are continuously interested to explore the synthesis and reaction of ruthenium complexes with other bidentate thiolate ligands, such as dithiocarbamate and dithiophosphate [5].

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In this article we report the syntheses of two ruthenium complexes with dithiodiethylphosphate ligands and their characterization by spectral data and single-crystal X-ray diffraction.

2. Experimental

2.1. *General*

All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. Solvents were purified, distilled and degassed by standard methods. $[Ru(PPh_3)_3Cl_2]$ [6] and $[RuHCl(CO)(PPh_3)_3]$ [7] were prepared according to literature methods. $K[S_2P(OEt)_2]$ was synthesized from the reaction of P_4S_{10}, EtOH and KOH [8]. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ^1H and ^{31}P, respectively. Chemical shifts (δ, ppm) were referenced to $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin–Elmer 16 PC FT–IR spectrophotometer and mass spectra on a Finnigan TSQ 7000 spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 273A potentiostat. The working and reference electrodes were glassy carbon and $Ag/AgNO_3$ (0.1 M in acetonitrile) electrodes, respectively. Potentials were reported with reference to the ferrocenium–ferrocene ($Cp_2Fe^{+/0}$) couple. Elemental analyses were performed by Medac Ltd, Surrey, UK.

2.2. *Preparations*

2.2.1. $[Ru\{S_2P(OEt)_2\}_2(PPh_3)_2]$ (1). A mixture of $[Ru(PPh_3)_3Cl_2]$ (144 mg, 0.15 mmol) and $K[S_2P(OEt)_2]$ (69 mg, 0.31 mmol) was dissolved in THF (20 mL) and then stirred overnight at room temperature. The solvent was pumped off under vacuum. The remaining solid was washed with hexane and further recrystallized from CH_2Cl_2/hexane. Dark red block crystals of **1** were obtained after three days. Yield: 86 mg, 58%. ^1H NMR ($CDCl_3$): δ 1.13 (m, 12H, OCH_2CH_3), 3.74 (m, 8H, OCH_2CH_3), 7.68–7.07 (m, 30H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 40.84 (s, 2P, PPh_3), 98.86 (s, 2P, $S_2P(OEt)_2$). MS (FAB): *m/z* 996 (M^+), 734 (M^+–PPh_3). $E_{1/2}$ (CH_2Cl_2, *V*) = 0.19 (Ru^{II}/Ru^{III}). Anal. Calcd for $C_{44}H_{50}O_4P_4S_4Ru$: C, 53.1; H, 5.07. Found: C, 53.3; H, 5.01.

2.2.2. $[RuH(CO)\{S_2P(OEt)_2\}(PPh_3)_2]$ (2). A mixture of $[RuHCl(CO)(PPh_3)_3]$ (150 mg, 0.16 mmol) and $K[S_2P(OEt)_2]$ (36 mg, 0.16 mmol) was dissolved in THF (20 mL) and then stirred overnight at room temperature. A colour change from yellow to pale orange was observed. The solvent was pumped off under vacuum. The remaining solid was washed with hexane and further recrystallized from CH_2Cl_2/hexane. Block orange crystals of **2** were obtained after one week. Yield: 80 mg, 60%. ^1H NMR ($CDCl_3$): δ 0.82 (t, 6H, OCH_2CH_3), 1.55 (s, 1H, RuH), 2.93–3.13 (m, 4H, OCH_2CH_3), 7.36–7.64 (m, 30H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 40.26 (s, 2P, PPh_3), 93.77 (s, 1P, $S_2P(OEt)_2$). IR (Nujol, cm^{-1}): 1926 ($\nu_{C\equiv O}$). MS (FAB): *m/z* 841 ($M^+ + 1$), 812 (M^+–CO), 577 (M^+–PPh_3), 549 (812 (M^+–PPh_3–CO)). $E_{1/2}$ (CH_2Cl_2, *V*) = 0.28 (Ru^{II}/Ru^{III}), 0.73 (irreversible, Ru^{III}/Ru^{IV}). Anal. Calcd for $C_{41}H_{41}O_3P_3S_2Ru$: C, 58.6; H, 4.93. Found: C, 58.8; H, 4.89.

2.3. *X-ray structure analyses*

Well developed single-crystals of **1** (0.55 × 0.42 × 0.30 mm) and **2** (0.28 × 0.25 × 0.20 mm) were mounted in random orientation on glass fibres. Diffraction data were collected on a Siemens *P*4 diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by using a 2θ scan technique (for **1**, $1.10° < \theta < 25.00°$; for **2**, $2.96° < \theta < 26.00°$). The collected frames were processed with the software SAINT [9]. The data were corrected for absorption using the program SADABS [10]. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [11]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C–H = 0.95 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or nitrogen atoms before the final cycle of least-squares refinement. Two carbon atoms in one ethyl moiety in **1** were disordered. Their site occupancies were 70/30 (C5/C5A), and 60/40 (C6/C6A). The disordered carbon atoms in the ethyl group were refined without hydrogen atoms. The O and C atoms in one of the OEt groups in **2** were clearly disordered. Their site occupancies, each set to 0.5, were isotropically refined and the corresponding carbon atoms were described without hydrogen atoms. Refinement converged to $R1 = 0.0408$, $wR2 = 0.0961$, and $S = 1.029$ for 5728 independent reflections with $I \geq 2.0\,\sigma(I)$ and 525 variables for **1**, and $R1 = 0.0262$, $wR2 = 0.0659$, and $S = 1.029$ for 4002 independent reflections with $I \geq 2.0\,\sigma(I)$ and 444 variables for **2**. Further details of the structure analyses of both complexes are given in table 1.

Crystal data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary

Table 1. Crystal data and structure refinement for complexes **1** and **2**.

Complex	**1**	**2**
Formula	$C_{44}H_{50}O_4P_4S_4Ru$	$C_{41}H_{41}O_3P_3S_2Ru$
Formula weight	996.03	839.84
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	$Pna2_1$
a (Å)	12.615(2)	18.898(1)
b (Å)	19.632(2)	12.519(1)
c (Å)	37.129(4)	16.831(1)
V (Å^3)	9195(2)	3981.9(4)
Z	8	4
D_{calcd} (g cm^{-3})	1.439	1.401
Temperature (K)	293(2)	293(2)
F(000)	4112	1728
μ(Mo Kα) (mm^{-1})	0.703	0.656
No. reflections measured	8205	4225
No. unique reflections	7948	7883
No. observed reflections	5728	4002
No. parameters	525	444
R_{int}	0.0164	0.0132
$R1^a$, $wR2^b$ ($I > 2\sigma(I)$)	0.0408, 0.0961	0.0262, 0.0659
$R1^a$, $wR2^b$ (all data)	0.0689, 0.1098	0.0294, 0.0681
GoF^c	1.029	1.029
Final difference peaks (e Å^{-3})	+0.395, −0.307	+0.310, −0.193

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$;
[b] $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$;
[c] $GoF = [\sum w(|F_o| - |F_c|)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

publication numbers CCDC-254333/254334. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

3. Results and discussion

Interaction of $[Ru(PPh_3)_3Cl_2]$ with $K[S_2P(OEt)_2]$ in THF afforded $[Ru\{S_2P(OEt)_2\}_2(PPh_3)_2]$ (**1**) as the sole isolable product. Complex **1** is stable in the solid but readily air oxidized in solution to give a paramagnetic green species, presumably a ruthenium(III) complex. The $^{31}P\{^1H\}$ NMR spectrum of **1** in $CDCl_3$ shows two intense singlets at δ 40.84 and 98.86 ppm, assignable to PPh_3 and $[S_2P(OEt)_2]^-$ [8], respectively. The positive ion FAB mass spectrum of **1** shows the molecular ions $[Ru\{S_2P(OEt)_2\}_2(PPh_3)_2]^+$ and $[Ru\{S_2P(OEt)_2\}_2(PPh_3)]^+$ with the characteristic isotopic distribution patterns. The solid-state structure of **1** has been established by X-ray crystallography, as shown in figure 1. The corresponding selected bond lengths and angles are listed in table 2. The molecule is mononuclear with an octahedral geometry. Two *cis*-PPh_3 ligands bind the ruthenium centre with a P–Ru–P angle of 99.83(4)°, and two chelating $[S_2P(OEt)_2]^-$ ligands form the basal plane. The four-membered RuS_2P rings are nonplanar and distorted. Each ring contains a pair of long and short Ru–S bonds [Ru(1)–S(1) = 2.5376(11) Å ('long') with Ru(1)–S(2) = 2.4535(11) Å ('short'); Ru(1)–S(4) = 2.5355(11) Å ('long') with Ru(1)–S(3) = 2.4521(12) Å ('short')]. The Ru–S bond lengths in **1** [av. 2.4974(11) Å] are comparable

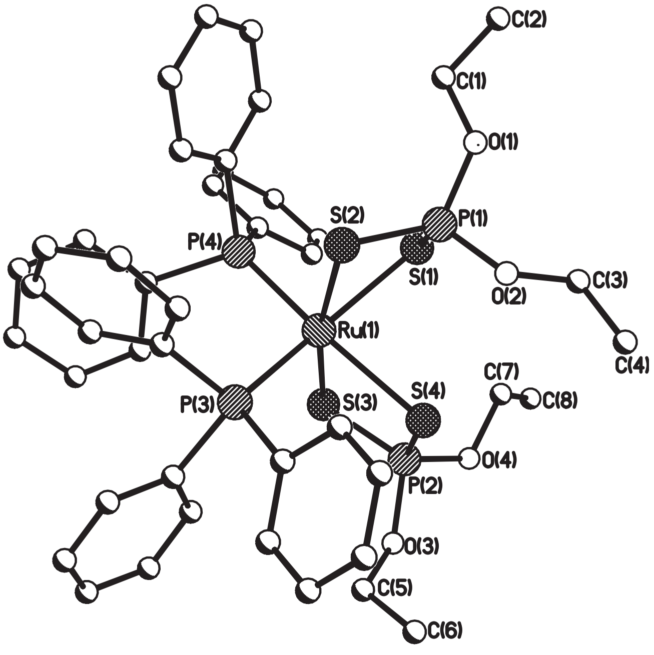

Figure 1. Perspective view of $[Ru\{S_2P(OEt)_2\}_2(PPh_3)_2]$ (**1**).

Table 2. Selected bond distances (Å) and bond angles (°) for complex **1**.

Ru(1)–P(3)	2.3518(10)	Ru(1)–P(4)	2.3130(11)
Ru(1)–S(1)	2.5376(11)	Ru(1)–S(2)	2.4535(11)
Ru(1)–S(3)	2.4521(12)	Ru(1)–S(4)	2.5355(11)
S(1)–P(1)	1.9865(16)	S(2)–P(1)	1.9792(15)
S(3)–P(2)	1.9908(16)	S(4)–P(2)	1.9710(17)
P(4)–Ru(1)–P(3)	99.83(4)	P(4)–Ru(1)–S(3)	92.68(4)
P(3)–Ru(1)–S(3)	99.94(4)	P(4)–Ru(1)–S(2)	92.92(4)
P(3)–Ru(1)–S(2)	89.03(4)	S(3)–Ru(1)–S(2)	168.47(4)
P(4)–Ru(1)–S(4)	168.34(4)	P(3)–Ru(1)–S(4)	89.29(4)
S(3)–Ru(1)–S(4)	78.49(4)	S(2)–Ru(1)–S(4)	94.51(4)
P(4)–Ru(1)–S(1)	86.30(4)	P(3)–Ru(1)–S(1)	165.87(4)
S(3)–Ru(1)–S(1)	92.42(4)	S(2)–Ru(1)–S(1)	77.89(4)
S(4)–Ru(1)–S(1)	86.47(4)	P(1)–S(1)–Ru(1)	83.11(5)
P(1)–S(2)–Ru(1)	85.51(5)	P(2)–S(3)–Ru(1)	88.87(5)
P(2)–S(4)–Ru(1)	86.96(5)		

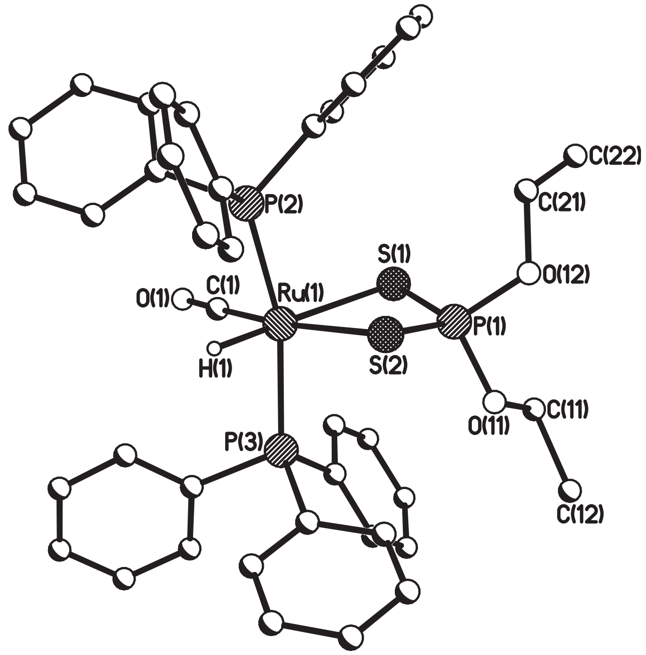

Figure 2. Perspective view of $[RuH(CO)\{S_2P(OEt)_2\}(PPh_3)_2]$ (**2**).

to those in $[(\eta^6\text{-}p\text{-cymene})Ru\{S_2P(OMe)_2\}(PPh_3)][BPh_4]$ [av. 2.4311(12) Å)] with a chelated dithiophosphate ligand [12], but slightly longer than for *cis*-$[Ru(S_2CNEt_2)_2(PPh_3)_2]$ [av. 2.3952(5) Å] with chelated dithiocarbamate [13]. The average Ru–P bond length of 2.3324(10) Å in **1** agrees well with those in related ruthenium(II) complexes with PPh_3 ligands [12, 13].

Treatment of $[RuHCl(CO)(PPh_3)_3]$ with an equivalent of $K[S_2P(OEt)_2]$ in THF gave $[RuH(CO)\{S_2P(OEt)_2\}(PPh_3)_2]$ (**2**) isolated as air-stable orange crystals. The chloride atom in the starting ruthenium compound was substituted by bidentate dithiophosphate, and one PPh_3 ligand was dissociated to make the ruthenium(II) centre of **2** keep six-coordination. The ^1H NMR spectrum of **2** displays a characteristic

Table 3. Selected bond distances (Å) and bond angles (°) for complex **2**.

Ru(1)–C(1)	1.829(4)	Ru(1)–P(2)	2.3494(8)
Ru(1)–P(3)	2.3608(10)	Ru(1)–S(1)	2.5590(12)
Ru(1)–S(2)	2.5358(11)	S(1)–P(1)	1.9779(17)
S(2)–P(1)	1.9863(17)		
C(1)–Ru(1)–P(2)	89.44(11)	C(1)–Ru(1)–P(3)	88.36(12)
P(2)–Ru(1)–P(3)	163.48(4)	C(1)–Ru(1)–S(2)	172.84(14)
P(2)–Ru(1)–S(2)	88.77(4)	P(3)–Ru(1)–S(2)	95.30(3)
C(1)–Ru(1)–S(1)	95.29(13)	P(2)–Ru(1)–S(1)	97.72(4)
P(3)–Ru(1)–S(1)	98.78(4)	S(2)–Ru(1)–S(1)	78.09(4)
P(1)–S(1)–Ru(1)	84.97(5)	P(1)–S(2)–Ru(1)	85.43(5)

proton of the Ru–H at δ 1.55 [7]. By comparison to $^{31}P\{^{1}H\}$ NMR data of **1**, the ^{31}P signal for $[S_2P(OEt)_2]^-$ in **2** is a singlet at δ 93.77, less down-field than in **1**; while the ^{31}P signal for PPh_3 in **2** (δ 40.84) is similar to that in **1** (δ 40.26). The C≡O stretching vibration mode was found at $1926\,cm^{-1}$ in the IR spectrum of **2**. The solid-state structure of **2** has been confirmed by X-ray crystallography. Figure 2 shows a perspective view of **2**; selected bond lengths and angles are given in table 3. The geometry around ruthenium is pseudo-octahedral with two trans-binding PPh_3 ligands. The P–Ru–P angle of 163.48(4)° has large deviation from linear. The $[S_2P(OEt)_2]^-$ ligand chelates the ruthenium centre with two nearly equal Ru–S bonds [2.5358(11) and 2.5590(12) Å] and the S–Ru–S angle of 78.09(4)°. Different from the unequal R–S bonds in four-membered RuS_2P rings for **1**, the elongation of the Ru–S bond *trans* to CO in **2** is due to π back-bonding to the C≡O bond. The Ru–H bond length of 1.624(2) Å is within the range reported for ruthenium-hydride complexes [14].

The cyclic voltammogram of **1** in CH_2Cl_2 shows a reversible couple at 0.19 V *versus* $Cp_2Fe^{+/0}$, which is assigned as the metal-centred Ru^{III}–Ru^{II} couple because $[S_2P(OEt)_2]^-$ ligand is redox inactive at this potential. The Ru^{III}–Ru^{II} for **1** is similar to that for *cis*-$[Ru(S_2CNEt_2)_2(PPh_3)_2]$. The CV of **2** shows a reversible Ru^{III}–Ru^{II} couple at 0.28 V along with an irreversible oxidation wave at 0.73 V, which is tentatively attributed to Ru^{III}–Ru^{IV} oxidation [15].

Acknowledgements

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