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Pentasulfide S_5^{2-} as the First Tridentate Chelating Ligand in $Ru(P(OE)_3)_3S_5$(E = Me and Et)

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Room temperature stirring of $H_2Ru(P(OE)_3)_4$ (E = Me and Et) and elemental sulfur in benzene afforded the optically active compounds $Ru(P(OMe)_3)_3S_5$ (**1**) and $Ru(P(OEt)_3)_3S_5$ (**2**). Compounds **1** and **2** are crystallized in the trigonal space group $P3_1$ with $a = 14.231(10)$ Å, $c = 10.24(1)$ Å, $V = 1794(2)$ Å^3, and $Z = 3$, and orthorhombic space group $P2_12_12_1$ with $a = 15.393(5)$ Å, $b = 18.126(6)$ Å, $c = 12.421(4)$ Å, $V = 3465(1)$ Å^3, and $Z = 4$, respectively. Solutions of **1** and **2** did not show any optical activity since the bulk materials are racemic mixtures. The X-ray analyses also reveal that in both compounds polysulfide S_5^{2-} ion acts as a novel tridentate ligand, resulting in an asymmetric bicyclic RuS_5 unit having three- and five-membered rings around the ruthenium atom. Fragmentation of the S_5^{2-} ring to S^{2-} ion was observed in the presence of sulfur-abstracting reagents such as PR_3 (R = Ph, OMe, and OEt) and also to S_2^{2-} ion when the compounds were reacted with $RuCl_2(P(OE)_3)_4$ (E = Me and Et).

Introduction

The catenating and reducible nature of the sulfur atom are the keys to generating polysulfides (S_x^{2-}, $x \geq 2$). It is well-known for a long time that cyclooctasulfur S_8 is reduced by sulfide or hydrogen sulfide to polysulfide ions S_x^{2-}.[1] Free polysulfide ions consist of nonlinear and nonbranched sulfur chains and are unstable, similar to the ring structures of neutral S_x ($x > 3$), which are also unstable, except S_8.[1−4] But it is remarkable that all possible S_x^{2-} ($x = 2-9$) ions occur in complexes with different types of stable chelate ring having metal as a heteroatom, although S_9^{2-} ion has not yet been reported in an isolated complex.[2] Among the several means for the synthesis of polysulfido complexes, oxidative addition of elemental sulfur to a coordinatively unsaturated electron-rich metal is a convenient one.[5] The structurally rich coordination chemistry of S_x^{2-} ions is due to their versatile chelating and bridging ligand behavior.[2] They can bridge two or more metal atoms in different fascinating modes resulting in flourishing structural data.[2,6,7] Due to their flexidentate and self-adjusting chain length according to the preference of the host metal, they can nicely glue metal aggregates such as $[Cu_6(S_4)_3(S_5)]^{2-}$, in which the six atoms are stabilaized by only four sulfur ligands.[8] $[Bi_2(S_6)(S_7)_4]^{4-}$ is a known novel complex which contains the highest portion of sulfur as the ligand.[9] $[Pd_2(S_7)_4]^{2-}$ is an interesting example where S_7^{2-} ion is a doubly bridging ligand, and a NH_4^+ ion is captured in the center of the cage.[10] $[Nb_2(OMe)_2(S_2)_3(S_5)O]^{2-}$ is the known polysulfido complex having the highest oxidation state (+5) of the metal.[11]

Polysulfide ligands differ from classical ligands as reactions such as scission of or insertion into the S−S bonds can occur. Polysulfido complexes can take part in different types of transformations such as (1) desulfurization of one or more sulfur atoms from polysufide rings by addition of sulfur-abstracting reagents such as PR_3.[12,13] (2) Other than the above nucleophilic attack, electrophilic attack of CS_2 to $[SMo(S_4)_2]^{2-}$ and ZnS_4(PMDETA) (PMDETA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) yielded $[SMo(CS_4)_2]^{2-}$ and ZnS_3CS(PMDETA), respectively.[14] (3) Several addition reactions can also occur; (a) addition of alkyne RCCR′ to S−S bonds to give dithiolene ligands RCSCSR′, for instance, (MeCOO)CC(COOMe) reacts with Cp_2TiS_5 (Cp = cyclopentadienyl) to give $Cp_2Ti(S_2C_2(CO_2Me)_2)$;[15] (b) insertion of the isoeletronic group $-CR_2-$ (R = H or alkyl) into a S−S bond without breaking the metal−sulfur bond; for instance, CH_2Br_2 and R_2CO react with Cp_2TiS_5 to produce 1,3-$Cp_2TiS_4CH_2$ and 1,4-$Cp_2TiS_4CR_2$, respectively.[16] (4) Finally, substitution reactions can also occur, such as $[ZnS_6$(TMEDA)] (TMEDA = tetramethylethylenediamine) reacting with methylimidazole (MeIm) to give $[Zn(MeIm)_6]^{2+}$.[17] The reactivity of polysulfido complexes also depends on ancillary ligands. Rauchfuss et al. showed that the reactvity toward CS_2 and (MeCOO)CC(COOMe) is in the order of [Zn(PMDETA)-

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S_4] > [Zn(TMEDA)S_6], and this enhanced nucleophilicity of the polysulfide ring in [Zn(PMDETA)S_4] is due to the third ancillary amine of the PMDETA ligand.[14,17] Our previous works on S_5^{2-}- and S_6^{2-}-coordinated diruthenium complexes suggested that these polysulfides are less electron-donating than S^{2-} and S_2^{2-} but is more stably coordinating than amine ligand.[18]

Interest in polysulfide complexes is not only due to their rich structural chemistry and reactivity but also to their possible uses in some vital industrial and biological processes.[2,6,19−21] In this context S_5^{2-} is of much current industrial interest, since it is believed to be the favored species during the sulfur rich stages of the discharge of Na−S battery (e.g. $Na_2S_3 + 2S \rightarrow Na_2S_5$).[22] Only a few complexes with bidentate S_5^{2-} ligand are known. The first reported complex was homoleptic optically active [Pt(S_5)$_3$].[23−28] The most thoroughly studied polysulfide compound of S_5^{2-} ion is Cp_2TiS_5, and similar compounds for zirconium, hafnium, and vanadium are also reported.[29−32] The MS_5 unit has the chair conformation in all known mononuclear complexes such as $[Cr(NH_3)_2(S_5)_2]^{2-}$ and $[(S_5)Mn(S_6)]^{2-}$.[11,33] The variation of the "bite" of S_5^{2-} is wide and the largest one is in $[(S_5)Fe(MoS_4)]^{2-}$.[34,35] In the case of ruthenium there is a striking paucity of polysulfido complexes and that with S_5^{2-} ion is rare,[35] although there is a number of ruthenium complexes with monodentate and/or polydentate organosulfur ligands coordinated through sulfur.[37] All hitherto reported possible polysulfides occurring in metal complexes act as bidentate chelating ligand, except the tridentate chelating behavior of S_7^{2-} ion in $(PMe_3)_3MS_7$ (M = Ru and Os).[38] Here we report the first tridentate chelating behavior of S_5^{2-} ion in $(P(OE)_3)_3RuS_5$ (E = Me and Et) complexes, which crystallize in noncentrosymmetric space groups by natural fractionation of the two optical isomers for both complexes.

Experimental Section

Typical Syntheses of Complexes 1 and 2. To a benzene solution of $H_2Ru(P(OE)_3)_4$ (E = Me and Et) (0.40 mmol), solid elemental sulfur (0.40 mmol) was added, and the solution was stirred at room temperature for about 2 days under nitrogen. The reaction mixture was evaporated to dryness and dissolved in CH_2Cl_2 and hexane (1:10). The solution was then subjected to silica gel chromatography by using dichloromethane and hexane (1:1) as an eluent. The single reddish orange band was collected and dried. The residue for the case of trimethyl phosphite complex was dissolved in pentane and kept for crystallization at −4 °C. Bright reddish orange prismatic crystals were isolated within a few days (69% yield). For the case of triethyl phsophite, crystals were obtained by slow evaporation of the CH_2Cl_2 solution of the residue layered by hexane (73% yield). Anal. Calcd for $C_9H_{27}O_9S_5P_3Ru$ (**1**): C, 17.04; H, 4.26. Found: C, 17.10; H, 4.30. ^1H NMR (CD_3CN, 270 MHz): δ 3.8−3.6 (m, 27H, 3P(OMe)$_3$). $^{31}P\{^1H\}$ NMR (CD_3CN, 109.4 MHz): δ 153.8 (t, 1P(OMe)$_3$), 147.1 (s, br, 1P(OMe)$_3$), 137.4 (s, br, 1P(OMe)$_3$). FABMS: *m/e* 633 (M^+), 569 ($M^+ - 2S$), 573 ($M^+ - 3S$). Anal. Calcd for $C_{18}H_{45}O_9S_5P_3Ru$ (**2**): C, 28.42; H, 5.92. Found: C, 28.54; H, 6.15. ^1H NMR (CD_3CN, 270 MHz): δ 1.24 (t, 27H, 3(OCH$_2$*CH$_3$*)$_3$, 4.08 (q, 18H, 3 (O*CH$_2$*CH$_3$)$_3$. ^{31}P $\{^1H\}$ NMR (CD_3CN, 109.4 MHz): δ 148.4 (t, 1P(OEt)$_3$), 147.8 (s, br, 1P(OEt)$_3$), 147.2 (s, br, 1P(OEt)$_3$). FABMS: *m/e* 759 (M^+), 695 ($M^+ - 2S$), 663 ($M^+ - 3S$).

Physical Measurements. Unless noted otherwise, all the operations were carried out in air. Commercially available chemicals were purchased and used without further purification. Solvents were purchased and used as received. $H_2Ru(P(OMe)_3)_4$ and $H_2Ru((P(OEt)_3)_4$ were prepared following the reported procedures.[39] The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL EX-270 instruments. The ^{31}P chemical shifts are referenced to an external standard of free $P(OMe)_3$ in $(CD_3)_2CO$ at 140 ppm.

Collection and Reduction of X-ray Data. Epoxy resin-coated crystals of compounds **1** and **2** were subjected to single-crystal X-ray analysis. The X-ray data were collected on a Rigaku AFC-7R diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å), and unit cell parameters were obtained from a least-squares fit of 25 reflections in the range 29° < 2θ < 30° for both compounds **1** and **2**. The data were processed and corrected for Lorentz−polarization effects and absorption. The intensities of the three representative reflections were measured every 150 reflections, and decay correction was not applied, as there was no serious deterioration of the crystals for **1** and **2** during the measurements. Relevant crystallographic information is summarized in Table 1.

Solution and Refinement of the Structures. The structure of compound **1** was solved by direct method, whereas that of compound **2** was solved by a heavy-atom method. All non-hydrogen atoms in the compounds were located and were refined anisotropically.

Results and Discussion

Sytheses and Properties of Compounds 1 and 2. Room temperature stirring of a benzene solution of $H_2Ru(P(OE)_3)_4$ (E = Me and Et) and elemental sulfur afforded compounds **1** and **2** in high yield. It is easy to follow the reactions by the distinct color change of the reaction mixtures from colorless to reddish orange. Use of ethanol or dichloromethane instead of benzene gave no product variation and also no effect on the yield of the complexes. They are fairly air stable and nicely soluble in all common organic nonpolar and polar solvents even in pentane.

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Table 1. Summary of Crystal Data for Complexes **1** and **2**

	1	**2**
formula	$C_9H_{27}O_9P_3S_5Ru$	$C_{18}H_{45}O_9P_3S_5Ru$
fw	633.60	759.84
cryst. system	trigonal	orthorhombic
space group	$P3_1$ (No. 144)	$P2_12_12_1$ (No. 19)
a (Å)	14.231(10)	15.393(5)
b (Å)		18.126(6)
c (Å)	10.24(1)	12.421(4)
V (Å$^{3)}$	1794(2)	3465(1)
λ, Å	0.71069	0.71069
T (deg)	25 ± 1	25 ± 1
Z	3	4
ρ_{calcd} (g cm^{-3})	1.758	1.456
crystal dimens (mm)	0.65 × 0.25 × 0.13	0.45 × 0.25 × 0.12
absorp coeff (cm^{-1})	13.3	9.3
2θ range (deg)	$5 < 2\theta < 55$	$5 < 2\theta < 55$
residual electron density (e/Å^3)	1.01	0.26
no. of params	245	326
R^a	0.076	0.048
$R_w{}^b$	0.077	0.053

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

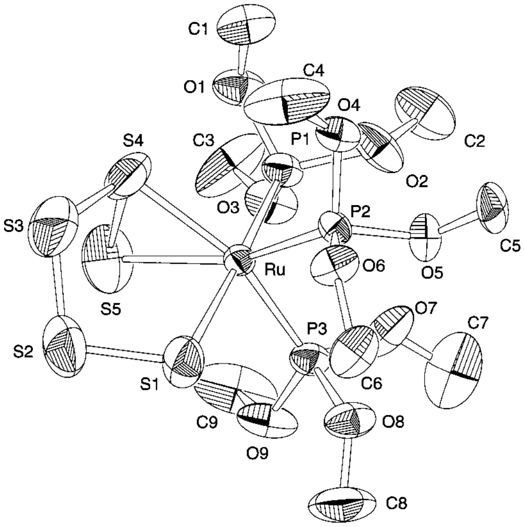

Figure 1. ORTEP drawing of Ru(P(OMe)$_3$)$_3$S$_5$ (**1**).

Behavior of 1 and 2 as a Sulfur Transferring Reagent. The nucleophiles PR$_3$ (R = Ph, OMe, and OEt) are too reactive toward **1** and **2** and abstract sulfur from the polysulfide ring, forming the respective sulfides. The products were identified by comparing their ^{31}P peaks with the reported values. We were not able to isolate any product from the ruthenium part, and the compound was thought to be decomposed. Room temperature stirring of compounds **1** and **2** in dichloromethane with RuCl$_2$(P(OE)$_3$)$_4$ (E = Me and Et) yielded the known disulfide-bridged dinuclear ruthenium compounds [{RuCl(P(OMe)$_3$)$_2$}$_2$-(μ-S$_2$)(μ-Cl)$_2$][40] and [{RuCl(P(OEt)$_3$)$_2$}$_2$(μ-S$_2$)(μ-Cl)$_2$][41] with SP(OE)$_3$. The above transformations reveal that polysulfide S_5^{2-} is fragmented to S^{2-} and S_2^{2-} ions.

Structures of 1 and 2. The molecular structures of **1** and **2** are shown in Figures 1 and 2.

The major bond distances and angles are listed in Tables 2 and 3, respectively.

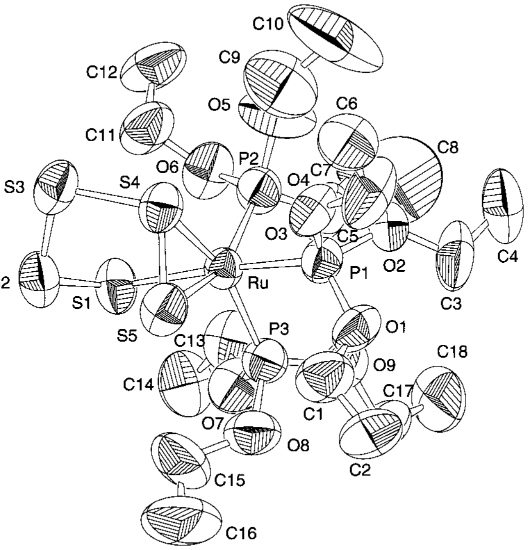

Figure 2. ORTEP drawing of Ru(P(OEt)$_3$)$_3$S$_5$ (**2**).

Table 2. Major Bond Distances (Å) of Complexes **1** and **2**

	1	**2**
Ru−S1	2.456(6)	2.469(3)
Ru−S4	2.403(7)	2.389(3)
Ru−S5	2.485(6)	2.472(3)
Ru−P1	2.248(6)	2.255(3)
Ru−P2	2.236(6)	2.230(3)
Ru−P3	2.233(6)	2.242(3)
S1−S2	1.986(10)	2.031(4)
S2−S3	2.06(1)	2.000(4)
S3−S4	2.05(1)	2.193(4)
S4−S5	2.19(1)	1.995(4)

Table 3. Major Bond Angles (deg) of Complexes **1** and **2**

	1	**2**		**1**	**2**
S1−Ru−S4	89.5(3)	91.26(9)	S5−Ru−P3	106.4(3)	108.1(1)
S1−Ru−S5	88.2(3)	90.45(10)	P1−Ru−P2	93.8(2)	92.8(1)
S1−Ru−P1	174.7(3)	176.0(1)	P1−Ru−P3	93.0(2)	90.4(1)
S1−Ru−P2	91.5(2)	89.6(1)	P2−Ru−P3	94.2(2)	95.9(1)
S1−Ru−P3	86.4(2)	86.2(1)	Ru−S1−S2	105.7(4)	103.8(1)
S4−Ru−S5	53.3(3)	48.42(10)	S1−S2−S3	103.2(5)	103.6(2)
S4−Ru−P1	89.3(2)	91.04(9)	S2−S3−S4	102.0(6)	97.8(2)
S4−Ru−P2	106.0(3)	107.6(1)	Ru−S4−S3	111.0(4)	107.9(1)
S4−Ru−P3	159.5(3)	156.4(1)	Ru−S4−S5	65.3(3)	68.0(1)
S5−Ru−P1	87.0(3)	88.67(10)	S3−S4−S5	99.6(6)	105.5(2)
S5−Ru−P2	159.3(3)	156.0(1)	Ru−S5−S4	61.4(2)	63.6(1)

There are no basic differences between the structures of **1** and **2**, and they have a few common interesting features. The ruthenium atom in each case is pseudo-octahedrally coordinated by phosphite and S_5^{2-} ligand. The S_5^{2-} unit is linked to the Ru atom via S1, S4, and S5 sulfur atoms and thus it is a novel tridentate chelating ligand. The distances of Ru−S1 (2.463 Å) (av) and Ru− S5 (2.479 Å) (av) are comparable to the reported values,[38,42,43] but Ru−S4 (2.396 Å) (av) is significantly shorter.[38,42,43] It suggests that the Ru−S4 bond is composed of donor and acceptor bonds and is represented as Ru$\rightleftarrows$S4.[38,42,43] The multipilicity of the Ru−S4 bond causes elongation of both adjacent S3−S4 (2.05(1) Å) and S4−S5 (2.19(1) Å) bonds in **1** but exceptionally only S3−S4 (2.193(4) Å) bond in complex **2**. These are longer than the usual S−S bonds (2.01−2.05 Å).[42,44−46] All other S−S bonds are normal but the terminal S1−S2 (1.986(10) Å) bond in **1** and the S4−S5 (1.995(4) Å)

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bond in **2** are shorter compared to the normal S−S bond. This is reasonable considering the Hordvik hypotheses that the terminal S−S bonds should reach a minimum value of about 2.02 Å in polysulfide chains.[47] The Ru−S bond distances trans to trimethyl phosphite ligands in **1** and trans to triethyl phosphite ligands in **2** are almost same, which suggests that there is no significant difference in trans effect between the two phosphite ligands. The Ru−P distances (2.239 Å) (av) for **1** and (2.243 Å) (av) for **2** are shorter compared to the reported Ru(II)−P distances (2.32−2.35 Å).[48,49] In both compounds Ru−P1 distances (2.251 Å) (av) are larger than those of Ru−P2 (2.233 Å) (av) and Ru−P3 (2.238 Å) (av). It reveals that P1 trans to S1 exerts a stronger trans effect than P2 trans to S5 and P3 trans to S4, as S1 is more linear to P1 (S1−Ru−P1 = 175.3°) (av) than S5 to P2 (S5−Ru−P2 = 157.6°) (av) and S4 to P3 (S4−Ru−P3 = 157.9°) (av). It is also notable that although the slight bendings of S5 to P2 and S4 to P3 are to the same extent, the Ru−P3 in average is still a little longer than that of the Ru−P2 distance due to the bond multipilicity of the Ru−S4 bond. The average bond angles in the sulfur chain, 103.4° (S1−S2−S3), 99.9° (S2−S3−S4), and 102.5° (S3−S4−S5), are smaller than the normal S−S−S angle in $\alpha-S_8$ (107°).[50] The Ru−S1−S2 bond angles are also smaller (104.7°) (av) than that reported for the RuSSRu core compounds, where the Ru−S−S is ca. 109°.[40,50]

During the reaction, there was a distinct smell of H_2S, and the formation of $SP(OMe)_3$ and $SP(OEt)_3$ was confirmed by ^{31}P NMR. It indicates that presumably the reactions occur according to eq 1.

$$H_2Ru(P(OE)_3)_4 + S_8 \rightarrow Ru(P(OE)_3)_3S_5 + H_2S + SP(OE)_3 + S \quad (1)$$

Rationale of Accommodation of S^{5-} and Optical Activity in 1 and 2. The complexes $M(PMe_3)_3S_7$ (M = Ru and Os) possess S_7^{2-} ion,[38] whereas $Ru(P(OE)_3)_3S_5$ contains S_5^{2-} ion. Steric factors and electronic effect are expected to dictate the ring size around the metal atom, but no definite explanation can be given here for the difference of the sulfur ring size of the two Ru complexes. The coligand in the complex $Ru(PMe_3)_3S_7$ is PMe_3, whereas that in **1** and **2** is $P(OE)_3$, and as the phosphites are bulkier than the corresponding phosphines, the accommodation of smaller S_5^{2-} ion seems reasonable in the case of **1** and **2**. The S_7^{2-} in $Os(PMe_3)_3S_7$ is coordinated to an Os atom, resulting in two 5-membered bicycles.[38] In our case S_5^{2-} is linked to Ru atom making three- and five-membered strained rings. The flexibility in S_7^{2-} will be more effective in minimizing the ring strain, resulting in two five-membered bicycles, and in attaining more symmetry than that for the case of S_5^{2-}. Since both crystals have optically active space groups and both **1** and **2** are optically active molecules, both crystals were checked for their activity in solution. However, both crystals were racemic mixtures and did not show any optical activity.

Supporting Information Available: An X-ray crystallographic file in CIF format for structures of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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