Synthesis and Crystal Structure of a Binuclear Ruthenium Compound Containing $[Ru_2(\mu\text{-}S_5)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ and $[Ru_2(\mu\text{-}S_6)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$: The First Ruthenium Compounds with Bridging S_5 and S_6 Ligands

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Several sulfur-bridged binuclear ruthenium compounds have recently been reported,[1–6] and the structures, the chemical properties and the redox potentials have been discussed. Ruthenium is noted for its strong back-donating nature among all metals, and multinuclear ruthenium compounds with sulfur bridging atoms seem promising for multielectron-redox reactions of coordinated molecules. However, most of the sulfur-bridged binuclear ruthenium compounds so far reported have cyclopentadienyl or bipyridine as the ligands, which are suitable for isolating stable and robust multinuclear compounds, but the resulting compounds are resistant to any ligand substitution or addition reactions. Only a few noteworthy reactions have been reported, which include substitution or addition of CO, RC═CH or *t*-BuNC to Cp*-coordinated binuclear ruthenium compounds (Cp* is pentamethyl cyclopentadienyl).[2,4] We have recently reported the syntheses of MS_4^{2-} (M = Mo, W) bridged compounds $[(L)Ru(CO)(PPh_3)]_2(MS_4)$ (L = PhNCHS, $CH_2CH_2(C_5H_4N)$, $CH_2CH_2(C_5H_4N)$, $CH_2CH_2C(O)OMe$)[7] and photosubstitution reactions of the coordinated ligands. Although such a photosubstitution reaction, with the multinuclear structure being retained, is rare for sulfur-bridged multinuclear compounds of any metals, the reaction is so far successful only for the substitution of the coordinated CO and PPh_3 with pyridine. In an attempt to widen the variety of sulfur-bridged multiruthenium compounds with coordinated CO and PPh_3 which seem essential to such substitution reactions, we obtained two binuclear ruthenium compounds having a S_5 or a S_6 bridging ligand. The two compounds exist in a crystal lattice which is randomly disordered, and these are the first examples in which S_5^{2-} and S_6^{2-} ligands bridge ruthenium atoms.

Experimental Section

Synthesis. The compound $RuH(S_2CNMe_2)(CO)(PPh_3)_2$[8] (0.775 g, 1 mmol) was stirred in 50 mL of benzene under nitrogen atmosphere with 0.8 g (~25 mmol) of elemental sulfur at room temperature for 4 days. The solution changed color during the reaction from yellow to orange, and orange microcrystals precipitated. The precipitate was removed by filtration and was collected to give $[Ru_2(\mu\text{-}S_{5.215})(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ (yield 66.1%). Anal. Calcd for $C_{44}H_{42}N_2O_2P_2S_{9.215}Ru_2$: C, 44.40; H, 3.56; N, 2.35. Found: C, 44.33; H, 3.64; N, 2.18. The crystals used for the X-ray diffraction study were obtained by the diffusion method from CH_2Cl_2–Et_2O. The formula of the crystal was $[Ru_2(\mu\text{-}S_{5.215})(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO_2)_2(PPh_3)_2]\cdot 0.5CH_2Cl_2$ (**1**) and the yield was 56.3%. Anal. Calcd for $C_{44.5}H_{43}N_2O_2P_2S_{9.215}ClRu_2$: S, 23.96; C, 43.36; H, 3.52; N, 2.27. Found: S, 24.05; C, 43.48; H, 3.43; N, 2.23. The formula was determined on the basis of the X-ray structure determination. Ir (KBr): 1948 (s) (ν_{CO}), 1532 (s), 1482 (m), 1434 (s), 1394 (s), 1156 (m), 1092 (m), 744 (m), 696 (s), 568 (m), 530 (s), 516 (m) cm^{-1}. UV–vis: 275.0 (sh) ($\epsilon = 4.79 \times 10^4$), 330.0 (sh) ($\epsilon = 2.03 \times 10^4$), 450.0 (sh) nm, ($\epsilon = 1.13 \times 10^3$ M^{-1} cm^{-1}). Both solvated and unsolvated compounds are stable in air.

Table I. Crystallographic Data for **1**

chem formula: $C_{44.5}H_{43}N_2O_2P_2S_{9.21}ClRu_2$
fw = 1232.82
cryst syst: monoclinic
space group: $P2_1/a$ (No. 14)
$a = 20.417\ (5)$ Å
$b = 15.150\ (3)$ Å
$c = 17.851\ (4)$ Å
$\beta = 111.95\ (2)°$
$V = 5121\ (2)$ Å
$Z = 4$
$\rho_{calcd} = 1.60$ g/cm^3
$\rho_{measd} = 1.58$ g/cm^3
$\mu = 10.89$ cm^{-1}
radiation: Mo Kα (0.710 68 Å)
$R^a = 0.0576$
$R_w{}^a = 0.0556$

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

Physical Measurements. The electrochemical measurement was performed on a Fuso 315A potentiostat with a platinum-disk working electrode and a platinum wire as a counter electrode. The measurement was performed with a three-electrode system by using Ag/AgCl as a reference electrode.

X-ray Structure Determination. An orange prism crystal with the approximate dimensions 0.35 × 0.20 × 0.12 mm^3 was mounted on a thin glass fiber. The diffraction data were collected on a Rigaku AFC-5R four-circle automated diffractometer. Standard peak search and automatic procedures, followed by least-squares refinement using 24 reflections ($20° \le 2\theta \le 25°$), yielded the cell dimensions given in Table I. A total of 7380 unique reflections in the range $2.0° < 2\theta < 55.0°$, among which were 5021 observed reflections ($|F_o| > 4.0\delta|F_o|$), were collected by scanning $\pm h$, $+k$, and $+l$ at a scan rate of 8°/min in 2θ. Lorentz, polarization, and anomalous dispersion corrections were applied. No absorption correction was applied since the linear absorption coefficient is small.

The coordinates of the two independent ruthenium atoms and sulfur atoms were deduced by direct methods (SHELX-86), and subsequent least-squares and Fourier calculations revealed positions for the remaining non-hydrogen atoms (SHELX-76). The positions of the hydrogen atoms were calculated and were included in the final structure factor calculation. All the non-hydrogen atoms except the sulfur atoms of the S_5^{2-} and S_6^{2-} ligands were refined with anisotropic temperature factors. The sulfur atoms of the S_5^{2-} and S_6^{2-} ligands were refined isotropically. In the course of the successive Fourier calculations, it was found that the bridging S_n (n = 5 and 6) ligands are disordered in the lattice, whereas all the remaining atoms are not disordered, and therefore the distribution ratios for the two chelates were also refined in the final full-matrix least-squares calculation.

Results and Discussion

The final refinement of the structure revealed that **1** contains 78.5% $[Ru_2(\mu\text{-}S_5)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ and 21.5% $[Ru_2(\mu\text{-}S_6)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$. Therefore, the formula of **1** is as described in the Experimental Section. The coordinates of all the other atoms except those of the S_5^{2-} and S_6^{2-} bridges are identical for the both complexes, and the final atomic parameters are listed in Table II. The ORTEP drawings[9] for the two complexes are separately shown in Figures 1 and 2. Several examples, which exhibit a similar disorder of S_5^{2-} and S_6^{2-} chains in the crystal lattice, i.e., $[Ph_4P]_2[(S_n)FeS_2MoS_2]$ (n = 5 and 6)[10] and $[Ph_4P]_2MnS_{11}$,[11] have already been reported. The present compound **1** is the first example in which

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Table II. Atomic Coordinates and Thermal Parameters for **1**[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2
Ru1	0.17495 (4)	0.37989 (5)	0.73963 (5)	2.33
Ru2	0.27349 (4)	0.58687 (5)	0.75166 (5)	2.38
P1	0.1859 (1)	0.2293 (1)	0.7225 (2)	2.78
P2	0.2575 (1)	0.7383 (2)	0.7665 (2)	2.80
S1	0.1314 (1)	0.4117 (2)	0.5943 (2)	3.72
S2	0.0486 (1)	0.3591 (2)	0.6855 (2)	4.34
S3	0.1593 (1)	0.5416 (1)	0.7505 (2)	2.67
S4	0.2836 (1)	0.5690 (2)	0.8940 (2)	3.25
S5	0.3980 (2)	0.6088 (3)	0.7808 (3)	3.66
S6	0.4239 (2)	0.5453 (3)	0.6950 (3)	4.51
S7	0.4221 (2)	0.4107 (3)	0.7120 (2)	4.45
S8	0.3174 (2)	0.3803 (3)	0.6682 (3)	3.86
S9	0.2921 (1)	0.4273 (1)	0.7629 (2)	2.80
S10	0.3876 (5)	0.6324 (8)	0.7579 (9)	2.40
S11	0.4575 (7)	0.5324 (9)	0.7808 (9)	4.59
S12	0.4493 (8)	0.4747 (9)	0.6766 (9)	5.13
S13	0.4014 (6)	0.3580 (8)	0.6775 (9)	3.90
S14	0.2965 (7)	0.3851 (9)	0.6525 (6)	2.76
O1	0.2140 (5)	0.3493 (5)	0.9177 (6)	6.18
O2	0.2377 (4)	0.5973 (5)	0.5740 (5)	4.90
N1	−0.0059 (5)	0.3706 (7)	0.5210 (8)	6.69
N2	0.1559 (5)	0.5499 (5)	0.9022 (6)	4.79
C1	0.1986 (5)	0.3595 (6)	0.8496 (8)	3.56
C2	0.2508 (5)	0.5925 (6)	0.6415 (8)	3.09
C11	0.0490 (5)	0.3806 (6)	0.5922 (7)	4.35
C12	−0.0004 (8)	0.3860 (9)	0.4416 (8)	7.22
C13	−0.0731 (6)	0.3373 (10)	0.5251 (10)	8.70
C21	0.1950 (5)	0.5537 (6)	0.8565 (6)	3.13
C22	0.0781 (6)	0.5295 (8)	0.8646 (8)	5.73
C23	0.1883 (7)	0.5609 (9)	0.9914 (7)	6.14
C110	0.1323 (5)	0.1873 (6)	0.6227 (7)	3.29
C111	0.0663 (5)	0.1481 (7)	0.6108 (7)	3.69
C112	0.0223 (6)	0.1208 (7)	0.5337 (8)	5.18
C113	0.0429 (7)	0.1323 (8)	0.4702 (9)	5.55
C114	0.1059 (7)	0.1711 (8)	0.4818 (8)	5.69
C115	0.1518 (6)	0.1991 (6)	0.5579 (7)	3.91
C120	0.1572 (5)	0.1559 (6)	0.7868 (6)	2.92
C121	0.1137 (6)	0.1828 (7)	0.8259 (7)	4.40
C122	0.0913 (6)	0.1226 (8)	0.8692 (8)	5.79
C123	0.1112 (8)	0.0373 (8)	0.8732 (8)	6.31
C124	0.1541 (8)	0.0094 (7)	0.8351 (9)	6.78
C125	0.1783 (6)	0.0676 (6)	0.7944 (7)	4.61
C130	0.2762 (5)	0.1905 (6)	0.7462 (7)	3.55
C131	0.3278 (5)	0.2202 (7)	0.8158 (7)	4.38
C132	0.3977 (6)	0.1944 (9)	0.8335 (10)	6.52
C133	0.4154 (8)	0.1404 (11)	0.7853 (12)	8.61
C134	0.3640 (8)	0.1070 (10)	0.7156 (11)	8.25
C135	0.2951 (7)	0.1322 (7)	0.6960 (8)	5.96
C210	0.1851 (5)	0.7600 (5)	0.8017 (6)	2.78
C211	0.1992 (5)	0.7791 (6)	0.8827 (7)	3.45
C212	0.1444 (6)	0.7887 (7)	0.9098 (8)	4.55
C213	0.0742 (6)	0.7811 (7)	0.8538 (9)	5.47
C214	0.0598 (5)	0.7610 (7)	0.7763 (9)	4.78
C215	0.1150 (5)	0.7492 (6)	0.7493 (6)	3.71
C220	0.3327 (5)	0.7990 (6)	0.8420 (6)	3.01
C221	0.3792 (6)	0.7568 (7)	0.9074 (7)	5.23
C222	0.4338 (7)	0.8025 (8)	0.9648 (8)	6.08
C223	0.4434 (6)	0.8901 (8)	0.9550 (8)	5.11
C224	0.3975 (7)	0.9325 (7)	0.8889 (9)	6.19
C225	0.3433 (6)	0.8873 (7)	0.8325 (7)	4.88
C230	0.2366 (5)	0.8095 (6)	0.6780 (6)	3.18
C231	0.1869 (6)	0.8755 (7)	0.6557 (7)	4.29
C232	0.1800 (8)	0.9310 (8)	0.5932 (8)	5.99
C233	0.2217 (9)	0.9248 (8)	0.5509 (8)	6.84
C234	0.2719 (8)	0.8583 (9)	0.5712 (8)	7.22
C235	0.2806 (6)	0.8021 (7)	0.6341 (8)	5.32
CL1	0.4662 (4)	0.4182 (6)	0.9821 (4)	16.7
C99	0.4658 (22)	0.5299 (11)	0.9543 (24)	47.8

[a] The atomic parameters for S5 to S8 and S10 and S14 are isotropic temperature factors.

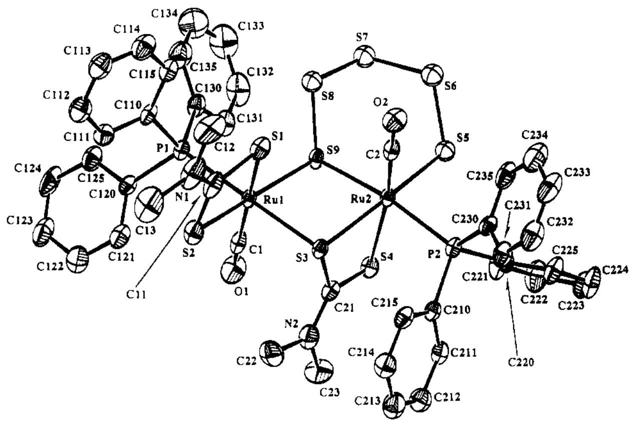

Figure 1. Structure of $[Ru_2(\mu\text{-}S_5)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ with thermal ellipsoids drawn at the 30% probability level.

Table III. Selected Bond Distances (Å) and Angles (deg) for **1**

Ru1–Ru2	3.688 (1)	Ru2–P2	2.346 (2)
Ru1–P1	2.323 (2)	Ru2–S3	2.424 (3)
Ru1–S1	2.455 (3)	Ru2–S4	2.485 (3)
Ru1–S2	2.414 (3)	Ru2–S5	2.419 (4)
Ru1–S3	2.488 (2)	Ru2–S9	2.444 (2)
Ru1–S9	2.381 (2)	Ru2–S10	2.392 (12)
Ru1–C1	1.863 (14)	Ru2–C2	1.846 (14)
S5–S6	2.039 (7)	S10–S11	2.02 (2)
S6–S7	2.064 (6)	S11–S12	2.00 (2)
S7–S8	2.036 (6)	S12–S13	2.02 (2)
S8–S9	2.069 (6)	S13–S14	2.06 (2)
		S14–S9	2.11 (1)
S3–Ru1–P1	177.0 (1)	S3–Ru2–P2	95.9 (1)
S1–Ru1–P1	93.9 (1)	S4–Ru2–P2	87.3 (1)
S1–Ru1–S3	83.3 (1)	S4–Ru2–S3	71.9 (1)
S2–Ru1–P1	87.7 (1)	S5–Ru2–P2	91.2 (1)
S2–Ru1–S3	90.6 (1)	S5–Ru2–S3	166.2 (1)
S2–Ru1–S1	72.1 (1)	S5–Ru2–S4	96.7 (1)
S9–Ru1–P1	100.4 (1)	S10–Ru2–P2	83.5 (3)
S9–Ru1–S3	80.8 (1)	S10–Ru2–S3	178.0 (4)
S9–Ru1–S1	93.9 (1)	S10–Ru2–S4	106.1 (4)
S9–Ru1–S2	164.4 (1)	S9–Ru2–P2	169.1 (1)
C1–Ru1–P1	88.6 (3)	S9–Ru2–S3	80.8 (1)
C1–Ru1–S3	94.1 (3)	S9–Ru2–S4	81.8 (1)
C1–Ru1–S1	173.9 (4)	S9–Ru2–S5	90.0 (1)
C1–Ru1–S2	102.6 (3)	S9–Ru2–S10	99.3 (3)
C1–Ru1–S9	91.0 (3)	C2–Ru2–P2	94.9 (3)
Ru1–S3–Ru2	97.3 (1)	C2–Ru2–S3	98.4 (3)
Ru1–S9–Ru2	99.7 (1)	C2–Ru2–S4	170.3 (3)
		C2–Ru2–S5	92.7 (3)
		C2–Ru2–S10	83.6 (5)
		C2–Ru2–S9	95.9 (3)

S_5^{2-} and S_6^{2-} chains coordinate to ruthenium atoms in any compound. Sulfur-bridged ruthenium compounds so far reported have their sulfur atoms in the form of MS_4^{2-} (M = Mo, W, Re),[1,2,5,12] disulfido,[3,13] RSH,[6] RS$^-$,[4] and S_3^{2-},[13] and it has become evident that the reactivity and the redox potential are very much dependent on the nature of the sulfur-containing ligands. Therefore, compound **1** adds a new class of sulfur-bridged ruthenium compound which is of value for the comparative study of such compounds.

The structure of the present compound should be compared to that of $[Os_2(\mu\text{-}S_5)(\mu\text{-}S_3CNEt_2)(S_2CNEt_2)_3]$,[14] whose S_5^{2-} ligand has a similar coordination mode, i.e., chelating to one Ru atom and bridging two Ru atoms at the same time. The major bond distances in **1** are listed in Table III. Of the four Ru–S(dithiocarbamate) distances, one with the bridging dithiocarbamate, Ru1–S3 (2.488 Å) is longer than the other three (average 2.446 Å). A similar tendency is observed in $[Ru(S_2CNEt_2)_2CO]_2$,[15] where Ru–S(bridging) is 2.55 Å, whereas the average of Ru–S(nonbridging) is 2.399 Å. The average S–S distance of the

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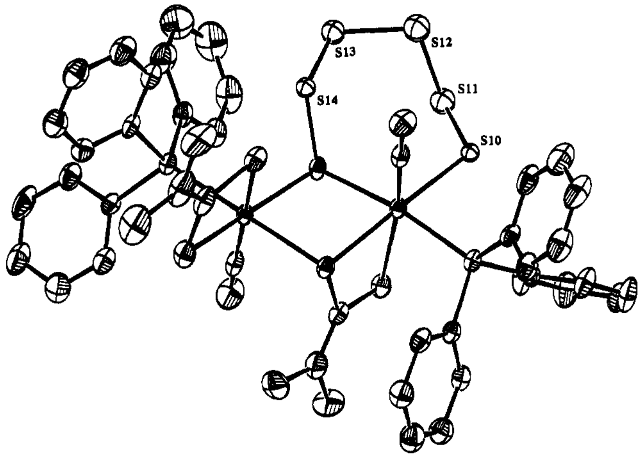

Figure 2. Structure of $[Ru_2(\mu\text{-}S_6)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ with thermal ellipsoids drawn at the 30% probability level.

S_5 chain is 2.06 Å, which is slightly shorter than that in $[Os_2(\mu\text{-}S_5)(\mu\text{-}S_3CNEt_2)(S_2CNEt_2)_3]$[14] where the value is 2.09 Å. The average S–S distance of the S_6 chain in **1** is 2.03 Å, which is slightly shorter than that of the S_5 chain in **1**. The recently reported polysulfido ruthenium complex $(PPh_4)[Ru(NO)(NH_3)(S_4)_2]$[16] is the first example in which a polysulfido ligand coordinates to a ruthenium atom, but the S_4 ligands only chelate to a ruthenium atom and there are no bridging ruthenium atoms.

The cyclic voltammogram of **1** in CH_2Cl_2 with *n*-Bu_4NClO_4 as the supporting electrolyte showed that **1** decomposes in the anodic scan at around 0.47 V (vs Ag/AgCl) and there was no other redox wave observed within the range −1.5 to +1.5 V. From this fact it can be at least concluded that the S_5^{2-} and S_6^{2-} ligands are weaker electron donors than the S_2^{2-} or RS^- ligands, since $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ exhibits two one-electron redox waves at +180 and −875 mV (vs Ag/AgCl)[6] and $[Cp^*Ru(\mu\text{-}SPh)_3RuCp^*]$ exhibits two redox waves at −0.42 and −1.0 V (vs SCE).[4] From the synthetic and electrochemical studies so far reported on sulfur-bridged binuclear ruthenium compounds, it is evident that the redox potential of the Ru(III/II) couple is drastically affected by the sulfur-containing ligand: MS_4^{2-} (M = Mo, W) is rather electron accepting, and the ruthenium redox potentials in MS_4^{2-}-coordinated compounds are relatively high,[1,2,5] whereas RS^- is strongly donating.[4] S_2^{2-} is also considerably donating, but as the present study shows, S_5^{2-} and S_6^{2-} are weaker electron donors and are unstable to oxidation. Another feature of these polysulfido ligands is expressed in the IR absorption of **1** at ν_{CO} = 1948 cm^{-1}, which is significantly higher than that of the mononuclear starting compound $RuH(S_2CNMe_2)(CO)(PPh_3)_2$, where ν_{CO} = 1922 cm^{-1}. This fact indicates that coordination of the S_5^{2-} and S_6^{2-} ligand, as in MS_4^{2-} (M = Mo, W) ligands,[7] also weakens the coordination of CO.

Supplementary Material Available: Tables of bond distances and angles, thermal parameters, and the coordinates of the hydrogen atoms (8 pages). Ordering information is given on any current masthead page.

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