3838 *Inorg. Chem.* **1995,** *34,* 3838−3840

Synthesis and Structure of a Hydride- and Sulfide-Bridged Tetranuclear Ruthenium(II,III) Cluster Complex

Kazuko Matsumoto,* Hiroshi Ohnuki, and Masaki Kawano

Department of Chemistry, Waseda University, Okubo, Shinjuku-ku, Tokyo 169, Japan

Received December 21, 1994

The authors have been synthesizing various dinuclear ruthenium complexes with a Ru−S−S−Ru bridging structure.[1−4] One of the complexes [{RuCl(P(OMe)$_3$)$_2$}$_2$(μ-Cl)$_2$(μ-S$_2$)] (**1**) reacts with anhydrous N$_2$H$_4$ to form [{RuCl(P(OMe)$_3$)$_2$}$_2$(μ-Cl)(μ-N$_2$H$_4$)(μ-S$_2$)] (**2**).[2] Another complex [{Ru(AN)$_3$(P(OMe)$_3$)$_2$}$_2$(μ-S$_2$)]$^{4+}$ (**3**) (AN is CH$_3$CN) reacts with anhydrous N$_2$H$_4$ to produce a triply bridged dinuclear complex [{Ru(AN)(P(OMe)$_3$)$_2$}$_2$(μ-S$_2$)(μ-NH$_2$NH$_2$)$_2$](CF$_3$SO$_3$)·Et$_2$O (**4**).[1] Complex **1** also forms [{Ru(P(OMe)$_3$)$_2$(AN)$_2$}(CH$_3$COCH$_2$S$_2$){Ru(P(OMe)$_3$)$_2$(AN)$_3$]$^{3+}$ (**5**), in which deprotonated acetone is bonded to one of the disulfide S atoms with the methylene carbon atom and the acetonate carbonyl oxygen is coordinated to one of the Ru atoms, by removing all the terminal and bridging chloride of **1** by Ag$^+$ [5] and addition of acetone. These facts suggest that the S$_2$-bridged starting complexes are suitable for coordinating a small molecule as a bridging ligand between the two metal centers. In the present study, we have reduced the triply bridged complex, [{Ru(AN)(P(OMe)$_3$)$_2$}$_2$(μ-Cl)$_2$(μ-S$_2$)](CF$_3$SO$_3$)$_2$ (**6**)[6] with magnesium metal in methanol under N$_2$, hopefully to accommodate N$_2$ between the two Ru atoms. What we have obtained, however, is a novel tetranuclear Ru(II,III) mixed-valent cluster complex [Ru$_4$(P(OMe)$_3$)$_8$(μ_2-H)$_2$(μ_2-S)$_2$(μ_4-S)$_2$] (**7**). The synthesis and the crystal structure of the interesting cluster structure are reported here.

Experimental Section

Synthesis. Complex **7** was prepared under N$_2$ as follows. To 2 mL of dry methanol containing 0.1 g (0.11 mmol) of **6**, which was prepared by adding 2 equiv of AgCF$_3$SO$_3$ to **1**,[6] was added excess magnesium powder (0.02 g, 0.82 mmol) at 0 °C, and the solution was stirred at 0 °C for 1 h. During this period, the solution turned from blue-green to light yellow and finally to reddish brown after further stirring at 50 °C for 9 h. The resulting solution was further stirred at 50 °C for 3 days. The solution was filtered to remove white precipitate, and the filtrate was set for crystallization by ether vapor diffusion. Brown plate crystals were obtained with 29% yield. Anal. Calcd for C$_{24}$H$_{74}$O$_{24}$P$_8$Ru$_4$S$_4$: C, 18.87; H, 4.89%. Found: C, 18.92; H, 4.93%.

NMR Measurements. ^{1}H NMR spectra were measured on a JEOL JNM-EX270WB. Since compound **7** is very unstable in solution, TMS was not added to the sample solution for fear that TMS may accelerate the decomposition of the compound. Therefore, all chemical shifts are referenced to external TMS.

Table 1. Summary of Crystal Data for **7**

formula	C$_{24}$H$_{74}$O$_{24}$P$_8$Ru$_4$S$_4$	Z	2
fw	1527.2	d_{calcd}, g cm^{-3}	1.83
cryst syst	monoclinic	abs coeff (μ), cm^{-1}	11.12
space group	$P2_1/n$ (No. 14)	radiation (λ, Å)	Mo Kα (0.710 69)
a, Å	12.085(1)	R^a	0.0430
b, Å	23.318(2)	$R_w{}^b$	0.0496
c, Å	10.550(1)	GOF^c	1.04
β, deg	110.91(2)	$T = 23$ °C	
V, Å^3	2777.2(5)		

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. $w = 1/(\sigma(F)^2 + 0.001222F^2)$. [c] GOF $= [\Sigma w(|F_o| - |F_c|)^2/\Sigma(N_{reflcns} - N_{params})]^{1/2}$.

Table 2. Atomic Parameters for [Ru$_2$(μ-H)(μ-S)(μ_4-S){P(OMe)$_3$}$_4$]$_2$

atom	x/a	y/b	z/c	K	B_{eq},^{a} Å^2
Ru1	0.08346(4)	0.07835(2)	0.55278(5)	1.000	2.03
Ru2	−0.14383(4)	0.05104(2)	0.38994(5)	1.000	2.07
S2	0.2639(1)	0.0315(1)	0.6799(2)	1.000	3.09
S1	0.0397(1)	−0.0024(1)	0.3814(1)	1.000	2.33
P1	0.1826(1)	0.1375(1)	0.4711(2)	1.000	2.91
P2	0.0854(2)	0.1382(1)	0.7165(2)	1.000	2.93
P3	−0.2789(1)	0.1020(1)	0.4358(2)	1.000	2.95
P4	−0.2035(2)	0.0864(1)	0.1820(2)	1.000	3.36
O11	0.1196(5)	0.1967(2)	0.4108(6)	1.000	4.86
O12	0.3074(5)	0.1614(3)	0.5778(6)	1.000	4.64
O13	0.2324(5)	0.1161(2)	0.3559(5)	1.000	4.34
C11	0.178(1)	0.2397(4)	0.357(1)	1.000	7.11
C12	0.4222(8)	0.1477(6)	0.581(1)	1.000	8.05
C13	0.1501(8)	0.1033(4)	0.2223(8)	1.000	5.00
O21	0.0962(5)	0.2064(2)	0.7102(5)	1.000	3.89
O22	−0.0294(5)	0.1291(2)	0.7577(5)	1.000	4.44
O23	0.1860(6)	0.1311(3)	0.8669(5)	1.000	4.89
C21	0.0053(7)	0.2418(3)	0.6164(9)	1.000	4.66
C22	−0.0473(9)	0.1585(4)	0.8683(9)	1.000	6.10
C23	0.3054(8)	0.1550(5)	0.897(1)	1.000	5.83
O31	−0.2412(5)	0.1660(2)	0.4828(6)	1.000	4.81
O32	−0.4023(5)	0.1184(3)	0.3186(6)	1.000	5.00
O33	−0.3342(6)	0.0807(3)	0.5457(8)	1.000	7.48
C31	−0.3200(8)	0.2055(4)	0.515(1)	1.000	6.74
C32	−0.4975(8)	0.0753(5)	0.266(1)	1.000	6.01
C33	−0.303(1)	0.0374(5)	0.638(1)	1.000	8.25
O41	−0.1352(5)	0.0668(3)	0.0820(5)	1.000	5.04
O42	−0.3390(5)	0.0700(3)	0.0916(5)	1.000	5.11
O43	−0.203(1)	0.1524(3)	0.1492(7)	1.000	3.17
C41	−0.1400(9)	0.0065(5)	0.0414(9)	1.000	6.22
C42	−0.394(1)	0.0917(6)	−0.0442(9)	1.000	7.62
C43	−0.1649(9)	0.1978(4)	0.221(1)	1.000	5.59
H	−0.074(5)	0.111(3)	0.458(6)	1.000	2.25

[a] $B_{eq} = 8/3\pi^2[a^2a^{*2}U_{11} + b^2b^{*2}U_{22} + c^2c^{*2}U_{33} + aba^*b^*(\cos\gamma)U_{12} + aca^*c^*(\cos\beta)U_{13} + bcb^*c^*(\cos\alpha)U_{23}]$.

Collection and Reduction of X-ray Data. A crystal of **7** (0.5 × 0.4 × 0.25 mm^3) was subjected to single-crystal X-ray diffraction analysis. Since the crystal was very unstable at room temperature, X-ray measurement was made on a epoxide-resin coated crystal. Unit cell parameters were obtained from a least-squares fit of 24 reflections in the range 21° < 2θ < 25° measured on a Rigaku AFC-5R four-circle diffractometer using graphite-monochromated Mo Kα radiation (0.710 69 Å). Under these conditions no significant deterioration of the crystal was observed during the measurement, therefore no decay correction was applied. Azimuthal scans of several reflections indicated no need for absorption correction. The crystal data are given in Table 1, and the details of the data collection are in supporting Table S1. The Lorentz−polarization correction was made to the collected data.

Solution and Refinement of the Structure. The structure of **7** was solved by a direct method and subsequent Fourier techniques. All the non-hydrogen atoms in the complex and the bridging hydrogen atom were located and were refined anisotropically by a full-matrix least-squares method, by using the program Shelxs 76/86. The bridging hydrogen atom was refined isotropically.

The final atomic positional and thermal parameters for **7** are listed in Table 2. The anisotropic thermal parameters are deposited in Table S2.

Results and Discussion

The formation of **7** is schematically illustrated in Figure 1. Crystals of **7** are not stable in air, and **7** is very unstable in

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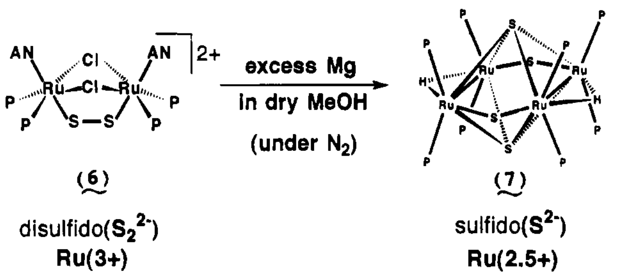

Figure 1. Formation reaction of **7**. The ligand P is P(OMe$_3$), and AN is CH$_3$CN.

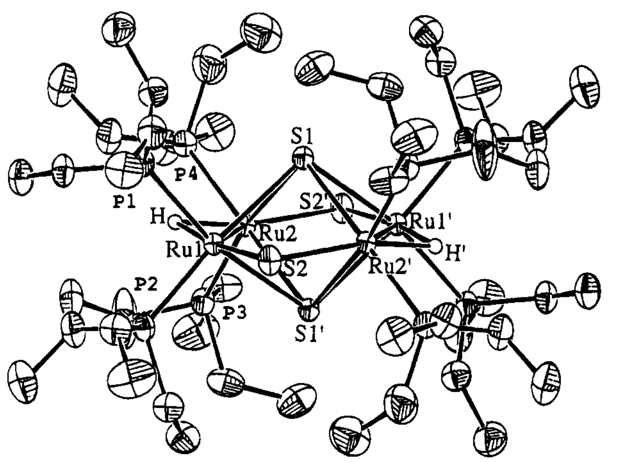

Figure 2. Structure of [{Ru$_4$(P(OMe$_3$)$_8$(μ_2-H)$_2$(μ_2-S)$_2$(μ_4-S)$_2$] (**7**). The thermal ellipsoids are drawn at the 30% level.

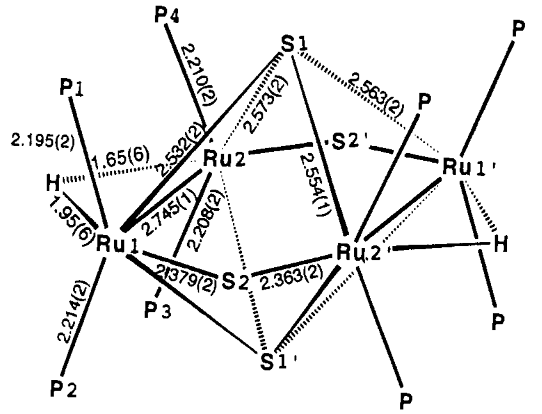

Figure 3. Selected interatomic distances (Å) in **7**.

Table 3. Bond Distances (Å) for [Ru$_2$(μ-H)(μ-S)(μ_4-S){P(OMe)$_3$}$_4$]$_2$

Ru2−Ru1	2.745(1)	Ru1−Ru2	2.745(1)
S2−Ru1	2.379(2)	S1−Ru2	2.573(2)
S1−Ru1	2.532(2)	P3−Ru2	2.208(2)
P1−Ru1	2.195(2)	P4−Ru2	2.210(2)
P2−Ru1	2.214(2)	H−Ru2	1.65(6)
H−Ru1	1.95(6)	Ru1···Ru2	3.112
Ru2···Ru1	3.112	S2···Ru2	2.364
S1···Ru1	2.563	S1···Ru2	2.554

Table 4. Bond Angles (deg) for [Ru$_2$(μ-H)(μ-S)(μ_4-S){P(OMe)$_3$}$_4$]$_2$

S2−Ru1−Ru2	139.22(4)	S1−Ru2−Ru1	56.76(3)
S1−Ru1−Ru2	58.20(4)	P3−Ru2−Ru1	113.0(1)
S1−Ru1−S2	88.7(1)	P3−Ru2−S1	169.2(1)
P1−Ru1−Ru2	117.7(1)	P4−Ru2−Ru1	115.7(1)
P1−Ru1−S2	89.5(1)	P4−Ru2−S1	97.2(1)
P1−Ru1−S1	101.0(1)	P4−Ru2−P3	90.7(1)
P2−Ru1−Ru2	111.4(1)	H−Ru2−Ru1	44.7(21)
P2−Ru1−S2	95.6(1)	H−Ru2−S1	96.2(21)
P2−Ru1−S1	165.2(1)	H−Ru2−P3	76.0(21)
P2−Ru1−P1	93.2(1)	H−Ru2−P4	93.1(20)
H−Ru1−Ru2	36.4(18)	Ru2−S1−Ru1	65.03(4)
H−Ru1−S2	173.3(18)		
H−Ru1−S1	90.1(17)		
H−Ru1−P1	97.2(18)		
H−Ru1−P2	84.0(17)		

solution even under N$_2$. No detailed pursuit of the decomposition products was carried out. The structure of **7** is shown in Figure 2. The major interatomic distances in the core are illustrated in Figure 3. The solid complex is unstable in air and its CH$_2$Cl$_2$ solution is unstable at room temperature even under N$_2$. The complex has a center of symmetry at the center of the molecule. The distance of Ru1−Ru2 is 2.745(1) Å, suggesting a metal−metal bonding, whereas the other distance Ru1···Ru2′ is 3.112(1) Å and is not a metal−metal bonding. The Ru atoms, originally Ru(III) in the starting complexes **1** and **6**, have been reduced to a Ru(II,III) mixed-valence state consisting of two Ru(II) and two Ru(III). The actual oxidation state of each Ru atom in **7** cannot, however, be assigned from the X-ray structural data. The Ru oxidation states seem to be averaged in the crystal structure as judged from the almost comparable distances of the corresponding bond groups Ru1−S2 (2.379(2) Å) and Ru2′−S2 (2.363(2) Å) as well as Ru1−S1 (2.532(2) Å), Ru2−S1 (2.573(2) Å), Ru1′−S1 (2.563(2) Å), and Ru2′−S1 (2.554(1) Å), and the four independent Ru−P distances are not significantly different for Ru1 and Ru2. The Ru−P distances (2.195(2), 2.214(2), 2.208(2), and 2.210(2) Å are closer to those of Ru(III)−P(phosphite) (2.24−2.30 Å)[4,7,8] than those of Ru(II)−P(phosphite) (2.32 to 2.35 Å).[9,10] The bond distances and angles are listed in Tables 3 and 4, respectively.

The disulfide ligand originally bridging the two Ru atoms in **6** is converted to monosulfide bridging ligand in **7**. The reaction does not seem to involve any release of inorganic sulfur, since inorganic sulfur did not precipitate even after concentration of the reaction solution. The Ru$_4$S$_4$ core in **7** seems to be produced rather by dimerization and reductive S−S bond cleavage of the starting RuSSRu core. Similar reductive coupling to form a new cluster framework has been reported for a S^{2-}-bridged Mo precursor.[11] A quadruply briding μ_4-S ligand like that in **7** is very rare in Ru complexes; several other examples reported are Ru carbonyl clusters, Ru$_6$(CO)$_{14}$(μ_3-MeC$_2$NMe$_2$)$_2$(μ_4-S)$_2$,[12] Ru$_6$(CO)$_{13}$(μ-MeC$_2$NMe$_2$)(μ_3-MeC$_2$NMe$_2$)(μ_4-S)$_2$,[12] and [(μ_2-H)-Ru$_3$(CO)$_9${μ_3-SRu(CO)$_3$(η^2-CH$_2$CMe$_2$NHCNHBu^t)}].[13] All the μ_4-S atoms in these compounds are, however, tetrahedrally surrounded by four Ru atoms, which is distinctly different from the square pyramidal capping mode of the μ_4-S ligand in **7**. Even apart from the μ_4-bridging mode, there are not many Ru complexes with S^{2-} ligands of any bridging mode; [(CpMe)$_4$-Ru(III,IV)$_4$(μ_3-S)$_4$] (**8**)[14] (CpMe is methylcyclopentadienide), [{Ru(IV)(Etda-H)}$_2$(μ-S)] (**9**)[15] (Edta-H is ethylenediaminetetraacetic acid), [(C$_5$Me$_5$)$_4$Ru(III,IV)$_4$(μ_3-S)$_4$] (**10**),[16] [Ru$_3$(C$_5$-

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$Me_5)_3(\mu_3\text{-}S)(\mu_3\text{-}Cl)]$,[17] and $[Ru_3(C_5Me_5)_3(\mu_3\text{-}S)(\mu_3\text{-}SPr^i)]$[17] are the only five complexes other than the above-mentioned Ru compounds with $\mu_4\text{-}S^{2-}$ ligands. If other metals are considered, a $M_4(\mu_4\text{-}S)_2$ cluster complex, $Fe_2Co_2(\mu_4\text{-}S)_2(CO)_{11}$, should be mentioned as a relevant complex, in which the two S^{2-} ligands bridge the square planar four metals from above and below the metal plane, similar to the S^{2-} ligands in **7**.[18] It is noteworthy that all the compounds **8**−**10** contain the high oxidation state Ru(IV), which is contrasted with the medium oxidation states (Ru(II,III)) of the present complex **7**. Among **8**−**10**, X-ray structure data are available only for the first compound. The Ru−S distances in **8** are in the range 2.300−2.379 Å, which is not much different from the Ru−(μ_2-S) distances in **7**, although the Ru oxidation states are different. The Ru−(μ_4-S) distances in **7** (2.532(2), 2.573(2), 2.563(2), and 2.554(1) Å) are extraordinarily long, even if the general tendency is taken into account that the Ru−S distance is increased as the sulfur atom bridges increasing number of Ru atoms. The Ru−(μ_4-S) distances in other compounds[12,13] are in the range 2.3−2.4 Å. The Ru1−H (1.95(6) Å) and the Ru2−H (1.65(6) Å) distances are significantly different, indicating that the hydride is more strongly associated with Ru2. Although several Ru−carbonyl clusters with bridging hydrides are known,[13,19−22] most of them have their bridging hydrides with equivalent Ru−H bridging distances in the range 1.6−1.8 Å. The 18 electron-rule is satisfied for the Ru(III) atom; it has 5 d-electrons, 2 × 6 = 12 electrons of the six ligands (=3 × S + 2 × P + H), and one electron from the Ru−Ru bond, whereas the total number is more than 18 for the Ru(II) atom. This difference might be the cause of the unusually long Ru1−H distance in **7**, and if it is so, the actual electronic state of Ru1 is closer to Ru(II), whereas Ru2 is closer to Ru(III).

In the ^1H NMR spectrum, the bridging hydride is observed at −1.71 ppm relative to TMS in CD_2Cl_2 at −50 °C (Figure 4). The hydride ligand originates from the solvent methanol, which was confirmed by preparing **7** in CD_3OD and measuring the ^1H NMR. In this case no signal was observed in the hydride region. The hydride signal is broad and no coupling structure due to J_{HP} was resolved. The chemical shift of −1.71 ppm is unusually low-field for a bridging hydride ligand coordinated to Ru; the values are usually in the range −19 to −10 ppm in Ru−carbonyl clusters with hydride bridges.[19,21,22] Other ^1H peaks in Figure 4 observed at 3.52 and 3.58 ppm are ascribed to the coordinated $P(OMe)_3$. A reliable ^{31}P NMR spectrum of **7** was not obtained, presumably because of the instability and/or small paramagnetism of the compound.

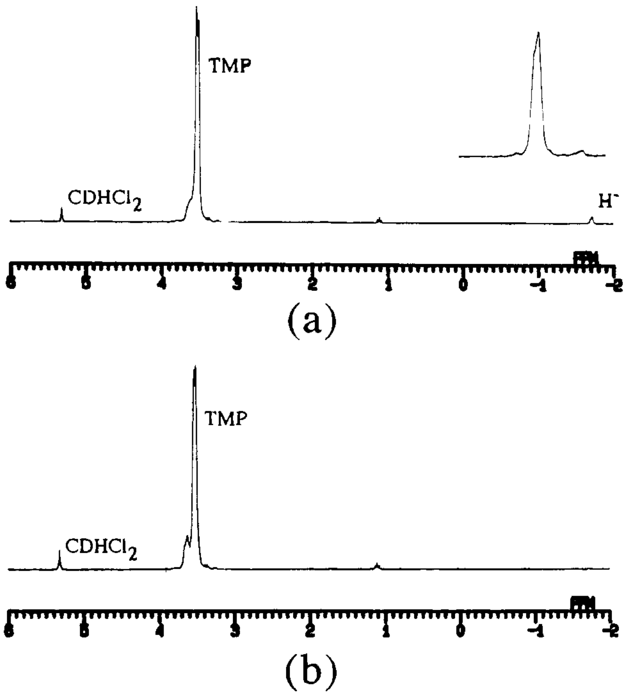

Figure 4. ^1H NMR spectra of **7** in CD_2Cl_2 at −50 °C: (a) **7** prepared in CH_3OH; (b) **7** prepared in CD_3OD. TMP is $P(OMe)_3$.

Acknowledgment. The present research was supported by Grants-in-Aid for Scientific Research on Priority Areas of "Activation of Small Molecules" (No. 04241225), and of "Reactive Organometallics" (No. 05236104) from the Ministry of Education, Science and Culture, Japan.

Supporting Information Available: Tables of crystal data, data collection, and refinement detail (Table S1) and anisotropic thermal parameters (Table S2) (3 pages). Ordering information is given on any current masthead page.

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