Synthesis of a μ,η^2-Disulfide-Bridged Hexanuclear $Ru^{II}-Na$ Cluster Formed from the Reductive Coupling of a μ,η^1-Disulfide-Bridged Dinuclear Ru^{III} Complex

Kazuko Matsumoto* and Yoichi Sano

Department of Chemistry, Advanced Research Center for Science and Engineering, Waseda University, Tokyo 169, Japan

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Upon reduction of the disulfide-bridged complex $[\{Ru^{III}Cl(P(OMe)_3)_2\}_2(\mu,\eta^1\text{-}S_2)(\mu\text{-}Cl)_2]$ (**3**) with Na metal in THF, the hexanuclear cluster complex $[Na_2Ru^{II}_4(P(OMe)_3)_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)_2(\mu,\eta^2\text{-}S_2)_2(\mu\text{-}P(OMe)_3\text{-}P,O)_4]\cdot THF$ (**4**) was obtained, and the X-ray crystal structure was solved. The crystal is triclinic with space group $P\bar{1}$. The cell constants are $a = 14.927(3)$ Å, $b = 21.063(7)$ Å, $c = 11.802(4)$ Å, $\alpha = 93.81(3)°$, $\beta = 94.73(2)°$, $\gamma = 69.24(2)°$, $V = 3455(1)$ Å^3, and $Z = 2$. Compound **4** is a hexanuclear cluster in the crystal, having two units of dinuclear compound **3**, bridged by two Na ions. Each Na ion is coordinated by two terminal chlorides, two bridging chlorides, and two phosphite oxygen atoms of the starting compound **3**. The other notable feature of **4** is that the disulfide ligand originally in a μ,η^1-bridging mode in **3** has been rotated by 90° in **4** and bridges the two Ru atoms in a μ,η^2-mode. The S−S distances of **4**, 2.050(8) and 2.046(8) Å, are significantly longer than that in **3**, 1.971(4) Å, and one of the two sulfur atoms of the disulfide ligand more strongly coordinates to one of the dinuclear Ru atoms, while the other coordinates more strongly to the other Ru atom. Therefore the four Ru−S distances are as follows: Ru(1)−S(1), 2.524(5) Å; Ru(1)−S(2), 2.334(5) Å; Ru(2)−S(1), 2.350(5) Å; Ru(2)−S(2), 2.527(5) Å. The same is observed for the other Ru(3)−Ru(4) dinuclear unit. The Na−Cl distances are normal, and the Na−O distances (2.37(1)−2.45(1) Å) are close to usual Na−O(carboxylate) distances.

Introduction

The disulfide ligand (S_2^{2-}) exhibits several distinct properties when coordinated to transition metals. These include (i) remarkably strong π-donation to metals,[1,2] often associated with a strong covalent nature between the disulfide ligand and the metals;[2−4] (ii) a strong absorption in the range 550−800 nm, typical of a M−S−S−M core, which is explained by a π-molecular orbital delocalized throughout the M−S−S−M core;[1,2,5] and (iii) stabilization of higher oxidation states of the metals, due to the strong donation of a disulfide ligand. In spite of these novel properties that are not easily provided by other ligands, relatively few complexes with disulfide ligands are reported. Two notable reactivities of disulfide complexes are that the coordinated η^2-disulfide in $MoOS_2(S_2CNR_2)_2$ reacts with various nucleophiles N (PR_3, CN^-, SO_3^{2-}, RS^-, RSH)[6] to give free NS and coordinated monosulfide, and that the disulfide in $Os(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2$ reacts with alkylating agents (CH_3I, $CH_3SO_3CF_3$)[7,8] to give alkyl sulfide with the sulfide coordination retained. Also noteworthy are several alkyne addition reactions to the coordinated $\mu,\eta^2\text{-}S_2$ in $(C_5Me_4Et)_2Ru_2(S_2)_2$[9] and, most strikingly, reaction of acetone with $\mu,\eta^1\text{-}S_2$ in $[\{Ru(CH_3CN)_3(P(OMe)_3)_2\}_2(\mu,\eta^1\text{-}S_2)]^{4+}$ [10] to form a C−S bond on the bridging disulfide. Redox reaction of the disulfide ligand is also notable. Conversion of disulfide to monosulfide on reduction is reported. Such a reaction may be a key step in the formation of a Mo−Fe−S cofactor of nitrogenase enzyme in nature,[11] and also in the mechanism of hydrodesulfurization catalysts.[12] Coordinated disulfide is expected to be reduced to two monosulfide ligands (S^{2-}), but the actual reduction reaction is not so simple, because both the central metal and the disulfide ligand can be the reduction site.

In our recent study, a novel tetranuclear Ru(II,III) complex, $[Ru_4(P(OMe)_3)_8(\mu\text{-}H)_2(\mu\text{-}S)_2(\mu_4\text{-}S)_2]$ (**1**), was synthesized.[13] The $Ru_4(\mu\text{-}H)_2(\mu\text{-}S)_4$ cluster core was formed by reductive coupling of a disulfide-bridged Ru^{III} dinuclear complex $[\{Ru(CH_3CN)(P(OMe)_3)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)](CF_3SO_3)_2$ (**2**) with Mg metal in MeOH.[2,13] It seems that the new Ru core was formed by the reduction of Ru^{III} by Mg metal, followed by dimerization of the two dinuclear Ru moieties. The $\mu\text{-}S_2$ ligand in **2** undergoes reductive cleavage to two monosulfides (S^{2-}) to make the tetranuclear core structure of **1**. Although such a reductive cleavage had been postulated for many years,[14] especially for molybdenum sulfide complexes with respect to the formation of the nitrogenase enzyme cofactor, the present synthetic reaction shows that such a reaction can actually occur and also reveals the necessity of research on the reactivities of this class of ligands. In the present study, another reduction using Na metal was attempted on $[\{Ru^{III}Cl(P(OMe)_3)_2\}_2(\mu,\eta^1\text{-}S_2)(\mu\text{-}Cl)_2]$ (**3**),[15] and a hexanuclear cluster complex $[Na_2Ru^{II}_4(P(OMe)_3)_4$-

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Table 1. Crystallographic Data for **4**

empirical formula	$C_{28}H_{80}O_{25}P_8S_4Cl_6Na_2Ru_4$
fw	1855.93
cryst syst	triclinic
space group	$P\bar{1}$
cryst params	
a	14.927(3) Å
b	21.063(7) Å
c	11.802(4) Å
α	93.81(3)°
β	94.73(2)°
γ	69.24(2)°
V	3455(1) Å^3
Z	2
T	21 °C
λ	0.71069 Å
ρ	1.784 g cm^{-3}
μ	14.73 cm^{-1}
transm factors	0.8679−0.9991
R^a	0.062
$R_w{}^b$ ($w = 1/\sigma^2(F)$)	0.076

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

$(\mu\text{-Cl})_2(\mu,\eta^2\text{-S}_2)_2(\mu\text{-P(OMe)}_3\text{-}P,O)_4]\cdot$THF (**4**) was obtained. This reaction demonstrates another new behavior of the η^1-$S_2{}^{2-}$ ligand, as well as novel incorporation of sodium and chloride ions in the cluster.

Experimental Section

The synthesis of **4** was carried out in a N_2 atmosphere at 0 °C as follows. To 25 mL of dry THF containing 200 mg of **3**[15] was added 70 mg of sodium metal. Although the starting compound **3** was insoluble in THF, it became soluble after the solution was stirred for 1−2 days and the original blue-green color of **3** (λ_{max} = 660 nm) became green with a slight tint of brown (λ_{max} = 700 nm). The reaction should not be continued for more than 2 days, as the solution becomes more brown, from which no pure material can be isolated. The reaction solution was filtered to remove unreacted Na metal and NaCl precipitate. The filtrate was condensed to 7 mL, to which 30 mL of diethyl ether was slowly added. After half a day the solution gave orange prismatic crystals of **4**. Anal. Calcd for $C_{28}H_{80}O_{25}P_8S_4Cl_6Na_2Ru_4$ (MW = 1855.93): C, 18.12; H, 4.35. Found: C, 19.20; H, 4.59. UV−vis spectrum in CH_2Cl_2: λ_{max} 231, 268, 329, 435 nm.

Physical Measurement. The X-ray data were collected on a Rigaku AFC-7R diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at 21 °C. A prismatic orange crystal of **4** (0.30 × 0.30 × 0.20 mm) was coated with epoxy resin and was used for X-ray measurement. Three standared reflections were measured after 150 reflections, and a decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The crystal data are summarized in Table 1, and further details of the data collection are summarized in the Supporting Information.

The teXsan crystal analysis package was used. The structure was solved by direct methods. Successive Fourier synthesis revealed all of the atoms except those of THF. All non-hydrogen atoms were refined anisotropically except the carbons, which were refined isotropically. Hydrogen atoms were not included in the calculation. The final cycle of the full-matrix least-squares refinement based on 5506 observed reflections ($F > 3.00\sigma(F)$) and 530 parameters converged the R and R_w values to 0.062 and 0.076. The definitions for R and R_w are $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$). Although the elemental analysis of **4** indicates the presence of one THF molecule per complex, it was not clearly located in the electron map and was not included in the analysis. The final atomic positional and thermal parameters, the full interatomic distances and angles are listed in the Supporting Information.

NMR spectra were recorded on a JEOL EX-270 instrument. The ^{31}P chemical shifts are expressed in parts per million, referenced to $P(OMe)_3$ in CD_3CN set at 140.0 ppm.

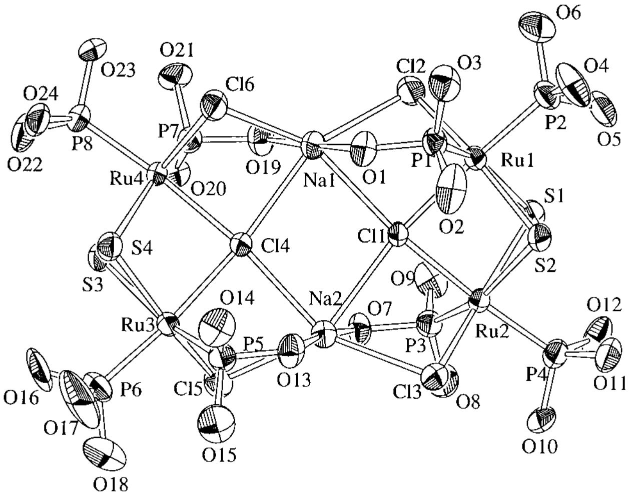

Figure 1. Perspective view of **4**. The methyl groups are omitted for clarity. The full structure including methyl groups is available as Figure S1 (Supporting Information).

Results and Discussion

X-ray Structure. The molecular structure of **4** is shown in Figure 1. The reaction scheme is shown in Scheme 1. One of the two chloride bridging ligands in **3** has been removed as the NaCl precipitate, and the disulfide ligand originally in a μ,η^1-mode in **3** now bridges the two Ru^{II} atoms in a μ,η^2-mode to satisfy the 18-electron rule. Similar η^1 to η^2 rotation by 90° of a bridging disulfide ligand is reported for $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\mu,\eta^1\text{-S}_2)(\mu,\eta^2\text{-S}_2)]$; however, in this case, the rotation occurs on electrochemical 2-electron oxidation of the two iron atoms.[16,17] Another striking feature of compound **4** is that two sodium ions bridge the two Ru^{II} dinuclear units, and thus the whole structure is hexanuclear. Both sodium ions are coordinated by four chloride ions and two oxygen atoms of $P(OMe)_3$. The two chloride ions in **4** bridge two Ru and two Na atoms in a μ_4-mode. The present reaction is a new type of reductive coupling, but, different from the usual one such as exemplified in the reduction of disulfide to monosulfide forming a new cluster framework, the dimerization is effected by the formation of a sodium ion bridge between the two dinuclear Ru units, and not by metal−metal bond formation or reorganization of the disulfide ligand. The two S−S distances in **4**, 2.050(8) and 2.046(8) Å (Table 2), are significantly longer than that in the starting complex **3**, 1.971(4) Å.[15] One of the two sulfur atoms of the disulfide coordinates more strongly to one of the dinuclear Ru atoms, while the other coordinates more strongly to the other Ru atom. Therefore, Ru(1)−S(1) (2.524(5) Å) is significantly longer than Ru(1)−S(2) (2.334(5) Å), while Ru(2)−S(1) (2.350(5) Å) is shorter than Ru(2)−S(2) (2.527(5) Å). The same is observed also for the other Ru(3)−Ru(4) dinuclear unit. The Na−O distances (2.37(1)−2.45(1) Å) are significantly short as Na−O(ether) distances; literature values of Na−O(ether) are in the range 2.70−2.94 Å, and the present distances are closer to the reported Na−O(carboxylate) distances.[18] In contrast to the relatively tight Na−O coordination in **4**, the Na−Cl distances (2.734(9)−2.848(9) Å) are long compared to that in the NaCl crystal lattice (2.82 Å).[19]

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Scheme 1

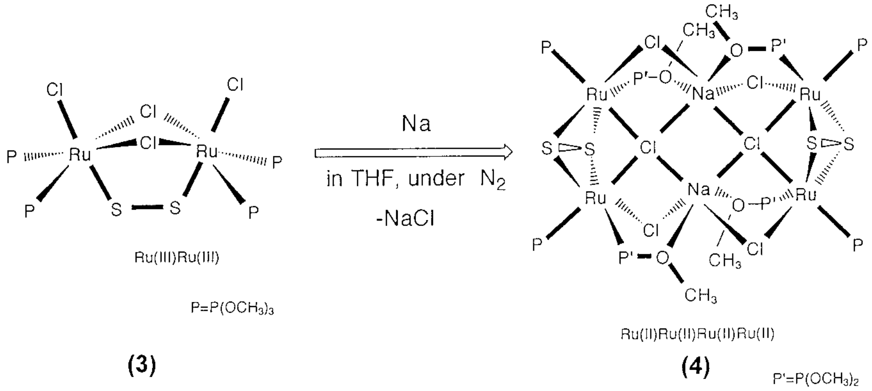

Table 2. Selected Bond Distances (Å) and Angles (deg) in **4**

Ru(1)−Cl(1)	2.526(5)	Ru(4)−S(3)	2.336(6)
Ru(1)−S(1)	2.524(5)	Ru(4)−P(7)	2.200(6)
Ru(1)−P(1)	2.197(6)	Ru(4)−Cl(6)	2.440(5)
Ru(1)−Cl(2)	2.446(5)	Ru(4)−S(4)	2.521(6)
Ru(1)−S(2)	2.334(5)	Ru(4)−P(8)	2.193(5)
Ru(1)−P(2)	2.204(6)	Ru(1)−Cl(1)	2.834(8)
Ru(2)−Cl(1)	2.514(5)	Na(1)−Cl(2)	2.756(9)
Ru(2)−S(1)	2.350(5)	Na(1)−Cl(4)	2.811(9)
Ru(2)−P(3)	2.197(5)	Na(1)−Cl(6)	2.734(9)
Ru(2)−Cl(3)	2.438(6)	Na(2)−Cl(1)	2.848(9)
Ru(2)−S(2)	2.527(5)	Na(2)−Cl(3)	2.766(9)
Ru(2)−P(4)	2.186(6)	Na(2)−Cl(4)	2.834(9)
Ru(3)−Cl(4)	2.533(5)	Na(2)−Cl(5)	2.768(9)
Ru(3)−S(3)	2.508(5)	Na(1)−O(1)	2.37(1)
Ru(3)−P(5)	2.198(6)	Na(1)−O(19)	2.43(1)
Ru(3)−Cl(5)	2.441(5)	Na(2)−O(7)	2.42(1)
Ru(3)−S(4)	2.345(5)	Na(2)−O(13)	2.45(1)
Ru(3)−P(6)	2.195(6)	S(1)−S(2)	2.050(8)
Ru(4)−Cl(4)	2.524(5)	S(3)−S(4)	2.046(8)
Ru(1)−S(1)−Ru(2)	92.1(2)	Ru(3)−S(3)−Ru(4)	93.3(2)
Ru(1)−S(2)−Ru(2)	92.5(2)	Ru(3)−S(4)−Ru(4)	92.8(2)
Ru(1)−Cl(1)−Ru(2)	88.4(1)	Ru(3)−Cl(4)−Ru(4)	88.4(2)
Ru(1)−S(1)−S(2)	60.3(2)	Ru(3)−S(3)−S(4)	61.0(2)
Ru(1)−S(2)−S(1)	60.7(2)	Ru(3)−S(4)−S(3)	69.3(2)
Ru(2)−S(1)−S(2)	60.3(2)	Ru(4)−S(3)−S(4)	69.9(2)
Ru(2)−S(2)−S(1)	60.7(4)	Ru(4)−S(4)−S(3)	60.5(2)
Cl(1)−Na(1)−Cl(4)	80.4(2)	Cl(1)−Na(2)−Cl(4)	79.7(2)
Ru(1)−Cl(1)−Na(1)	87.7(2)	Ru(3)−Cl(4)−Na(2)	87.8(2)
Ru(2)−Cl(1)−Na(2)	87.4(2)	Ru(4)−Cl(4)−Na(1)	86.3(2)
Ru(1)−Cl(2)−Na(1)	91.2(2)	Ru(3)−Cl(5)−Na(2)	91.2(2)
Ru(2)−Cl(3)−Na(2)	90.8(2)	Ru(4)−Cl(6)−Na(1)	89.7(2)

It is noteworthy that such Na bridges stabilize the whole cluster framework only with Na−O and Na−Cl coordination. Different from the lithium ion, which is known to make various chloride complex ions,[20] the sodium ion is usually not incorporated into discrete complex ions and clusters with chloride ligands. It is important to see whether the structure of **4** remains stable in THF solution. The $^{31}P\{^1H\}$ spectrum of **4** in THF shows two doublets of equal intensity at 154.48 and 146.50 ppm both with $^2J_{pp} = 79.4$ Hz. This AB pattern shows that the two $P(OMe)_3$ groups on a Ru atom are not equivalent. A number of monosulfide- and disulfide-bridged dinuclear Ru complexes with two terminal $P(OMe)_3$ ligands without Na^+ ion have been synthesized in our laboratory, and all of them show that the coordinated $P(OMe)_3$ gives a high-field shift compared to 140 ppm of the free ligand;[2,21] the complexes so far synthesized include μ-S_2, μ-S, and μ,η^2-S^2 bridged Ru(III) dimer and Ru(II)Ru(III) dimer complexes, and they exhibit the ^{31}P signal of the coordinated terminal $P(OMe)_3$ in the range 115−125 ppm. The present low-field shift of **4** can be interpreted in two ways: the structure in Figure 1 is retained, and as a result of the sodium coordination to one of the $P(OMe)_3$ groups and to the bridging chloride that is trans to the other $P(OMe)_3$, the ^{31}P chemical shift is at low field. The other interpretation is that the structure is disrupted to two disulfide-bridged Ru(II) dimer molecules and sodium ions, and the Ru(II) dimer complex exhibits the low-field shift. The authors have very recently prepared another disulfide-bridged Ru(II) complex with the $P(OMe)_3$ ligand, which shows a similar low-field shift.[22] Therefore, it is more likely that **4** is disrupted to a dimer complex and a sodium ion. The ^1H NMR spectrum shows two doublets with an intensity ratio of ca. 1:1 at 3.64 and 3.77 ppm both with $^3J_{PH} = 11.22$ Hz. This is in accordance with the disulfide-bridged Ru(II) dimer complex produced on dissolution in THF.

Compound **4** has several notable features with regard to the chemistry of the disulfide ligand. It should be noted that **4** is the first $Ru^{II}SSRu^{II}$ core and does not exhibit the intense blue to green color typical of a $Ru^{III}SSRu^{II}$ or $Ru^{III}SSRu^{III}$ core with an end-on S_2 bridge. The first fully reduced $Ru^{II}SSRu^{II}$ core is highly reactive toward air, and it easily exhibits a blue color on air oxidation. The oxidation reaction and other reactivities of **4** are presently under investigation.

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Supporting Information Available: Crystal data collection procedures and an unabbreviated ORTEP representation of **4** (4 pages). An X-ray crystallographic file in CIF format for compound **4** is available on the Internet only. Ordering and access information is given on any current masthead page.

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