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A Novel Binuclear Ruthenium(III) Compound Triply Bridged by Chloride and Disulfide Ligands, $[RuCl\{P(OMe)_3\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)RuCl\{P(OMe)_3\}_2]$

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A diruthenium compound with a novel $Ru_2(S_2)Cl_2$ core has been synthesized. The X-ray crystal study shows that the disulfide ligand bridges the ruthenium atoms in a cis manner with the S-S distance of 1.971(4) Å. The compound has a redox potential of -0.57 V (vs. Ag^+/Ag) and a characteristic absorption band at 737 nm.

The authors have attempted to synthesize sulfur-bridged multinuclear ruthenium compounds which functionally mimic and behave like nitrogenase enzymes. Although Ru is not employed in any natural enzyme, it seems suitable for preparing such artificial enzyme mimics because of its strong back-donating nature compared to other metals. In our previous studies, trinuclear compounds, $[\{(TMP)_4Ru\}_2(\mu\text{-}MS_4)](PF_6)_2$$^{1)}$ and $[\{(L)(CO)(PPh_3)Ru\}_2(\mu\text{-}MS_4)]$$^{2)}$ (TMP = $P(OMe)_3$, L = PhNCHS, $CH_2CH_2(C_5H_4N)$, $CH_2CH_2C(O)OMe$, M = Mo, W), were synthesized and their chemical properties were investigated. Although the compounds were found to exhibit novel photosubstitution reactions, it turned out that the bridging ligand MS_4^{2-} is strongly electron-accepting, and accordingly the redox potentials of Ru(III/II) in such trinuclear compounds shift to higher values. No redox wave was observed in the cyclic voltammetry of these compounds in the range -1.3— +0.8 V (vs. Ag^+/Ag). Disulfide ligand S_2^{2-} has recently come up to be noted for its strong electron-donating ability, which is exemplified in $[\{CpRu(PPh_3)_2\}_2(\mu\text{-}S_2)](BF_4)_2$$^{3)}$ and 1,4-$[\{(MeCp)Ru(PPh_3)\}_2\text{-}(\mu\text{-}S_2)_2]$$^{4)}$ (Cp = cyclopentadienyl, MeCp = pentamethylcyclopentadienyl), and seems promising for lowering the redox potential and leading to multielectron reduction of the coordinated molecules. We report here the synthesis and the crystal structure of a new sulfide cluster with a novel $Ru_2(S_2)Cl_2$ core. The compound is also the first example that has a substitution active ligand like terminal chloride.

trans-$RuCl_2(TMP)_4$$^{5)}$ (1 mmol) and S_8 (10 mmol) were suspended in 0.05 dm^3 of CH_2Cl_2 and were reacted at room temperature for 24 h. The solution was concentrated to 5×10^{-3} dm^3 under reduced pressure, then was added with 5×10^{-3} dm^3 of acetone, and was filtered to remove unreacted sulfur. The filtrate was further concentrated to 3×10^{-3} dm^3 under reduced pressure and was added with ether until green powder precipitated. The precipitate was recrystallized from acetone/ether. The yield was 65%. Anal. Found: C, 15.82; H, 4.09%. Calcd for $[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$: C, 15.94; H, 4.01%.

A crystal of approximate dimensions of $0.5 \times 0.1 \times 0.1$ mm^3 was used for the X-ray crystallographic study. The crystal data are as follows: FW = 904.4, monoclinic, space group $P2_1/n$, a = 23.739(8), b = 15.665(4), c = 8.794(1) Å, β = 99.93(2)°, V = 3221(2) Å^3, D(calcd) = 1.86 g/cm^3, and Z = 4. The X-ray diffraction intensities were collected in the range of $5° < 2\theta < 55°$ on a Rigaku AFC-5R diffractometer with graphite monochromoted Mo Kα radiation (λ=0.71068 Å). Absorption correction was not applied, since the absorption coefficient was small (μ = 16.21 cm^{-1}). A total of 3053 independent reflections with $|Fo| > 4\sigma(|Fo|)$, corrected for Lorentz and polarization effects, were used for the calculation. The structure was solved by a direct mathod (program SHELX-86). All the non-hydrogen atoms were treated anisotropically. The final discrepancy indices were R = 0.040 and R_w = 0.050 ($w = 1/\sigma^2(Fo)$).

The structure of the compound is shown in Fig.1. The two ruthenium atoms are triply bridged by two chloride and a S_2^{2-} ligands. The major interatomic distances and angles are summarized in Table 1. The S-S distances in the bridging disulfide ligands of the ruthenium compounds so

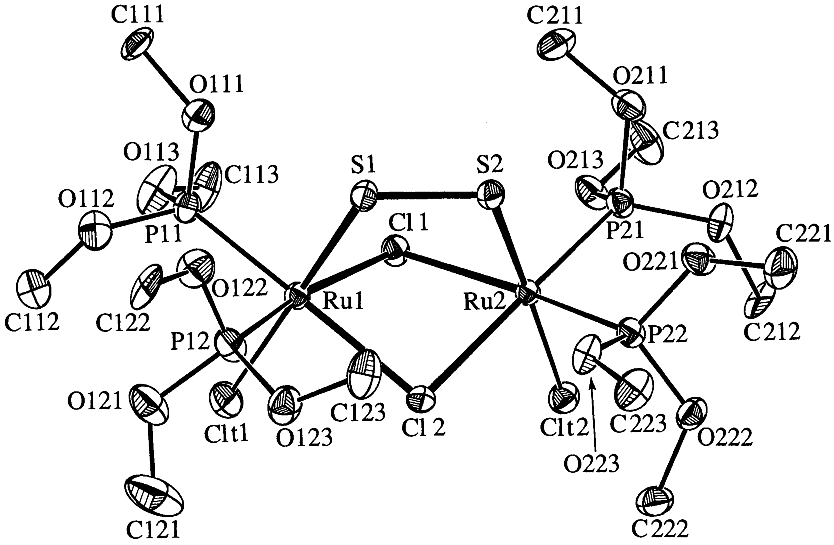

Fig. 1. Structure of $[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$.

far reported are listed in Table 2. It is clear that the S-S distance in the present compound is among the shortest of all the cis and trans S-S bridges, and is the shortest within the four cis S-S bridges.

Table 1. Interatomic Distances and Angles

	Distances(Å)		
Ru1-Ru2	3.579(1)	S1-S2	1.971(4)
Ru1-Cl1	2.530(2)	Ru2-Cl1	2.504(2)
Ru1-Cl2	2.484(3)	Ru2-Cl2	2.488(2)
Ru1-Clt1	2.420(2)	Ru2-Clt2	2.426(3)
Ru1-S1	2.205(2)	Ru2-S2	2.198(3)
Ru1-P11	2.248(3)	Ru2-P21	2.258(2)
Ru1-P12	2.242(3)	Ru2-P22	2.252(2)

	Angles(deg)		
Cl1-Ru1-Cl2	79.01(8)	Cl1-Ru2-Cl2	79.44(6)
Cl1-Ru1-Clt1	90.25(8)	Cl1-Ru2-Clt2	89.44(8)
Cl1-Ru1-S1	87.66(8)	Cl1-Ru2-S2	88.11(9)
Cl1-Ru1-P11	98.26(8)	Cl1-Ru2-P21	96.43(7)
Cl1-Ru1-P12	171.49(8)	Cl1-Ru2-P22	170.69(10)
Cl2-Ru1-Clt1	88.98(8)	Cl2-Ru2-Clt2	87.42(8)
Cl2-Ru1-S1	92.65(8)	Cl2-Ru2-S2	92.51(9)
Cl2-Ru1-P11	174.77(9)	Cl2-Ru2-P21	172.38(9)
Cl2-Ru1-P12	92.95(9)	Cl2-Ru2-P22	93.43(7)
Clt1-Ru1-S1	177.06(8)	Clt2-Ru2-S2	177.53(7)
Clt1-Ru1-P11	86.56(9)	Clt2-Ru2-P21	86.13(9)
Clt1-Ru1-P12	92.40(9)	Clt2-Ru2-P22	96.26(10)
S1-Ru1-P11	91.70(9)	S2-Ru2-P21	93.75(10)
S1-Ru1-P12	89.96(9)	S2-Ru2-P22	86.22(10)
P11-Ru1-P12	89.97(10)	P21-Ru2-P22	91.31(8)
Ru1-Cl1-Ru2	90.61(6)	Ru1-Cl2-Ru2	92.07(7)
Ru1-S1-S2	111.3(2)	Ru2-S2-S1	111.5(1)

Table 2. A comparison of the selected distances

	Ru-S(Å)	S-S(Å)	-s-s-Type	ref.
$[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$	2.202(av.)	1.971	cis	this work
$[\{CpRu(PPh_3)_2\}_2(\mu\text{-}S_2)](BF_4)_2$	2.208	1.962	trans	3
$[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]Cl_4\cdot 2H_2O$	2.193(av.)	2.014	trans	6, 7
1,4-$[\{(MeCp)Ru(PPh_3)\}_2(\mu\text{-}S_2)_2]$	2.295(av.)	2.046	trans	4
$[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}SPr^i)_2(\mu\text{-}S_2)]$	2.212(av.)	2.008	cis	8
$[(\mu^2\text{-}S_2)\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu^3\text{-}S)(\mu^2\text{-}S)_2WS]$	2.220(av.)	1.991	cis	8
$[\{(\eta^5\text{-}C_5Me_4Et)Ru\}_2(\mu,\eta^2\text{-}S_2)(\mu,\eta^1\text{-}S_2)]$	2.195	2.020	cis	9

The UV-vis spectrum of the compound showed strong absorption bands at 472 nm (ε = 2.36 x 10^3 $M^{-1}cm^{-1}$) ($M=mol\cdot dm^{-3}$), 334 nm (ε = 2.97 x 10^3 $M^{-1}cm^{-1}$), and 737 nm (ε = 6.33 x 10^3 $M^{-1}cm^{-1}$). The resonance Raman spectral measurements of the compound in CH_2Cl_2 with the excitation by 568.2 nm and 647.1 nm showed that the band at 385 cm^{-1} ((Ru-S)) is greatly enhanced by the exicitation with 647.1 nm, whereas it is not by 568.2 nm. Therefore, the visible band at 737 nm is assigned to the transition within the Ru_2S_2 core. The cyclic voltammetry of the compound and the starting material trans-$RuCl_2(TMP)_4$ in acetonitrile, measured with a Pt working electrode and Bu_4NClO_4 supporting electrolyte, revealed a single reversible redox wave corresponding to Ru(III/II) at -0.57 V and +0.41 V (vs. Ag^+/Ag), respectively. Similar large cathodic shift of the redox potential on disulfide coordination was reported for $[\{CpRu(PPh_3)_2\}_2(\mu-S_2)](BF_4)_2$ (-0.875 V vs. AgCl/Ag) compared to $CpRu(PPh_3)_2Cl$ (0.594 V vs. AgCl/Ag), and this cathodic shift is believed to be due to the strong donating ability of the $S_2{}^{2-}$ ligand.

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