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Synthesis and Structure of a Disulfido-Bridged Mixed-Valent Ru(II)Ru(III) Complex $[\{Ru(AN)_3(TMP)_2\}_2(\mu\text{-}S_2)](PF_6)_3$ (AN = acetonitrile, TMP = $P(OMe)_3$)

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The first structural analysis of a S_2^{2-}-bridged Ru(II)Ru(III) compound is reported. The compound was isolated from an acetonitrile solution of $[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$ with the addition of $NaPF_6$. The two Ru atoms are equivalent and are bridged by a S_2^{2-} ligand in trans positions.

Disulfur S_2 in free state is unstable and only poorly characterized,[1] but S_2^{n-} (n = 1, 2) ligands have been proved to coordinate to metal centers and form stable complexes. Various coordination modes of S_2^{n-} have been reported,[2] which include side-on coordination to a metal, bridging two or more metals, and cis and trans end-on bridging coordination.[2] Bridging of metal centers by a trans η^1-η^1-S_2 unit is relatively rare[2] and the crystal structures are reported only to $[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]Cl_4 \cdot 2H_2O$,[3-5] $[\{Mn(Cp)(CO)_2\}_2(\mu\text{-}S_2)]$,[6] $[\{Ru(MeCp)(PPh_3)\}_2(\mu\text{-}S_2)](SbF_6)_2$,[7] $[\{Ru(Cp)(PMe_3)_2\}_2(\mu\text{-}S_2)](SbF_6)_2$,[8] $[\{Fe(Cp)\}_2(\mu\text{-}SC_2H_5)_2(\mu\text{-}S_2)]$,[9] $[\{Ru(MeCp)\}_2(\mu\text{-}S_2)(WS_4)]$,[10] $[\{Ru(MeCp)\}_2(\mu\text{-}SPr^i)_2(\mu\text{-}S_2)]$,[10] $[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$,[11] and $[\{Ru(PPh_3)\text{'}S_4\text{'}\}_2(\mu\text{-}S_2)]$[12] (Cp = cyclopentadienyl, MeCp = methylcyclopentadienyl, SPr^i = iso-propylthiolato, and 'S_4' = 1,2-bis[(2-mercaptophenyl)thio]ethane(2-)). We have recently reported synthesis and crystal structure of a $Ru(III)_2$ dimer complex with a trans S_2^{2-} bridge and two chloro bridges, $[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$.[11] The complex has a novel $Ru(III)_2(S_2)Cl_2$ core structure. We report here the first paramagnetic S_2^{2-}-bridged Ru(II)Ru(III) mixed-valent compound which is derived from $[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$. The isolation of such a singly S_2^{2-}-bridged compound from the $Ru_2(S_2)Cl_2$ core compound revealed unexpectedly high reactivity of the bridging chloro compared to that of the terminal ones in the starting compound.

The compound $[\{Ru(AN)_3(TMP)_2\}_2(\mu\text{-}S_2)](PF_6)_3$ was prepared as follows. To a CH_3CN solution (0.05 dm^3) of $[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$ (0.90 g, 1.0 mmol), 1.01 g (6.0 mmol) of $NaPF_6$ in 0.1 dm^3 of H_2O was added and the solution was stirred at room temperature for 3 h under N_2. The solution turned blue from green during the reaction. To the solution 0.15 dm^3 of CH_2Cl_2 was added and the blue CH_2Cl_2/CH_3CN layer was separated from the aqueous layer by a separatory funnel. The blue organic layer was filtered and was concentrated to 10 dm^3. Blue plate crystals were obtained by ether vapor diffusion to the filtrate in a freezer (≈ -14 ℃). The yield was 72%. Anal. Found: C, 19.92; H, 3.67; N, 5.84%. Calcd for $C_{24}H_{54}N_6O_{12}F_{18}P_7S_2Ru_2$: C, 19.97; H, 3.77; N, 5.82%.

A crystal of approximate dimensions of 0.45 x 0.20 x 0.15 mm^3 was used for the X-ray crystallographic study. The crystal data are as follows: FW = 1443.8, triclinic, space group $P\bar{1}$, a = 12.469(3), b = 13.427(4), c = 11.834(3) Å, α = 121.12(2), β = 70.06(2), γ = 123.64(2)°, V = 1408.0(8) Å^3, D_c = 1.70 g/cm^3, and Z = 1. The X-ray diffraction intensities were collected in the range of $5° < 2\theta < 55°$ on a Rigaku AFC-5R diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71068 Å). Absorption correction was not applied, since the absorption coefficient is small (μ = 9.12 cm^{-1}). A total of 4023 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 method (SHELX-86). All the non-hydrogen atoms were treated anisotropically. Some of the methoxy groups were found to be

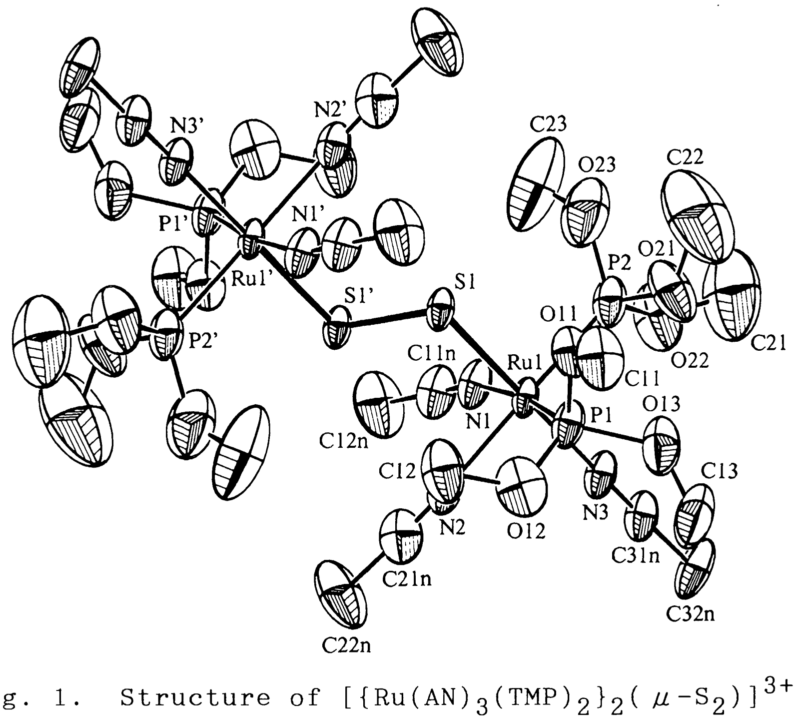

Fig. 1. Structure of $[\{Ru(AN)_3(TMP)_2\}_2(\mu\text{-}S_2)]^{3+}$.

disordered in two positions (O13 and O14, C13 and C14, and O21 O23 and O24 O26), and all the fluorine atoms of the hexafluorophosphate ions were also disordered in two orientations. The relative statistical weight of the two positions were determined by a full-matrix least-squares refinement to be 62.37 : 37.63 for the methoxy groups and 56.78 : 43.22 for the fluorine atoms. The final discrepancy indices were R = 0.082 and $R_w = 0.070$ ($w = 1/\sigma^2(Fo)$).

The structure of the major component of the complex cation is shown in Fig. 1. The major structure parameters are listed in Table 1 and are compared with those of other singly S_2^{2-}-bridged $Ru(III)_2$ dimer complexes in Table 2. The S-S distance of the present compound is comparable to those of the previously reported compounds, while the Ru-S distance of 2.322(2) Å is significantly longer than those of other Ru(III) dimer compounds in Table 2. This is possibly caused by the difference of the Ru oxidation states. The present complex has a center of symmetry at the midpoint of the S-S bond and the two Ru atoms are crystallographically equivalent. The structure in Fig. 1 is therefore considered to be the average structure of the mixed-valence state Ru(II)Ru(III).

Table 1. Interatomic Distances

Distances / Å			
Ru1-S1	2.322(2)	Ru1-N1	2.127(7)
Ru1-P1	2.234(3)	Ru1-N2	2.154(9)
Ru1-P2	2.232(4)	Ru1-N3	2.054(7)
S1-S1'	1.995(3)		

Table 2. A Comparison of the Selected Distances

	Ru-S(Å)	S-S(Å)	-S-S-Type	Ref.
$[\{Ru(AN)_3(TMP)_2\}_2(\mu\text{-}S_2)](PF_6)_3$ a)	2.322	1.995	trans	this work
$[\{Ru(Cp)(PMe_3)_2\}_2(\mu\text{-}S_2)](SbF_6)_2$ b)	2.208	1.962	trans	8
$[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]Cl_4\cdot 2H_2O$ c)	2.193(av.)	2.014	trans	4
$[\{Ru(PPh_3)'S_4'\}_2(\mu\text{-}S_2)]$ d)	2.243(av.)	1.991	trans	12

Ru oxidation state; a)Ru(II)Ru(III), b)$Ru(III)_2$, c)$Ru(III)_2$, d)$Ru(III)_2$.

The present compound is paramagnetic and the acetonitrile solution exhibits an isotropic signal at $g = 2.053$ at -50 ℃. At -85 ℃ the spectrum exhibits rhombic signal at $g_1 = 2.109$, $g_2 = 2.047$, and $g_3 = 1.994$. These values are comparable to those previously reported for sulfur-coordinated octahedral Ru(III) compounds.[13)]

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