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A Novel Diruthenium(II,III) Complex, $[\{Ru(AN)(TMP)_2\}_2(\mu\text{-}S_2)\text{-}(\mu\text{-}NH_2NH_2)_2](CF_3SO_3)_3 \cdot Et_2O$, with Two Hydrazine Bridges (AN = acetonitrile, TMP = $P(OMe)_3$)

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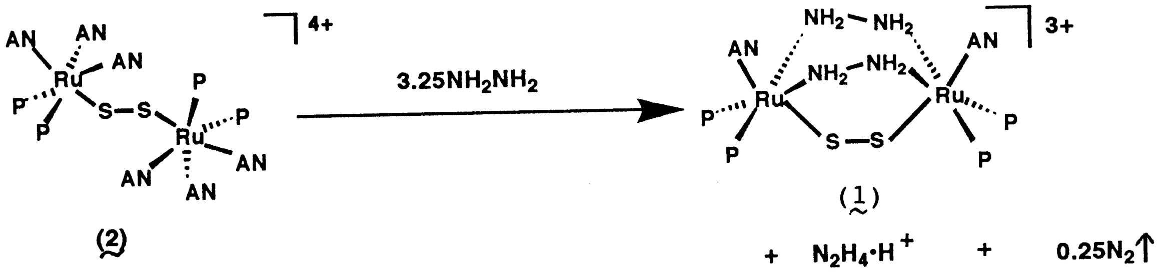
The title compound having two hydrazine bridges between the two ruthenium centers has been synthesized, and the structure is compared to that of the previously reported complex with a single hydrazine bridge, $[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)(\mu\text{-}N_2H_4)(\mu\text{-}S_2)]$.

The authors have reported several crystal structures of dinuclear Ru complexes with a RuSSRu core.$^{1-3)}$ One of the complexes has a N_2H_4 and a Cl^- bridges in the stable RuSSRu core.$^{1)}$ In the present study, we report another Ru(II)-Ru(III) complex with a similar RuSSRu core, but the complex has two N_2H_4 bridges within the RuSSRu core. Only three transition metal complexes$^{1,4,5)}$ are known, which have a N_2H_4 bridge between the two metal centers, and there is no precedent of any metal, which has two N_2H_4 bridges. Considering the high reactivity and unstable nature of N_2H_4 and the general scarcity of N_2H_4 complexes of any metals with any coordination mode, the synthesis and the crystal structure of the title compound are valuable to the chemistry of coordinated N_2H_4.

All the reactions were carried out under N_2. The title compound (1) was prepared from the reaction of $[\{Ru(AN)_3(TMP)_2\}_2(\mu\text{-}S_2)](CF_3SO_3)_4$ (2) with dry N_2H_4 as the following equation shows.



Compound **2** was prepared by reacting 4 equiv of $AgCF_3SO_3$ with $[\{RuCl((TMP)_2\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$2) in AN at 50 °C for 40 h. After the resulting AgCl was removed by filtration, the filtrate was dried under vacuo. Compound **2** was obtained as dark blue plate crystals by Et_2O vapor diffusion to a CH_2Cl_2 solution of the dried residue. Anal. Found: C, 21.09; H, 3.49; N, 5.16%. Calcd for $C_{28}F_{12}H_{54}N_6O_{24}P_4Ru_2S_6$: C, 20.95; H, 3.39; N, 5.24%.

Compound **1** was prepared by the reaction of **2** with 2 equiv of dry N_2H_4 in AN at 0 °C. The color of the solution changes slightly from blue to bluish green on addition of N_2H_4. After a week reaction at 0 °C, the solution was dried under vacuo and CH_2Cl_2 was added to the residue. Red-brown plate crystals of **1** were obtained by diffusing Et_2O to the CH_2Cl_2 solution in less than 10% yield. The compound is very unstable in air and must be stored under dry N_2. The structure of the complex cation was comfirmed with single crystal X-ray diffraction analysis as shown in Fig. 1.

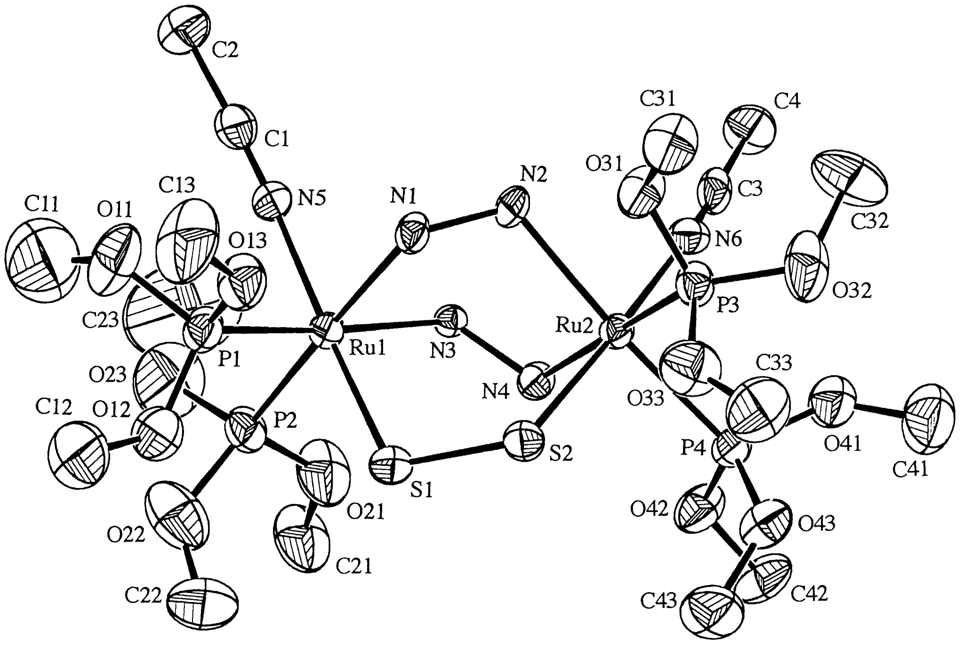


Fig.1. Molecular structure of $[\{Ru(AN)(TMP)_2\}_2(\mu\text{-}S_2)(\mu\text{-}N_2H_4)]^{3+}$.

The crystal data for **1** are as follows: FW = 1430.1, monoclinic, space group $P2_1/n$, a = 23.345(3), b = 17.536(2), c = 13.869(4) Å, β = 91.84(2)°, V = 5674(2) Å^3, D(calcd) = 1.67 g/cm^3, and Z = 4. The X-ray diffraction intensities were collected with an epoxide-resin coated crystal at -30 C in the range of $3° < 2\theta° < 50$ on a Rigaku AFC-5R diffractometer with graphite monochromated Mo K_α radiation (λ = 0.71068 Å). Absorption correction was not applied, since the absorption coefficient was small (μ = 9.15 cm^{-1}). A total of 4729 independent reflections with $|Fo| > 4\sigma(1|Fo|)$, corrected for Lorentz and polarization effects, were used for the calculation. The structure was solved by a direct method (program SHELX-86). All the non-hydrogen atoms were located and were refined anisotropically. The final discrepancy indices are R = 0.077 and R_w = 0.069 ($w = 1/(\sigma(F)^2 + 0.000590F^2)$).

Both N_2H_4 bridges in **1** are cis coordinated to Ru1 and Ru2 in a staggered manner. The two dihedral angles, Ru1-N1-N2-Ru2 and Ru1-N3-N4-Ru2, and the dihedral angle of Ru1-S1-S2-Ru2 are 60.4(9)°, 66.9(8)°, and 31.9(3)°, respectively, and are distinctively different from the Ru-N-N-Ru and Ru-S-S-Ru angles of 56.5(7)° and 16.1(2)° in similar Ru^{II}-Ru^{III} mixed-valent compound [{RuCl(TMP)$_2$}$_2$(μ-Cl)(μ-S_2)(μ-N_2H_4)]. The Ru atoms in **1** are reduced to a Ru^{II}-Ru^{III} mixed-valence state from the Ru^{III}-Ru^{III} of the starting complex **2**, but the two Ru atoms in **1** seem equivalent in their coordination distances and angles.

The major coordination and core distances in **1** are listed in Table 1. The N-N distances are not very much different from those of the bridging N_2H_4 (1.442 (1) Å) in [{RuCl(TMP)$_2$}$_2$(μ-Cl)(μ-S_2)(μ-N_2H_4)]$^{1)}$ and of other complexes with terminal N_2H_4.$^{6,7)}$

Table 1. Major Distances (Å) in **1**

Ru1 Ru2	3.996(2)		
Ru1-S1	2.306(4)	Ru1-N1	2.197(9)
Ru1-P1	2.238(4)	Ru1-N3	2.219(9)
Ru1-P2	2.250(4)	Ru1-N5	2.055(11)
Ru2-S2	2.299(4)	Ru2-N2	2.219(10)
Ru2-P3	2.245(4)	Ru2-N4	2.206(10)
Ru2-P4	2.254(4)	Ru2-N6	2.063(12)
S1-S2	2.009(5)		
N1-N2	1.465(14)	N3-N4	1.477(13)

The central Ru ··· Ru distance shows that there is no metal-metal bonding. The literature values of S-S distances in disulfide complexes are mostly in the range 2.01-2.05Å.$^{8)}$ The S-S distance of 2.009(5) Å in **1** is, therefore, relatively short but is almost similar to the value of 2.002(3) Å in the closely related complex [{RuCl(TMP)$_2$}$_2$(μ-Cl)(μ-N_2H_4)(μ-S_2),$^{1)}$ but is slightly longer than the corresponding distance of 1.971(4) Å in [{RuCl(TMP)$_2$}$_2$(μ-Cl)$_2$(μ-S_2)].$^{2)}$ These distances lie between the values of free S_2 (1.887 Å)$^{9)}$ and H_2S_2 (2.055 Å),$^{10)}$ indicating the partial double-bond character of the μ-S_2 bridge. The Ru-S and S-S distances of **1** are listed together with those of other ruthenium complexes in Table 2.

Table 2. A Comparison of the Selected Distances (Å)

	Ru-S	S-S	-S-S-type	Ref.
$[\{Ru(AN)(TMP)_2\}_2(\mu\text{-}S_2)(\mu\text{-}N_2H_4)_2]\text{-}(CF_3SO_3)_3\cdot Et_2O$	2.302(av.)	2.009	cis	this work
$[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)(\mu\text{-}S_2)(\mu\text{-}N_2H_4)]$	2.281(av.)	2.002	cis	1)
$[\{Ru(AN)_3(TMP)_2\}_2(\mu\text{-}S_2)](PF_6)_3$	2.322	1.995	trans	3)
$[\{Ru(Cp)(PMe_3)_2\}_2(\mu\text{-}S_2)](SbF_6)_2$	2.208	1.962	trans	11)
$[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)Cl_4\ 2H_2O$	2.202(av.)	1.971	cis	2)
$[\{\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}SPr^i)_2(\mu\text{-}S_2)]$	2.212(av.)	2.008	cis	13)
$[(\mu^2\text{-}S_2)\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu^3\text{-}S)(\mu^2\text{-}S)_2WS]$	2.220(av.)	1.991	cis	13)
$[\{(\eta^5\text{-}C_5Me_4Et)Ru\}_2(\mu,\eta^2\text{-}S_2)(\mu,\eta^1\text{-}S_2)]$	2.195	2.020	cis	14)

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