Synthesis, Properties, and Crystal Structure of a Novel μ-Hydrazine-Bridged Mixed-Valence Ruthenium(II,III) Complex Stabilized by Hydrazine Hydrogen Bonds, $[RuCl(TMP)_2]_2(\mu\text{-}Cl)(\mu\text{-}N_2H_4)(\mu\text{-}S_2)$ (TMP = $P(OMe)_3$)

Masaki Kawano, Chikara Hoshino, and Kazuko Matsumoto*

Department of Chemistry, Waseda University, Tokyo 169, Japan

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Transition metal complexes with coordinated hydrazine are currently of considerable interest as possible intermediates in the chemistry of coordinated dinitrogen and its reduction to NH_3 catalyzed by nitrogenases.[1-4] Numerous complexes with coordinated hydrazine or its derivatives have been synthesized, but only a few complexes are known which have been characterized by X-ray crystallography: coordinated NNH_2, $[Mo(NNH_2)F(dpe)_2](BF_4)\cdot CH_2Cl_2$ (dpe = $Ph_2PCH_2CH_2PPh_2$),[4c] $[WCl_3(NNH_2)(PMe_2Ph)_2]$;[4d] μ-N_2H_2, $[\mu\text{-}N_2H_2\{Ru(PPh_3)dttd\}_2]$ (dttd = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2-));[5] η-$N_2H_3^-$, $W(NAr)[N(NTs)_2](\eta\text{-}NHNH_2)Cl$ (Ar = 2,6-C_6H_3-*i*-Pr_2; $N(NTs)_2$ = 2,6-$NC_5H_3(CH_2NTosyl)_2$),[6] $WCp^*Me_4(\eta\text{-}NHNH_2)$,[7] and $[WCp^*Me_3(\eta\text{-}NHNH_2)](SO_3CF_3)$ ($Cp^* = \eta^5\text{-}C_5Me_5$);[7] and μ_3-$N_2H_3^-$, $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}NHNH_2)$.[8] Coordinated N_2H_4 moieties are even more scarce: to our knowledge, only $[W(NPh)Me_3]_2(\mu\text{-}\eta^1,\eta^1\text{-}NH_2NH_2)(\mu\text{-}\eta^2,\eta^2\text{-}NHNH)$,[9a] $[(tripod)Co(\eta^2\text{-}N_2H_4)]^{2+}$ (tripod = $CH_3C(CH_2PPh_2)_3$),[9b] and $[MoFe_3S_4Cl_2(Cl_5\text{-}cat)]_2(\mu\text{-}S)(\mu\text{-}N_2H_4)$ (cat = catecholate)[10] compounds contain the N_2H_4 ligand and have been structurally elucidated by X-ray diffraction, but the structures of latter two complexes have not been well determined due to the poor quality of the crystals. We report here the synthesis, the properties, and the crystal structure of $[RuCl(TMP)_2]_2(\mu\text{-}Cl)(\mu\text{-}N_2H_4)(\mu\text{-}S_2)$ (**1**) (TMP = trimethylphosphite), the first mixed-valence ruthenium(II,III) complex, in which Cl^-, NH_2NH_2 and a strong π-donor ligand, S_2^{2-}, bridge two ruthenium centers.

Compound **1** was synthesized by the reaction of $[Ru^{III}Cl(TMP)_2]_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)$ (**2**)[11] (0.30 g, 0.33 mmol) with RHNNHR (R = $SiMe_3$) (145 μL, 0.67 mmol)[12] or anhydrous hydrazine (22.2 μL, 0.68 mmol) in 10 mL of dichloromethane at 0 °C for 12 h. The color of the solution gradually changed from green to yellowish-brown. When NH_2NH_2 was used, the reacted solution was filtered in order to remove which powders of $NH_2NH_2\cdot n$HCl (n = 1 or 2). Diethyl ether was slowly added to the solution. After the solution stood at 0 °C for 3 d, reddish-brown microcrystalline product[13] formed and was filtered. The product was recrystallized from CH_2Cl_2/ether; yield 0.18 g, 60% (0.23 g, 80% with the use of anhydrous hydrazine). The hydrazine derivative RHNNHR seems to undergo the reaction shown in Scheme Ia and/or Scheme Ib, though we have not been able to obtain the reaction products, R_2NNR_2, RCl, and R_2NNHR. The stoichiometries of the reactions shown in Scheme I seem probable, since the reaction does not proceed when only equimolar RHNNHR is added. The reaction proceeds successfully only when the molar ratio of RHNNHR to **2** exceeds 2:1. The overall stoichiometry of the reaction with NH_2NH_2 is shown in Scheme I, parts c and d. Hydrazine hydrochloride salts were identified by IR spectroscopy and elemental analysis.

The molecular structure of **1** is shown in Figure 1.[14] Compound **1** is a 35 electron dimer and yet lacks a direct metal-metal bond (Ru···Ru, 3.800 (1) Å). The literature values of sulfur-sulfur distances in disulfide complexes are mostly in the range 2.01-2.05 Å.[15] The S-S distance of 2.002 (3) Å in **1** is, therefore, relatively short and lies between the values of free S_2 (1.887 Å)[16] and H_2S_2 (2.055 Å),[17] indicating the partial double-bond character of the μ-S_2 unit in **1**. Double-bond character is also indicated for the Ru-S bonds. They are comparatively shorter (2.266 (2) and 2.296 (2) Å) than the Ru-S bond distances as found in $[(NH_3)_5Ru^{II}\{S(CH_3)(C_2H_5)\}](PF_6)_2$ (2.316 (1) Å),[18] $[(NH_3)_5Ru^{III}\{S(CH_3)(C_2H_5)\}](PF_6)_{1.5}(F)_{1.5}$ (2.3711 (5) Å),[19] and the S-bound thiophene complex $[(2\text{-}(SC_4H_3)CH_2C_5H_4)Ru^{II}(PPh_3)_2](BF_4)$ (2.408 Å).[20] The S-S and Ru-S bond distances in **1** are longer than the corresponding ones in **2** (34e; S-S, 1.971 (4) Å, Ru-S, 2.205 (2) Å, and 2.198 (2) Å), while the S-S and Ru-S distances in **1** are, respectively, shorter and longer than those in $[(NH_3)_5Ru]_2(\mu\text{-}S_2)Cl_4\cdot 2H_2O$ (34e; S-S, 2.014 (1) Å, and Ru-S, 2.191 (1) and 2.195 (1) Å).[21,22] As Rauchfuss et al.[23] have suggested, π-donation from sulfur to ruthenium is invoked in electron-deficient complexes, thus causing shorter Ru-S distances. The short Ru-S distances in **1** (35e dimer) are therefore caused by such strong π-donation of the coordinated S_2^{2-} ligand. The mixed-valence interaction between the two metal centers is obviously

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(13) Anal. Calcd for $C_{12}Cl_3H_{40}N_2O_{12}P_4Ru_2S_2$ (MW = 900.97): C, 16.00; H, 4.48; N, 3.12. Found: C, 15.88; H, 4.46; N, 3.12.

(14) Crystal data for $C_{12}Cl_3H_{40}N_2O_{12}P_4Ru_2S_2$ at 23 °C: monoclinic, space group $P2_1/c$, a = 17.850 (3) Å, b = 12.468 (2) Å, c = 16.497 (4) Å, β = 115.07 (1)°, Z = 4, ρ_{calc} = 1.800 g cm^{-1}, μ = 14.88 cm^{-1}. A total of 7889 reflections were collected in the range 5° < 2θ < 55° ($\pm h,k,l$). Of these, 5296 were unique and 3897 with $F_o > 5.00\sigma(F_o)$ were used in the structure solution. $R(F)$ = 0.057, $R(F_w)$ = 0.062 ($w = 1/(\sigma(F)^2 + 0.001922F^2)$). All non-hydrogen atoms were anisotropically refined. The positions of the NH_2NH_2 hydrogen atoms were located by difference Fourier synthesis in the final step and were not refined.

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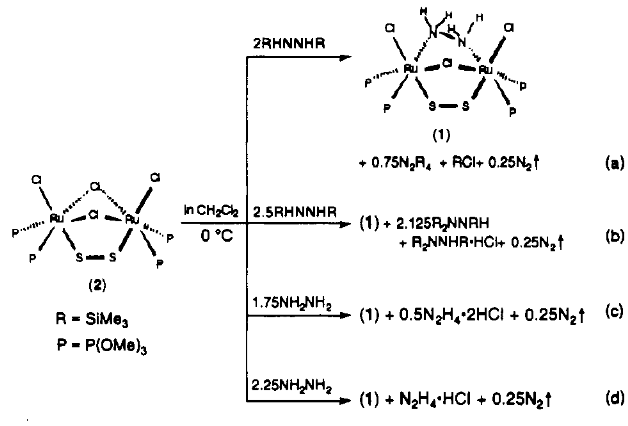
Scheme I



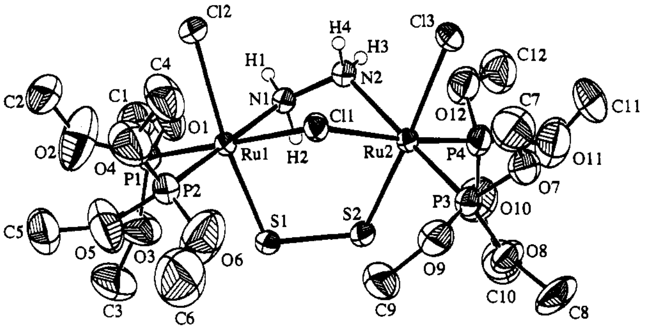


Figure 1. Molecular structure of $[RuCl(TMP)_2]_2(\mu\text{-}Cl)(\mu\text{-}N_2H_4)(\mu\text{-}S_2)$ (H atoms omitted for clarity except hydrazine hydrogen atoms).

mediated by the disulfide ligand. The Ru–P distances in **1**, 2.223 (3) (trans to Cl1), 2.221 (2) (trans to N1), 2.223 (3) (trans to N2), and 2.210 (3) Å (trans to Cl1), are 0.02–0.03 Å shorter than those (all trans to bridging chloride) in **2**, 2.242 (3), 2.248 (3), 2.258 (2), and 2.252 (2) Å. The decrease of Ru–P distances is ascribed to the increase of back-donation of $Ru(t_{2g})$ to $P(\pi)$, since the electron density on the ruthenium atoms is increased by 1e reduction. Both Ru1–P and Ru2–P distances are shortened to an approximately equal degree. This fact suggests that the unpaired electron delocalizes over the Ru_2S_2 core. The shortest Ru–Cl (bridging) distance, 2.477 (2) Å, is longer than both terminal Ru–Cl bonds, 2.454 (2) and 2.430 (2) Å, as expected. The Ru–S–S–Ru torsion angle in **2** is 0.4 (2)°, whereas that in **1** is 16.1 (2)°. The increased torsional distortion in **1** is due to the staggered conformation of Ru1–N1 and Ru2–N2 (the Ru–N–N–Ru torsion angle is 56.5 (7)°).

The N–N distance of 1.442 (1) Å is comparable to those of $[W(NPh)Me_3]_2(\mu\text{-}\eta^1,\eta^1\text{-}NH_2NH_2)(\mu\text{-}\eta^2,\eta^2\text{-}NHNH)$ (NH_2–NH_2, 1.434 (14) Å; cf. NH–NH, 1.391 (15) Å)[9a] and $[(tripod)Co(\eta^2\text{-}N_2H_4)]^{2+}$ (1.446 (17) Å)[9b] and falls in the range found for η-coordinated organohydrazines $R_mN_2H_{(4-m)}$ (m = 1, 2).[24,25] The $Ru\text{–}NH_2$ bond distances of 2.170 (7) and 2.172 (7) Å in **1** are slightly longer than a Ru–N bond of 2.12 Å which is a sum of the covalent radii of Ru and N, 1.42[26] and 0.70 Å,[27] respectively. This is probably due to the trans influence of $P(OMe)_3$. In the IR spectrum of a CH_2Cl_2 solution, two NH symmetric and antisymmetric stretches are observed (ν = 3316, 3244 cm^{-1}) as expected for symmetric N_2H_4. However, the IR spectrum (KBr pellet) showed four bands (ν = 3304, 3240, 3204, 3132 cm^{-1}) in the NH stretch range. N1···O1 and N2···O12 distances are 2.765 (10) and 2.936 (10) Å, respectively. The close approaches of N1 to O1 and N2 to O12 are comparable to, within experimental error, the border value of 2.89 (2) Å suggested by Kuleshova et al.[28] as indicative of a hydrogen bonding.

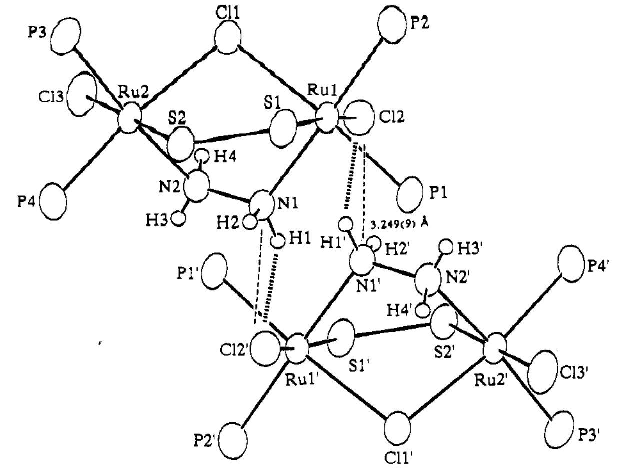


Figure 2. Association of two enantiomers via N–H···Cl hydrogen bonds (methoxy groups omitted for clarity).

In the unit cell, two enantiomers of **1** are related by a center of symmetry and are associated via two NH···Cl hydrogen bonds to give a cyclic centrosymmetric tetramer (Figure 2). The N1···Cl2 distance is 3.237 (7) Å, which is comparable to the NH···Cl bond distance of 3.23 Å, which is in ref 29 reported as the border value of a hydrogen bond.

The visible spectrum is dominated by an absorption at 812 nm ($\epsilon = 3.35 \times 10^3\ M^{-1}\ cm^{-1}$), which can possibly be attributed to intervalence charge transfer.[30] The replacement of Cl^- in **2** (λ_{max} = 737 nm, $\epsilon = 5.82 \times 10^3\ M^{-1}\ cm^{-1}$) by N_2H_4 results in a red-shift of 75 nm. The EPR spectrum in dichloromethane at 77 K shows a rhombic pattern (g_1 = 2.12, g_2 = 2.07, g_3 = 1.989). No signal was observed at room temperature.

The cyclic voltammetry of **1** revealed a single reversible redox wave corresponding to Ru(II)–Ru(III)/Ru(III)–Ru(III) at –0.09 V vs Ag/AgCl ($Fc^{0/+}$ = 0.45 V).[31] The reversible half-wave potential of the starting material for **2**, *trans*-$RuCl_2(TMP)_4$, is 0.77 V vs Ag/AgCl and that of **2** is –0.21 V. These large cathodic shifts from the mononuclear to binuclear compounds are due to a strong π-donating contribution of the S_2^{2-} ligand. A similar large cathodic shift was reported for $[\{CpRu(PPh_3)\}_2(\mu\text{-}S_2)](BF_4)_2$ (–0.875 V vs Ag/AgCl) compared to $CpRu(PPh_3)_2Cl$ (0.597 V vs. Ag/AgCl).[23] As expected from the redox potential, the yellowish-brown solution of **1** is readily oxidized in air and turns greenish-blue. The isolation of the oxidized complex is in progress.

The present study indicates the capability of the $Ru_2(\mu\text{-}Cl)(\mu\text{-}S_2)$ core to capture a hydrazine molecule and the existence of significant inter- and intramolecular hydrogen bonds of the coordinated hydrazine in **1**. The reactivities of the complex and the coordinated hydrazine are now under investigation and will be reported separately.

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Supplementary Material Available: Tables of crystal data and data collection and refinement detail, positional parameters, anisotropic thermal parameters, and bond distances and angles for **1** and a figure showing the ESR spectrum of **1** (8 pages). Ordering information is given on any current masthead page.

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