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First Example of μ_3-Sulfido Bridged Mixed-Valent Triruthenium Complex Triangle $Ru^{III}_2Ru^{II}$(*O*,*O*-acetylacetonate)$_3$(μ-*O*,*O*,γ-*C*-acetylacetonate)$_3$(μ_3-S) (1) Incorporating Simultaneous O,O- and γ-C-Bonded Bridging Acetylacetonate Units. Synthesis, Crystal Structure, and Spectral and Redox Properties

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The reaction of mononuclear ruthenium precursor [$Ru^{II}(acac)_2(CH_3CN)_2$] (acac = acetylacetonate) with the thiouracil ligand (2-thiouracil, H_2L^1 or 6-methyl –2-thiouracil, H_2L^2) in the presence of NEt_3 as base in ethanol solvent afforded a trinuclear triangular complex Ru_3(*O*,*O*-acetylacetonate)$_3$(μ-*O*,*O*,γ-*C*-acetylacetonate)$_3$(μ_3-sulfido) (**1**). In **1**, each ruthenium center is linked to one usual O,O-bonded terminal acetylacetonate molecule whereas the other three acetylacetonate units act as bridging functions: each bridges two adjacent ruthenium ions through the terminal O,O-donor centers at one end and via the γ-carbon center at the other end. Moreover, there is a μ_3-sulfido bridging in the center of the complex unit, which essentially resulted via the selective cleavage of the carbon–sulfur bond of the thiouracil ligand. In diamagnetic complex **1**, the ruthenium ions are in mixed valent $Ru^{III}Ru^{III}Ru^{II}$ state, where the paramagnetic ruthenium(III) ions are antiferromagnetically coupled. The single crystal X-ray structure of **1** showed two crystallographically independent C_3-symmetric molecules, Ru_3(*O*,*O*-acetylacetonate)$_3$(μ-*O*,*O*,γ-C-acetylacetonate)$_3$(μ_3-S) (**1**), in the asymmetric unit. Bond distances of both crystallographically independent molecules are almost identical, but there are some significant differences in bond angles (up to 6°) and interplanar angles (up to 8°). Each ruthenium atom exhibits a distorted octahedral environment formed by four oxygen atoms, two from each of the terminal and bridging acetylacetonate units, one γ-carbon of an adjacent acetylacetonate ligand, and the sulfur atom in the center of the complex. In agreement with the expected 3-fold symmetry of the complex molecule, the ^{1}H and ^{13}C NMR spectra of **1** in $CDCl_3$ displayed signals corresponding to two types of ligand units. In dichloromethane solvent, **1** exhibited three metal center based successive quasireversible redox processes, $Ru^{III}Ru^{III}Ru^{III}$–$Ru^{III}Ru^{III}Ru^{II}$ (couple I, 0.43 V vs SCE); $Ru^{III}Ru^{III}Ru^{IV}$–$Ru^{III}Ru^{III}Ru^{III}$ (couple II, 1.12 V); and $Ru^{III}Ru^{II}Ru^{II}$–$Ru^{III}Ru^{II}Ru^{II}$ (couple III, –1.21 V). However, in acetonitrile solvent, in addition to the three described couples [(couple I), 0.34 V; (couple II), 1.0 V; (couple III), –1.0], one irreversible oxidative response ($Ru^{III}Ru^{III}Ru^{IV} \rightarrow Ru^{III}Ru^{IV}Ru^{IV}$ or oxidation of the coordinated sulfide center) appeared at E_{pa}, 1.50 V. The large differences in potentials between the successive couples are indicative of strong coupling between the ruthenium ions in the mixed-valent states. Compound **1** exhibited a moderately strong charge-transfer (CT) transition at 654 nm and multiple ligand based intense transitions in the UV region. In the $Ru^{III}Ru^{III}Ru^{III}$ ($\mathbf{1}^+$) state, the CT band was slightly blue shifted to 644 nm; however, the CT band was further blue shifted to 520 nm on two-electron oxidation to the $Ru^{III}Ru^{III}Ru^{IV}$ ($\mathbf{1}^{2+}$) state with a reduction in intensity.

Introduction

Metal complexes encompassing simultaneous an oxygen and γ-carbon bonded bridging acetylacetonate moiety are relatively rare.[1] Only a few selective examples are reported in dinuclear complexes, $(C_4Ph_4C{=}O)_2Rh^{II}_2$($\mu$-*O*,*O*,$\gamma$-*C*-acetylacetonate)$_2$,[2a] [$(C_5Me_5)_2Rh^{III}_2$($\mu$-*O*,*O*,$\gamma$-*C*-acetylacetonate)$_2$]$(BF_4)_2$,[2b] $(Cp^*)_2Ru^{II}_2$(μ-*O*,*O*,γ-*C*-acetylacetonate)$_2$,[2c−e] Ir^{III}_2(*O*,*O*-acetylacetonate)$_2$(μ-*O*,*O*,γ-*C*-acetylacetonate)$_2$(γ-*C*-

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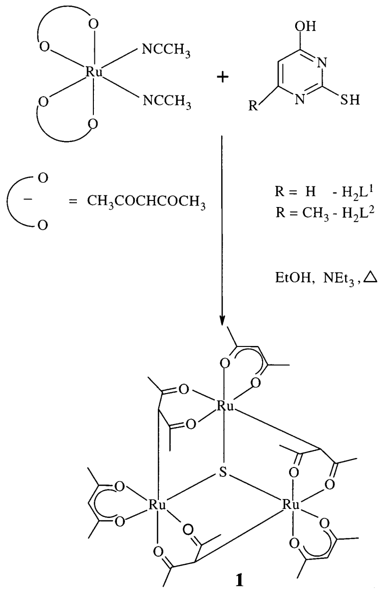
acetylacetonate$)_2$,[2f,g] $(CH_3)_6Pt^{IV}_2(\mu\text{-}O,O,\gamma\text{-}C\text{-acetylacetonate})_2$,[2h] where acetylacetonate ligands bind with one metal ion through the usual O,O-donor sites and the other metal ion via the γ-carbon center. Similarly in heteronuclear complexes, $NBu_4[(C_6F_5)_2Pd^{II}(O,O,\gamma\text{-}C\text{-acetylacetonate})Ag^{I}(O,O,\gamma\text{-acetylacetonate})Pd^{II}(C_6F_5)_2]$,[2i] $Ag^{I}Ni^{II}(O,O,\gamma\text{-}C\text{-acetylacetonate})_3\cdot 2AgNO_3\cdot H_2O$,[2j] and $Ag^{I}Ni^{II}(O,O,\gamma\text{-}C\text{-acetylacetonate})_3\cdot AgNO_3\cdot H_2O$,[2j] acetylacetonate ligands bind with Pd or Ni ions through oxygen centers and the Ag ion via the γ-carbon atom. In $(HgCl)_2C(COCH_3)_2$,[2k] the acetylacetonate ligand binds with one Hg ion via the γ-carbon center, and the other Hg is linked with one of the oxygen centers. The present article illustrates a unique example of symmetric triangular mixed-valent triruthenium complex $(Ru^{III})_2Ru^{II}(O,O\text{-acetylacetonate})_3(\mu\text{-}O,O,\gamma\text{-}C\text{-acetylacetonate})_3(\mu_3\text{-}S)$, **1**, where the complex unit possesses three simultaneous O,O- and γ-carbon bonded bridging acetylacetonate functions in addition to the usual terminal O,O-bonded three acetylacetonate units and one μ_3-bridged sulfido group. Complex **1** has been obtained in an unexpected but facile manner while reacting the precursor mononuclear ruthenium−acetylacetonate complex $Ru^{II}(acac)_2(CH_3CN)_2$, with the thiouracil molecule. Although the thiouracil molecule is well-known to function as a versatile ambidentate ligand with varying coordination modes, including monodentate S-donor,[3] bidentate chelating N,S-donor,[4] bridging N,S-donor,[5] or bridging through terminal N,S- and N,O-donor sites,[6] and retains its structural identity in all these occasions, when it is in contact with $Ru^{II}(acac)_2(CH_3CN)_2$, the selective cleavage of the C−S bond of the thiouracil unit takes place, leading to the preferential formation of μ_3-sulfido bridged triruthenium complex triangle **1**. This unprecedented ruthenium ion mediated selective cleavage of the carbon−sulfur bond of the thiouracil moiety in **1** deserves special attention due to its relevance to the hydrodesulfurization (HDS) process.[7,8] Moreover, it may be noted that the metal−sulfido clusters are important components in fundamental processes such as electron-transfer and reduction of dinitrogen.[9] To the best of our knowledge, the present work demonstrates the first example of a discrete triangular mixed-valent trinuclear metal complex (**1**) incorporating simultaneous *γ-C-* and *O,O-*bonded bridging acetylacetonate moieties and the formation of a μ_3-S unit in **1** via the cleavage of the C−S bond of the thiouracil function. In this paper, we report the synthesis, crystal structure, and spectroscopic and electrochemical properties of **1**.

Scheme 1



Results and Discussion

The reaction of the thiouracil ligand (2-thiouracil, H_2L^1, or 6-methyl-2-thiouracil, H_2L^2) with the mononuclear ruthenium precursor $[Ru^{II}(acac)_2(CH_3CN)_2]$, in the presence of NEt_3 as base, in ethanol solvent afforded initially a dark solution. Chromatographic workup of the dark solution using a neutral alumina column yielded one green complex, $Ru_3(O,O\text{-acetylacetonate})_3(\mu\text{-}O,O,\gamma\text{-}C\text{-acetylacetonate})_3(\mu_3\text{-}S)$ (**1**) (Scheme 1).

In **1**, the terminal acetylacetonate molecules are bonded to the ruthenium centers via the normal O,O-mode whereas the other three acetylacetonate units, acting as bridging functions, each bridge the two ruthenium ions through the terminal O,O-donor centers at one end and via the γ-carbon

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center at the other end. Moreover, there is a μ_3-sulfido bridging in the center of the complex unit, which essentially resulted via the selective cleavage of the carbon−sulfur bond of the thiouracil ligand. In the neutral and diamagnetic complex **1**, the ruthenium ions are in the mixed-valent $\mathrm{Ru^{III}Ru^{III}Ru^{II}}$ state where one-electron paramagnetic ruthenium(III) ions are antiferromagnetically coupled at room-temperature.

The apparent rate and yield of the reaction seemed to be independent of the R groups present in the thiouracil framework. The reaction in Scheme 1 preferentially took place under atmospheric conditions; therefore, aerial oxygen might be responsible for the selective oxidation of the two ruthenium centers in **1**. The presence of strongly σ-donating C, O, and S^{2-} functions in the complex molecule certainly facilitated the stabilization of the metal ions in relatively higher valence states.

Ruthenium, osmium, and cobalt ions mediated selective and facile cleavage of the carbon−sulfur bond of the xanthate molecule {(RO)C(=S)S$^-$},[10a−e] and the cobalt ion assisted C−S bond cleavage of diethyldithiocarbamate{(Et)$_2$N−C-(=S)S$^-$} molecule[10f] has been reported recently; therefore, the reaction in Scheme 1 was tested using xanthate and diethyldithiocarbamate as possible sources of sulfur instead of thiouracil unit, but the desired product, **1**, did not form at all. Similarly, the reaction was also checked with thiophenol and Na_2S instead of thiouracil, but the reactions failed to give desired product **1**, indicating the selective role of thiouracil function in forming complex **1**.

The usual O,O-bonding mode of the acac unit present in the precursor complex [$\mathrm{Ru^{II}(acac)_2(CH_3CN)_2}$] has been observed to retain its identity in the mononuclear and polynuclear complexes derived from it so far.[11] However, during the course of the reaction (Scheme 1), the γ-carbon atom of one of the coordinated acetylacetonate units of the parent Ru(acac)$_2$ core linked to the ruthenium ion of the adjacent second Ru(acac)$_2$ unit. The same process was repeated between the second and third Ru(acac)$_2$ units, and then between the third and first units, which in turn resulted in a symmetric triangular product **1**, in which the bridging units exist in the diketoacetylacetonate form. The presence of the μ_3-bridged sulfido group at the midway of the complex triangle (**1**) possibly suggests the initial coordination of the thiol function of the thiouracil ligand with the Ru(acac)$_2$ core followed by cleavage of the C−S bond and subsequent nucleation processes. The factors which are primarily involved in the ruthenium ion mediated C−S bond cleavage process of the well-known stable thiouracil ligand in **1** are not clear at present. However, it may be noted that the similar μ_3-S bridged triruthenium clusters (Cp*Ru)$_3$(μ-H)$_2$(μ_3-S)(μ_3-CCH$_2$C$_6$H$_5$) and (Cp*Ru)$_3$(μ-H)$_3$(μ_3-S) were reported to form during the reactions of a preformed triruthenium cluster unit, (Cp*Ru)$_3$(μ-H)$_3$(μ_3-H)$_2$, with benzothiophene and dibenzothiophene, respectively, where the insertion of the μ_3-S unit into the cluster framework took place via the cleavage of the C−S bond of the thiophene derivatives.[7] Similarly, in the trinuclear cobalt complex [$\mathrm{Co^{III}{}_3}$(μ_3-S)(μ-CNEt$_2$)(μ-SCNEt$_2$)$_2$(PPh$_3$)$_2$Cl]·2CH$_3$CN, the μ_3-S center inserted in the cluster unit via the C−S bond cleavage of diethyldithiocarbamate molecule.[10f]

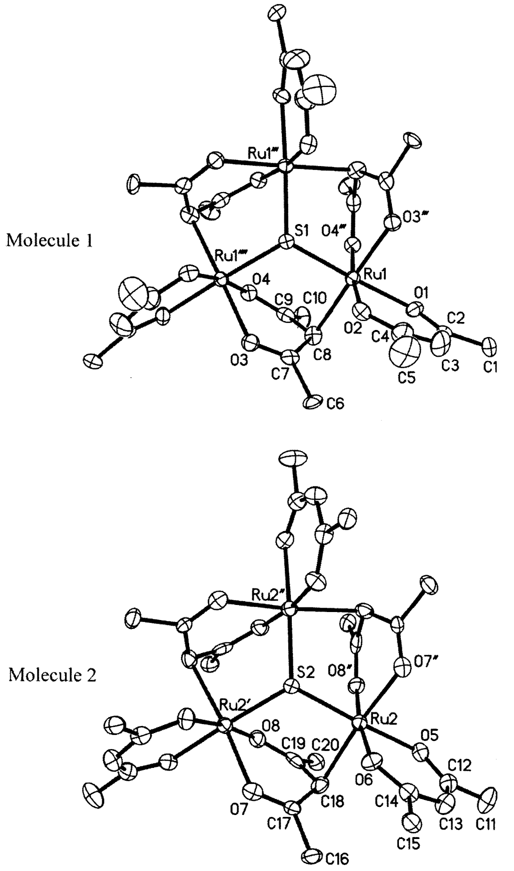

Figure 1. Molecular structures of the crystallographically independent two molecules of $\mathrm{Ru^{III}{}_2Ru^{II}}$(*O,O*-acetylacetonate)$_3$($\mu$-*O,O,γ-C*-acetylacetonate)$_3$(μ_3-S) (**1**). Ellipsoids are drawn at 50% probability level.

The formation of **1** has been authenticated by its single crystal X-ray structure. Mixed-valent complex **1** crystallized with two independent molecules in the unit cell (Figure 1). Important crystallographic data are summarized in Table 1, and selective bond distances and angles are set in Table 2. The C_3-symmetric molecules show two different sets of coordinated acetylacetonate ligands. One acetylacetonate ligand is terminally bonded to one Ru atom via its oxygen atoms, whereas the other bridges two metal centers via the O,O-coordination to one Ru atom and γ-C-coordination to the other. Therefore, each ruthenium atom exhibits a distorted octahedral environment formed by four oxygen atoms, two from each of the terminal and bridging ligands, one γ-carbon of an adjacent bridging ligand, and the sulfur atom in the center of the cluster.

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Table 1. Crystallographic Data for Complex Ru$_3$(*O,O*-acetylacetonate)$_3$(μ-*O,O,*γ-*C*-acetylacetonate)$_3$(μ_3-S) (**1**)

molecular formula	$C_{60}H_{84}O_{24}Ru_6S_2$
fw	1859.8
radiation	Mo Kα
temp/ K	173(2)
cryst symmetry	rhombohedral
space group	$R\bar{3}$
a/Å	16.458 (2)
c/Å	47.153 (9)
V/Å^3	11061(3)
Z	6
μ/mm^{-1}	1.325
D_{calcd}/g cm^{-3}	1.675
2θ range/deg	3−52
unique data (R_{int})	4855 (0.042)
data with $I > 2\sigma(I)$	3095
R1 ($I > 2\sigma(I)$)	0.0617
wR2 (all data)	0.1168
GOF	1.041

Table 2. Important Bond Distances (Å) and Angles (deg) for Crystallographically Independent Two Molecules of Ru$_3$(*O,O*-acetylacetonate)$_3$(μ-*O,O,*γ-*C*-acetylacetonate)$_3$(μ_3-S) (**1**)[a]

molecule 1		molecule 2	
Ru1−O1	2.113(5)	Ru2−O5	2.109(5)
Ru1−O2	2.035(5)	Ru2−O6	2.034(5)
Ru1−O3‴	2.085(5)	Ru2−O7″	2.075(5)
Ru1−O4‴	2.055(5)	Ru2−O8″	2.070(5)
Ru1−S1	2.1714(8)	Ru2−S2	2.1877(10)
Ru1−C8	2.236(8)	Ru2−C18	2.249(8)
O1−C2	1.272(9)	O5−C12	1.280(9)
O2−C4	1.288(10)	O6−C14	1.280(9)
O3−C7	1.258(9)	O7−C17	1.235(9)
O4−C9	1.284(9)	O8−C19	1.267(10)
O1−Ru1−S1	173.17(18)	O5−Ru2−S2	169.87(17)
O1−Ru1−O2	90.0(2)	O5−Ru2−O6	91.7(2)
O1−Ru1−O3‴	89.7(2)	O5−Ru2−O7″	89.3(2)
O1−Ru1−O4‴	85.5(2)	O5−Ru2−O8″	83.4(2)
O1−Ru1−C8	89.1(3)	O5−Ru2−C18	87.1(2)
O2−Ru1−S1	96.86(17)	O6−Ru2−S2	98.35(17)
O2−Ru1−O3‴	85.3(2)	O6−Ru2−O7″	87.7(2)
O2−Ru1−O4‴	172.9(2)	O6−Ru2−O8″	173.4(2)
O2−Ru1−C8	95.0(2)	O6−Ru2−C18	88.9(3)
O3‴−Ru1−S1	90.82(15)	O7″−Ru2−S2	92.55(15)
O3‴−Ru1−O4‴	89.2(2)	O7″−Ru2−O8″	87.9(2)
O3‴−Ru1−C8	178.7(3)	O7″−Ru2−C18	175.0(3)
O4‴−Ru1−S1	87.66(16)	O8″−Ru2−S2	86.75(17)
O4‴−Ru1−C8	90.4(2)	O8″−Ru2−C18	95.2(3)
S1−Ru1−C8	90.4(2)	S2−Ru2−C18	91.6(2)
Ru1−S1−Ru1⁗	117.83(4)	Ru2−S2−Ru2″	116.47(6)

[a] Atoms marked by primes are generated by the following symmetry operations: (″) $-x + y$, $1 - x$, z; (‴) $1 - y$, $x - y$, z; (⁗) $1 - x + y$, $1 - x$, z.

Table 3. Average Selected Bond Distances (Å) in the Six-Membered Chelate Rings in **1** and Ru(acac)$_3$

bond	bridging *O,O,*γ-*C*-bonded ligand in **1**	terminal *O,O*-bonded ligand in **1**	Ru(acac)$_3$
Ru−O	2.071	2.073	2.00
C−C	1.462	1.393	1.40
C−O	1.261	1.280	1.27

Structurally characterized transition metal complexes which contain both O- and γ-C-bonded acetylacetonate ligands are relatively rare.[2] In agreement with the mixed-valent (Ru^{III}Ru^{III}Ru^{II}) character of **1**, the average Ru−O bond length of 2.072 (5) Å is slightly longer than that in Ru^{III}−acetylacetonates with a hexacoordinated metal atom [2.00 (2) Å].[12] It may be noted that the trans influence of the sulfide ligand results in significantly longer Ru(1)−O(1) [2.113(5) Å] and Ru(2)−O(5) [2.109(5) Å] bond lengths. With 2.243 Å, the average Ru−C distance in **1** is ca. 0.17 Å shorter than that in the dimeric Ru^{II} complexes [Cp*Ru(μ-*O,O,*γ-*C*-acetylacetonate)]$_2$[2d] and [Cp*Ru(μ-*O,O,*γ-*C*-benzacetylacetonate)]$_2$[2e] but comparable to the corresponding value in [(Cp*)$_2$Rh$_2$((μ-*O,O,*γ-*C*-acetylacetonate)$_2$](BF$_4$)$_2$.[2b] The average Ru−(μ_3-S) distance of 2.1796 Å seems to be the shortest of this kind reported so far.[13]

Although bond distances of both crystallographically independent molecules are almost identical (Table 2), there are some significant differences in bond angles (up to 6°) and interplanar angles (up to 8°). As can be seen by looking at the distances of the Ru atoms from least-squares C_2O_2 planes [Supporting Information (Table S1a)], the biggest difference concerns the conformation of the six-membered RuO_2C_3 rings in the terminally coordinated acac ligands, which are *planar* in molecule 2 but *envelope* in molecule 1. In contrast, both γ-C-bonded chelate rings possess the *boat* conformation [Supporting Information (Table S1a)].

Unlike the delocalized O,O-bonded enolic terminal acetylacetonate moiety, the μ-O,O,γ-C-bonded bridging unit is expected to exist in the diketonic form where the γ-C center should exhibit sp^3 hybridization. In fact, in **1** the average angle around the γ-C center corresponds to ~109° whereas the same angle in the terminal unit is ~120° as expected from the sp^3- and sp^2-hybridized centers, respectively. The corresponding C−C distances are also supportive of the diketonic form of the bridging unit [the average values of selective bond distances for the two independent molecules (molecule 1 and molecule 2), and those reported for complex Ru(acac)$_3$[12] are set in Table 3]. However, the diketonic form of the bridging unit is not much reflected in the Ru−O and C−O distances (see Table 3). Therefore, the bond distances and angles involving the bridging ligand are essentially suggestive of its ketonic form where a sizable contribution from the corresponding enolic form is also apparent. It should be noted that the presence of similar keto−enol tautomerism for the simultaneous O, O, and γ-C-bonded bridging acetylacetonate unit has also been commented on in earlier occasions.[1,2b,f,h,i]

In agreement with the expected 3-fold symmetry of the complex molecule, the ^{1}H NMR spectrum of **1** in CDCl$_3$ [Supporting Information (Figure S1a)] displayed signals corresponding to two different acetylacetonate units. The coordinated CH proton of the bridging acetylacetonate ligand and the free CH proton associated with the terminal acetylacetonate molecule appeared at δ 4.57 and 5.92 ppm, respectively. The four distinct methyl signals appeared at δ 2.55, 2.23, 2.08, and 1.40 ppm. Similarly, the ^{13}C NMR spectrum of **1** in CDCl$_3$ [Supporting Information (Figure S1b)] showed resonances due to the bridging acetylacetonate

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(13) Research in the CCDC database (version April 2002) for Ru−S distances within a Ru$_3$(μ_3-S) fragment gave 58 hits in the range 2.262−2.443 Å.

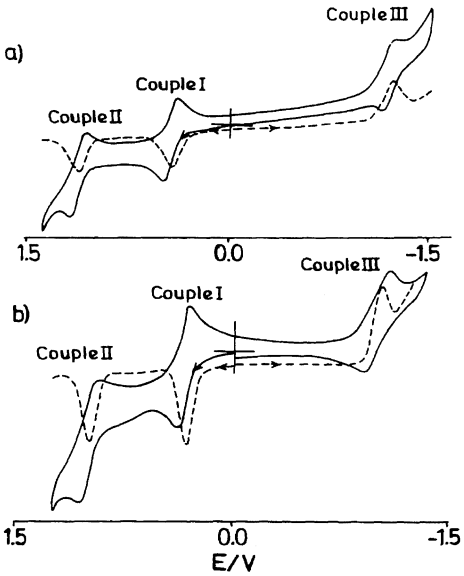

Figure 2. Cyclic voltammograms (—) and differential pulse voltammograms (- - -) of $Ru^{III}{}_2Ru^{II}$(*O,O*-acetylacetonate)$_3$(μ-*O,O,γ-C*-acetylacetonate)$_3$(μ_3-S) (**1**) (a) in dichloromethane and (b) in acetonitrile at 298 K.

unit at δ/ppm 59.34 (coordinated − CH), 220.27/215.39 (C=O), 30.88/30.54 (CH_3), and resonances due to terminal acetylacetonate at 100.84 (free CH), 188.63/186.48 (C=O), 28.95/28.31(CH_3).

The redox properties of **1** have been studied by cyclic voltammetric and differential pulse voltammetric experiments using a platinum working electrode in dichloromethane and acetonitrile solvents. It exhibited two successive quasi-reversible oxidative couples; $E°_{298}$, V (ΔE_p, mV) values follow: 0.43(100) (couple I), 1.12 (100) (couple II) and one reductive response at −1.21 (150) (couple III) versus SCE in dichloromethane solvent (Figure 2a). The one-electron nature of couple I was established by constant-potential coulometry, and the same for couples II and III was established by comparing their differential pulse voltammetric current heights with that for couple I. The observed couples are assigned to stepwise electron-transfer processes involving the metal centers: $Ru^{III}Ru^{III}Ru^{III}-Ru^{III}Ru^{III}Ru^{II}$ (couple I), $Ru^{III}Ru^{III}Ru^{IV}-Ru^{III}Ru^{III}Ru^{III}$ (couple II), and $Ru^{III}Ru^{III}Ru^{II}-Ru^{III}Ru^{II}Ru^{II}$ (couple III). In acetonitrile solvent, in addition to the three described couples [$E°_{298}$, V(ΔE_p, mV): 0.34(80) (couple I), 1.0(90) (couple II), −1.0 (couple III) (Figure 2b)], one irreversible oxidative response appeared at E_{pa}, 1.50 V (which is not shown in the figure). This irreversible oxidative response could be due to the metal centered $Ru^{III}Ru^{III}Ru^{IV} \rightarrow Ru^{III}Ru^{IV}Ru^{IV}$ process or oxidation of the coordinated sulfide function.

The large separations in potentials between the successive couples (Figure 2a), 690 mV for couple I/couple II and 1640 mV for couple I/couple III, respectively, in the dichloromethane solvent [the same in acetonitrile solvent were calculated to be 665 mV and 1340 mV, respectively (Figure 2b)] are indicative of the bridging function mediating strong electronic coupling between the ruthenium ions in the respective mixed-valent states.[6a,14] It is to be noted that the μ_3-oxo−triruthenium acetate complexes also exhibited similar successive metal based redox processes where the ruthenium centers are strongly coupled in the mixed-valent states, as has been observed in the present case.[15]

Although the responses (couples I−III) are reasonably reversible at the cyclic voltammetric time scale, coulometrically oxidized ($\mathbf{1}^+$, $\mathbf{2}^+$) and reduced species ($\mathbf{1}^-$) were found to be unstable at 298 K. Therefore, no specific attempt was made to isolate the higher and lower congeners of **1**.

In dichloromethane, **1** exhibited a moderately strong charge-transfer (CT) band in the visible region and multiple ligand based intense transitions in the UV region [λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 654 (6700); 430 (9500); 352 (15930); 276 (32400); 231 (46500)] [Supporting Information (Figure S2)]. Electrochemically generated bluish green one-electron oxidized species $Ru^{III}Ru^{III}Ru^{III}$ ($\mathbf{1}^+$) was found to be reasonably stable under a dinitrogen atmosphere at room-temperature. On oxidation to $\mathbf{1}^+$, the 654 nm CT band of **1** was slightly blue shifted to 644 nm without a change in intensity [Supporting Information (Figure S2)] [λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 644 (6750); 326 (16100); 266 (28200); 231 (49860)]. The electrochemically generated two-electron oxidized species $Ru^{III}Ru^{III}Ru^{IV}$($\mathbf{1}^{2+}$) was unstable even under dinitrogen atmosphere at 298 K, slowly decomposing to an unidentified product. The CT band for $\mathbf{1}^{2+}$ was further blue shifted to 520 nm with a reduction in intensity [Supporting Information (Figure S2)] [λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 520 (4360); 346 (16960); 286 (31850); 233 (45360)]. On the other hand, the reduced species $Ru^{III}Ru^{II}Ru^{II}$ ($\mathbf{1}^-$) was too unstable to be handled at room-temperature.

Conclusion

We have thus observed the formation of an unusual μ_3-sulfido bridged triangular mixed-valent triruthenium complex, $Ru^{III}{}_2Ru^{II}$(*O,O*-acetylacetonate)$_3$(μ-*O,O,γ-C*-acetylacetonate)$_3$(μ_3-S) (**1**), encompassing simultaneous O,O- and γ-carbon-bonded bridging acetylacetonate moieties. The unexpected formation of **1** from the mononuclear ruthenium precursor complex [$Ru^{II}(acac)_2(CH_3CN)_2$], in the presence of a thiouracil ligand, primarily involves the cleavage of the C−S bond of the thiouracil moiety and subsequent nucleation processes via the active participation of the γ-carbon center of the acac units and the insertion of a μ_3-S unit in the complex triangle. Thus, the present work illustrates the following important features: (i) the first example of

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ruthenium mediated selective and facile cleavage of the carbon−sulfur bond of the thiouracil molecule; (ii) the first example of μ_3-sulfido bridged triruthenium complex triangle (**1**) incorporating simultaneous oxygen and γ-carbon bonded bridging acetylacetonate moieties; (iii) preferential stabilization of the metal ions in mixed valent $Ru^{III}Ru^{III}Ru^{II}$ state in **1**, where the paramagnetic ruthenium(III) centers are antiferromagnetically coupled at room-temperature; (iv) **1** exhibiting successive electron-transfer processes to $Ru^{III}Ru^{III}Ru^{III}$ ($\mathbf{1}^+$)−$Ru^{III}Ru^{III}Ru^{II}$ (**1**), $Ru^{III}Ru^{III}Ru^{IV}$ ($\mathbf{1}^{2+}$)−$Ru^{III}Ru^{III}Ru^{III}$ ($\mathbf{1}^+$), $Ru^{III}Ru^{IV}Ru^{IV}$ ($\mathbf{1}^{3+}$)−$Ru^{III}Ru^{III}Ru^{IV}$ ($\mathbf{1}^{2+}$) (or oxidation of the coordinated sulfide center), and $Ru^{III}Ru^{III}Ru^{II}$ (**1**)−$Ru^{III}Ru^{II}Ru^{II}$ ($\mathbf{1}^-$).

Experimental Section

The starting complex, $Ru(acac)_2(CH_3CN)_2$, was prepared according to the reported procedure.[11d] 2-Thiouracil (H_2L^1) and 6-methyl-2-thiouracil (H_2L^2) were obtained from Aldrich. Other chemicals and solvents were reagent grade and used as received. For spectroscopic and electrochemical studies, HPLC grade solvents were used. Commercial tetraethylammonium bromide was converted into pure tetraethylammonium perchlorate by following an available procedure.[16]

UV−vis spectra were recorded with a Shimadzu-2100 spectrophotometer. FT-IR spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. Solution electrical conductivity was checked using a Systronic 305 conductivity bridge. Magnetic susceptibility was checked with a PAR vibrating sample magnetometer. $^1H/^{13}C$ NMR spectra were obtained with a 300 MHz Varian FT spectrometer. Cyclic voltammetric, differential pulse voltammetric, and coulometric measurements were carried out using a PAR model 273A electrochemistry system. Platinum wire working and auxiliary electrodes and an aqueous saturated calomel reference electrode (SCE) were used in a three electrode configuration. The supporting electrolyte was $[NEt_4]ClO_4$, and the solute concentration was $\sim 10^{-3}$ M. The half-wave potential $E°_{298}$ was set equal to $0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetric peak potentials, respectively. A platinum wire-gauze working electrode was used in coulometric experiments. All experiments were carried out under a dinitrogen atmosphere and were uncorrected for junction potentials. The elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. The electrospray mass spectrum was recorded on a Finnigan LCQ ADVANTAGE mass spectrometer.

Synthesis of Ru_3(*O,O*-acetylacetonate)$_3$(μ-*O,O,γ-C*-acetylacetonate)$_3$(μ_3-S)·0.5NEt$_3$ (1). Starting complex $Ru(acac)_2(CH_3CN)_2$ (100 mg, 0.26 mmol), 2-thiouracil ligand (H_2L^1, 12.8 mg, 0.13 mmol), and excess triethylamine (0.1 mL 0.72 mmol) were taken in 20 mL of ethanol, and the mixture was heated at reflux for 4 h. The initial orange color of the solution gradually changed to dark. The solvent was then removed under reduced pressure. The solid mass thus obtained was purified by using a neutral alumina column. Initially, a red solution corresponding to $Ru(acac)_3$ was eluted by $C_6H_6-CH_2Cl_2$ (2/1). With $CH_2Cl_2-CH_3CN$ (25/1), a green solution corresponding to **1** was separated later on, leaving behind a dark mass at the top of the column. Evaporation of solvent under reduced pressure afforded complex **1**. It was necessary to repeat the same operations using a second alumina column in order to obtain pure complex **1**. Yield: 25 mg (30%). Anal. Calcd (Found) for **1**: C, 44.06 (43.83); H, 5.81 (5.82); N, 0.070 (0.074).

The positive ion electrospray mass spectrum of **1** showed a strong molecular ion peak centered at *m*/*z* 933.3 (calculated molecular weight, 931.95).

Crystal Structure Determination. Single crystals of **1** were grown by slow evaporation of its dichloromethane solution. The X-ray data were collected at 173 K using a Siemens P3 diffractometer. Selected data collection parameters and other crystallographic data are summarized in Table 1. Calculations were carried out with the SHELXTL PC 5.03[17] and SHELXL-97[18] program systems installed on local personal computers. The phase problem was solved by direct methods, and the structure was refined on F_0^2 by full-matrix least-squares refinement. An absorption correction was applied by using semiempirical ψ-scans. Anisotropic thermal parameters were refined for all non-hydrogen atoms. H atoms were placed in the idealized positions and refined in a riding model approximation, including free rotation for the methyl group. A common isotropic displacement parameter was refined for CH and CH_3 hydrogen atoms, respectively. During the refinement, severely disordered triethylamine and acetonitrile molecules were located in three solvent accessible cavities (total volume 1134 Å^3). Since the disordered molecules could not be successfully modeled, their contribution was eliminated from the reflection data, using the BYPASS[19] method as implemented in the SQUEEZE routine of the PLATON98[20] package. Final *R* values are listed in Table 1.

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Supporting Information Available: X-ray crystallographic data for **1** in CIF format. ^1H and ^{13}C NMR spectra (Figure S1) and electronic spectra of **1**, $\mathbf{1}^+$, and $\mathbf{1}^{2+}$ at 298 K (Figure S2). Distances from least-squares planes (Å) and interplanar angles (deg) in the two crystallographically independent molecules for **1** (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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