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New μ-Disulfido and μ-Diselenido Complexes of Ruthenium(III). Crystal Structure of $[\{LRu^{III}(acac)\}_2(\mu\text{-}S_2)](PF_6)_2$ (L = 1,4,7-Trimethyl-1,4,7-triazacyclononane; acac = Pentane-2,4-dionate)

Ralf Schneider and Karl Wieghardt*

Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-44780 Bochum, Germany

Bernhard Nuber

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270,
D-69120 Heidelberg, Germany

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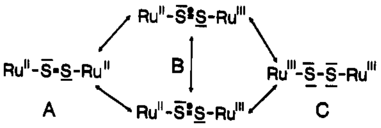
Reaction of the mononuclear species $[LRu(acac)(OH)]PF_6\cdot H_2O$ in alkaline aqueous solution with $Na_2S\cdot xH_2O$ and H_2Se yields the dinuclear species $[\{LRu(acac)\}_2(\mu\text{-}S_2)](PF_6)_2$ (**1**) and $[\{LRu(acac)\}_2(\mu\text{-}Se_2)](PF_6)_2$ (**2**), respectively, where L represents 1,4,7-trimethyl-1,4,7-triazacyclononane and acac = pentane-2,4-dionate. The crystal structure of **1** has been determined by X-ray crystallography at 295 K: triclinic space group $P\bar{1}$, $a = 8.157(5)$ Å, $b = 11.526(6)$ Å, $c = 12.184(6)$ Å, $\alpha = 76.11(4)°$, $\beta = 86.52(4)°$, $\gamma = 77.51(4)°$, $V = 1085.6(15)$ Å^3, $Z = 1$, $R = 0.038$, and $R_w = 0.035$. The Ru–S and S–S bond distances of 2.202(2) and 1.989(2) Å, respectively, the electronic spectrum, the electrochemistry, and the diamagnetism of **1** are indicative of an exchange-coupled dinuclear ruthenium(III) species containing an S_2^{2-} bridge. Similar results are reported for the μ-diselenido species **2**.

Introduction

Since the original synthesis and spectroscopic characterization of the first dinuclear ruthenium(III) complex containing a μ-disulfido bridge, namely $[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]^{4+}$, in 1973,[1] a small number of such complexes with organometallic ligands such as the cyclopentadienyl anion and phosphines have been prepared and structurally characterized.[2,3] A μ-disulfido-bridged species containing coordinated thioether and thiolato ligands has been described recently by Sellmann and co-workers.[4,5] The impetus for this work stems mainly from the puzzling electronic and magnetic properties of these seemingly simple compounds.[6] Their electronic structure has been discussed in the frame of the resonance structures depicted in Scheme I. For example, Elder and Trkula[7] proposed a supersulfide S_2^- bridge and ruthenium(II,III) ions in $[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]^{4+}$ whereas Isied et al.[8] showed later by using resonance Raman spectroscopy that a description with localized oxidation states (Ru(III)) and a S_2^{2-} bridge is more appropriate. On the other hand, Isied et al.[8] and subsequently Sellmann et al.,[5] have adopted the view that the [Ru–S–S–Ru]$^{4+}$ core is best described by a delocalized molecular orbital scheme (4c–6e π-system). The corresponding μ-diselenido moiety has only recently been structurally characterized in $[\{CpRu(PPh_3)_2\}_2(\mu\text{-}\eta^1,\eta^1\text{-}Se_2)](OTf)_2$.[9]

Scheme I



We describe here the synthesis and characterization of two complexes, namely $[\{LRu(acac)\}_2(\mu\text{-}\eta^1,\eta^1\text{-}S_2)](PF_6)_2$ (**1**) and its μ-η^1,η^1-diselenido analogue **2**. In the companion paper we have reported a series of mononuclear and μ-oxo-bridged dinuclear ruthenium(III) complexes containing the stable fragment LRu^{III}(acac), where L represents the macrocyclic triamine 1,4,7-trimethyl-1,4,7-triazacyclononane and acac is the chelating ligand pentane-2,4-dionate.[10] It is therefore possible to gain detailed insight from structural and spectroscopic data of this series of complexes into the electronic structure of the μ-disulfido and μ-diselenido species **1** and **2**.

Experimental Section

Preparation of Complexes. The starting material $[LRu(acac)(OH)]PF_6\cdot H_2O$ has been prepared as described previously.[10]

$[\{LRu^{III}(acac)\}_2(\mu\text{-}S_2)](PF_6)_2$ (1). To a solution of $Na_2S\cdot xH_2O$ (0.15 g; ~1.1 mmol) in water (15 mL) was added with vigorous stirring dropwise a solution of $[LRu(acac)(OH)]PF_6\cdot H_2O$ (0.10 g; 0.19 mmol) in water (5 mL) at ambient temperature in the presence of air. The pH of the solution was adjusted to 10 by addition of solid NaOH. The resulting solution was stirred for 3 h, during which time a color change from brown to dark green was observed. Addition of $NaPF_6$ (0.5 g) and cooling to 0 °C initiated the precipitation of green microcrystals, which were collected by filtration, washed with cold water, and dried in vacuo over $CaCl_2$. Yield: 0.06 g (58%). Anal. Calcd for $C_{28}H_{56}F_{12}N_6O_4P_2Ru_2S_2$: C, 30.7; H, 5.2; N, 7.7; S, 5.9. Found: C, 29.9; H, 4.9; N, 7.4; S, 6.1.

Suitable single crystals for an X-ray structure determination were grown from a warm (~50 °C), saturated aqueous solution of **1** by slow evaporation of the solvent within 4 days.

Fast atom bombardment mass spectrum FABMS (positive ion, ^{101}Ru, ^{32}S, m/z): 953 ($[\{LRu(acac)\}_2(\mu\text{-}S_2)]PF_6^+$), 808 ($[\{LRu(acac)\}_2(\mu\text{-}S_2)]^+$), 436 ($[LRu(acac)S_2]^+$), 404 ($[LRu(acac)S]^+$), 372 ($[LRu(acac)]^+$).

$[\{LRu(acac)\}_2(\mu\text{-}Se_2)](PF_6)_2$ (2). All manipulations were carried out under an argon-blanketing atmosphere in a well-ventilated hood. Only diffuse light was allowed to illuminate the closed all glass apparatus.

[•] Abstract published in *Advance ACS Abstracts,* October 1, 1993.

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Table I. Crystallographic Data for $[\{LRu(acac)\}_2(\mu\text{-}S_2)](PF_6)_2$

chem formula	$C_{28}H_{56}F_{12}N_6O_4P_2Ru_2S_2$
fw	1097
space group	$P\bar{1}$
a, Å	8.157(5)
b, Å	11.526(6)
c, Å	12.184(6)
α, deg	76.11(4)
β, deg	86.52(4)
γ, deg	77.51(4)
V, Å^3	1085.6(15)
Z	1
ρ_{calcd}, g·cm^{-3}	1.68
temp, °C	20
radiation (λ, Å)	Mo Kα (0.710 73)
abs coeff, mm^{-1}	0.94
min/max transm coeff	0.93–1.0
R^a	0.038
$R_w{}^a$	0.035

[a] Residuals: $R = \sum\|F_o| - |F_c\|/\sum|F_o|$; $R_w = \{\sum w(F_o - F_c)^2/\sum w|F_o|^2\}^{1/2}$.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $C_{28}H_{56}F_{12}N_6O_4P_2Ru_2S_2$ (**1**)

atom	x	y	z	U(eq)^a
Ru(1)	593(1)	1798(1)	3173(1)	32(1)
S(1)	555(1)	−25(1)	4254(1)	43(1)
O(1)	−1859(3)	2468(2)	3593(2)	40(1)
O(2)	1480(3)	2363(2)	4442(2)	46(1)
C(11)	−4140(4)	3307(4)	4633(3)	59(2)
C(12)	−2276(5)	2926(3)	4457(3)	42(1)
C(13)	−1177(5)	3087(3)	5218(3)	46(1)
C(14)	555(5)	2806(3)	5190(3)	47(2)
C(15)	1500(6)	3032(4)	6110(3)	80(2)
N(1)	618(4)	3522(3)	1963(3)	48(1)
N(2)	−45(4)	1291(3)	1712(2)	44(1)
N(3)	3076(3)	1312(3)	2544(2)	44(1)
C(1)	−655(6)	3539(4)	1118(3)	68(2)
C(2)	−333(5)	2389(4)	739(3)	66(2)
C(3)	1455(5)	356(4)	1486(3)	62(2)
C(4)	3042(5)	749(4)	1551(3)	63(2)
C(5)	3613(5)	2512(4)	2173(3)	60(2)
C(6)	2343(5)	3489(4)	1454(4)	68(2)
C(7)	61(5)	4612(3)	2449(3)	66(2)
C(8)	−1561(5)	746(4)	1854(3)	66(2)
C(9)	4257(4)	477(4)	3422(3)	66(2)
P(1)	5363(2)	3113(1)	8509(1)	65(1)
F(11)	7218(5)	3108(5)	8275(3)	196(3)
F(12)	3495(4)	3071(4)	8797(3)	178(3)
F(13)	5846(5)	1905(3)	9431(3)	139(2)
F(14)	4893(7)	4230(4)	7585(3)	228(3)
F(15)	5438(6)	3754(4)	9463(3)	191(3)
F(16)	5402(5)	2371(3)	7596(3)	138(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Caution! *H_2Se is extremely poisonous.* Unreacted H_2Se gas was passed through a cascade of semiconcentrated nitric acid containing flasks generating red elemental selenium in a hood.

Method A. H_2Se was prepared under an argon atmosphere from ZnSe (3.34 g) by slow dropwise addition of concentrated HCl. Excess HCl was removed from the resulting H_2Se gas by passing it through degassed H_2O in a gas-scrubbing column. The HCl free gas was then passed through a solution of $[LRu(acac)(OH)]PF_6 \cdot H_2O$ (0.25 g; 0.47 mmol) and NaOH (2.0 mmol) in water (25 mL) in a period of time of ~5 h at room temperature. The resulting turbid brown-green mixture was filtered under an argon atmosphere. The green residue was washed with small amounts of dioxygen-free H_2O, ethanol, and diethyl ether and dried under reduced pressure for 1 h at room temperature. The yield was ~40% based on the ruthenium starting complex.

Method B. A three-necked flask containing a suspension of elemental gray selenium (1.15 g; 14.5 mmol) and water (15 mL) was fitted with two dropping funnels containing a degassed solution of $Na[BH_4]$ (1.15 g; 30.5 mmol) in H_2O (10 mL) and an alkaline aqueous solution (10 mL) of $[LRu(acac)(OH)](PF_6) \cdot H_2O$, respectively. The first solution was added dropwise within 15 min to the solution containing the selenium. *Caution*! *This is a reaction with vigorous evolution of hydrogen and heat.* After cooling of the reaction mixture to room temperature, the solution of the second funnel containing the ruthenium complex was added dropwise with stirring. The resulting solution was stirred at room temperature for 4 h, during which time a green precipitate formed. The workup was as described above. The yields were similar as for method A, but the product was found to be not quite as pure. Anal. Calcd for $C_{28}H_{56}F_{12}N_6O_4P_2Ru_2Se_2$: C, 28.2; H, 4.7; N, 7.0; Se, 13.3. Found: C, 27.9; H, 4.5; N, 7.0; Se, 15.0. FABMS (positive ion, ^{101}Ru, ^{79}Se, m/z): 1044 ($[\{LRu(acac)\}_2(\mu\text{-}Se_2)]PF_6^+$), 899 ($[\{LRu(acac)\}_2(\mu\text{-}Se_2)]^+$), 529 ($[LRu(acac)(Se_2)]^+$), 452 $[LRu(acac)Se]^+$), 372 ($[LRu(acac)]^+$).

Physical Measurements. The equipment used for UV/vis/near-IR, infrared, NMR, and ESR spectroscopy, cyclic voltammetry, and measurements of temperature-dependent magnetic susceptibilities is the same as described in ref 10.

X-ray Structure Determination. Intensities and lattice parameters of a brown-green dichroic, irregularly shaped crystal of **1** were measured on an AED II (Siemens) diffractometer at ambient temperature by using monochromated Mo Kα radiation. Crystal parameters and details of the data collection and refinement are summarized in Table I (for full details, see supplementary material). An empirical absorption correction (ψ-scans of seven reflections in the range $10 \leq 2\theta \leq 47°$) was carried out. The structure was solved by conventional Patterson and difference Fourier methods. The Siemens program package SHELXTL-PLUS was used. The function minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F)$. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 11. The positions of hydrogen atoms of the methylene groups were placed at calculated positions with d(C–H) = 0.96 Å and isotropic thermal parameters, while the methyl groups were treated as rigid bodies each with three rotational variables. All non-hydrogen atoms were refined with anisotropic thermal parameters. Table II gives the atom coordinates of **1**.

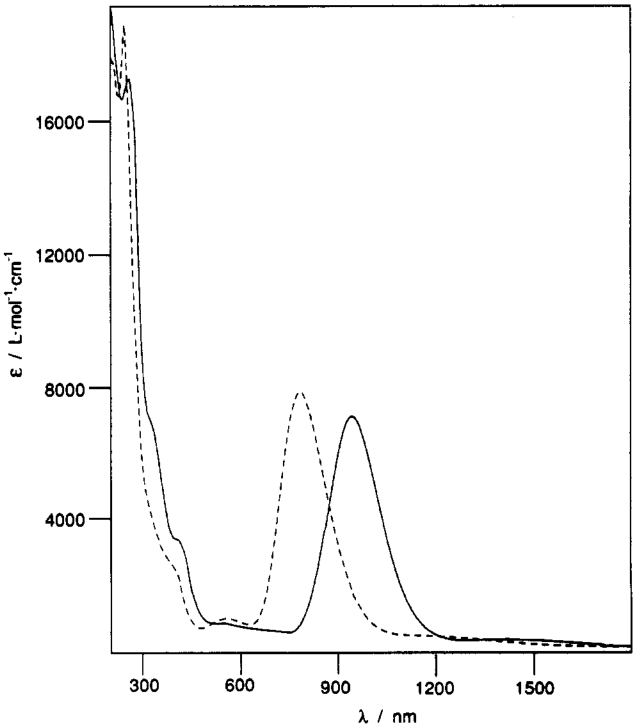

Figure 1. Electronic spectra of **1** (- - -) and **2** (—) in acetonitrile at ambient temperature.

Results and Discussion

Synthesis and Characterization of Complexes 1 and 2. The reaction of $[LRu(acac)(OH)]PF_6 \cdot H_2O^{10}$ in an alkaline aqueous solution with excess sodium sulfide in the presence of air at ambient temperature affords a deep green solution from which upon addition of $NaPF_6$ green crystals of $[\{LRu(acac)\}_2(\mu\text{-}\eta^1,\eta^1\text{-}S_2)]$-

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(11) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

Table III. Comparison of Electronic Spectra of μ-η^1,η^1-S_2^{2-} and μ-η^1,η^1-Se_2^{2-} Bridged Ruthenium Complexes

complex[a]	solvent	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	ref
$[\{LRu(acac))\}_2(\mu\text{-}Se_2)]^{2+}$	*b*	274 (1.71×10^4), 340 (6.9×10^3) sh, 415 (3.4×10^3) sh, 560 (950) sh, 670 (810) sh, 946 (7.0×10^3), 1400 (450)	this work
$[\{(\eta^5\text{-}Cp)Ru(PPh_3)_2\}_2(\mu\text{-}Se_2)](OTf)_2$	*c*	370 sh, 480 sh, 790 (8.18×10^3)	9
$[\{LRu(acac)\}_2(\mu\text{-}S_2)]^{2+}$	*b*	262 (1.91×10^4), 410 (2.6×10^3) sh, 569 (975), 798 (8.0×10^3), 1210 (390)	this work
$[\{Ru'S_4(PPh_3)\}_2(\mu\text{-}S_2)]$	*c*	640 (8.97×10^3), 1049 (1.37×10^4)	5
$[\{\eta^5\text{-}Cp)Ru(PPh_3)_2\}_2(\mu\text{-}S_2)]^{2+}$	*c*	362 (1.9×10^4), 445 sh, 718 (3.2×10^4), 820 sh	3
$[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]^{4+}$	*d*	235 (2.2×10^4), 284 (5.4×10^3), 390 (1.2×10^3), 720 (1.7×10^4)	1

[a] Abbreviations: L = 1,4,7-trimethyl-1,4,7-triazacyclononane, acac = pentane-2,4-dionate, Cp = cyclopentadienylate, Ph = phenyl, 'S$_4$' = 2,2'-(ethylenedithio)bis(thiophenolate)(2–). [b] CH_3CN. [c] CH_2Cl_2. [d] H_2O.

$(PF_6)_2$ (**1**) precipitated in 50% yield. The corresponding μ-diselenido species $[\{LRu(acac)\}_2(\mu\text{-}\eta^1,\eta^1\text{-}Se_2)](PF_6)_2$ (**2**) was prepared analogously in 40% yield by using H_2Se or sodium selenide as reagent. Complex **1** is air-stable both in the solid state and in solution, whereas **2** decomposes rapidly in solution and slowly in the solid state in the presence of oxygen with formation of red elemental selenium. The positive-ion fast atom bombardment mass spectra of **1** and **2** show envelopes of peaks corresponding to the ions $[\{LRu(acac)\}_2(X_2)](PF_6)^+$ and several of its fragments, where X is sulfur and selenium, respectively, indicating the dinuclear character of **1** and **2**.

The electronic spectra of **1** and **2** in acetonitrile are shown in Figure 1; Table III summarizes electronic spectral data of (μ-disulfido)- and (μ-diselenido)ruthenium(III) complexes. Complexes containing the $[Ru_2(\mu\text{-}\eta^1,\eta^1\text{-}S_2)]^{4+}$ core and their μ-diselenido counterparts all display very intense absorption maxima ($\epsilon > 10^3$ L mol^{-1}) in the visible and one less intense absorption in the near-infrared region (near-IR). Sellmann's complex $[\{Ru\text{'}S_4\text{'}\}_2(\mu\text{-}S_2)]$ is very interesting in this respect because the near-IR band at 1049 nm is more intense than the absorption in the visible at 798 nm.[4,5] For $[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]^{4+}$ the near-IR band has not been reported but the published spectrum has only been recorded up to 850 nm.[8] Sellmann et al. have assigned these bands to $\pi \rightarrow \pi^*$ transitions within the $[Ru\text{–}S\text{–}S\text{–}Ru]^{4+}$ core (4c–6e π system). In line with this interpretation is the observation that substitution of the μ-S_2^{2-} by a μ-Se_2^{2-} bridge induces a shift of these two absorption maxima to lower energy. A μ-diselenido ligand is expected to be a stronger π-donor than a μ-S_2 group, and it therefore destabilizes the HOMO π-orbital to a greater extent. Interestingly, the same trend has been reported for the organometallic species $[\{CpRu(PPh_3)_2\}_2\mu\text{-}X_2]^{2+}$ (X = S, Se).[3,9]

The magnetic susceptibility of a powder sample of **1** was measured in the temperature range 2.0–295 K by using a SQUID magnetometer; the data were corrected for underlying diamagnetism by use of tabulated Pascal constants. The effective magnetic moment was found to decrease monotonically from 1.11 μ_B per dinuclear unit at 295 K to 0.46 μ_B at 2.0 K. The same solid sample was found to be ESR silent at 4.2 K. In agreement with Isied's[8] and Sellmann's[4,5] results we attribute this small residual paramagnetism to a mononuclear Ru(III) or Ru(IV) impurity. In accord with this interpretation are the ^{1}H NMR results presented below which clearly indicate diamagnetism for both **1** and **2**.

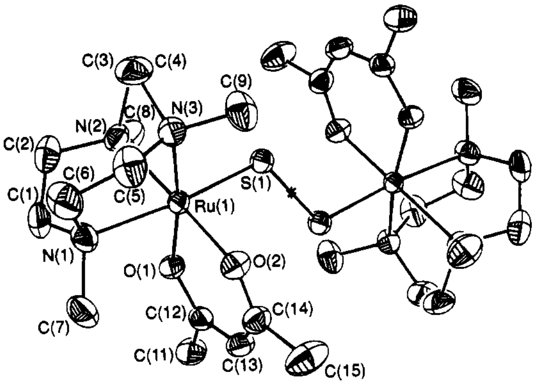

Figure 2. Perspective view and atom-labeling scheme for the dication in crystals of **1**. The asterisk denotes a crystallographic inversion center.

Table IV. Selected Bond Distances (Å) and Angles (deg) of the Dication in Crystals of $[\{LRu(acac)\}_2(\mu\text{-}S_2)](PF_6)_2$

Ru(1)–S(1)	2.202(2)	Ru(1)–N(2)	2.127(3)
Ru(1)–O(1)	2.063(2)	Ru(1)–N(3)	2.128(3)
Ru(1)–O(2)	2.040(3)	S(1)–S(1A)	1.989(2)
Ru(1)–N(1)	2.174(3)	O(1)–C(12)	1.284(5)
O(2)–C(14)	1.278(5)	C(11)–C(12)	1.506(5)
C(12)–C(13)	1.397(6)	C(13)–C(14)	1.380(6)
C(14)–C(15)	1.501(7)		
S(1)–Ru(1)–O(1)	92.0(1)	O(1)–Ru(1)–N(1)	89.6(1)
S(1)–Ru(1)–O(2)	92.6(1)	O(2)–Ru(1)–N(1)	92.8(1)
O(1)–Ru(1)–O(2)	91.5(1)	S(1)–Ru(1)–N(2)	92.3(1)
S(1)–Ru(1)–N(1)	174.3(1)	O(1)–Ru(1)–N(2)	94.7(1)
O(2)–Ru(1)–N(2)	172.0(1)	N(1)–Ru(1)–N(2)	82.2(1)
S(1)–Ru(1)–N(3)	95.4(1)	O(1)–Ru(1)–N(3)	172.2(1)
O(2)–Ru(1)–N(3)	90.8(1)	N(1)–Ru(1)–N(3)	82.9(1)
N(2)–Ru(1)–N(3)	82.5(1)	Ru(1)–S(1)–S(1A)	113.4(1)

X-ray photoelectron data of **1** and its oxo-bridged analogue $[\{LRu^{III}(acac)\}_2(\mu\text{-}O)](PF_6)_2$[10] were recorded in the range 275–300 eV. Peaks occur in this region due to ruthenium (Ru $3d_{3/2}$ and Ru $3d_{5/2}$) and carbon (C 1s) electron transitions. Oxygen signals (O 1s) of the coordinated pentane-2,4-dionate have been recorded at 535.6 eV for the oxo complex and at 534.9 eV for **1**. All binding energies reported in this work were measured relative to an arbitrarily assigned value of 284.4 eV for the C 1s peak due to the methylene carbon atoms of the cyclic amine and acac ligands. This approach has been adopted for the sake of consistency of our data with those reported by Meyer et al.[12] for $[\{(bpy)_2ClRu^{III}\}_2(\mu\text{-}O)](PF_6)_2$, $[Ru^{III}(bpy)_2Cl_2]Cl$, and $[Ru^{II}(bpy)_2Cl_2]$ for which Ru $3d_{5/2}$ binding energies of 280.5, 281.9, and 279.9 eV have been reported. Binding energies for **1** and $[\{LRu(acac)\}_2(\mu\text{-}O)](PF_6)_2$ were found at 279.4 and 280.0 eV, respectively. Two interesting facts emerge from these measurements. First, the two oxo-bridged diruthenium complexes have very similar Ru $3d_{5/2}$ binding energies and they are closer to the value expected for ruthenium(II) than the value expected for ruthenium(III). This has already been noted by Meyer et al. and indicates a consistent trend for complexes with the Ru^{III}–O–Ru^{III} core irrespective of the nature of other terminal ligands. Second, substitution of the oxo by a bridging, softer disulfido ligand in otherwise identical diruthenium species lowers the Ru $3d_{5/2}$ binding energy only marginally. One could argue that the Ru XPS data for **1** support the assignment of Ru(II) rather than Ru(III), but in this case this would also have to be true for the oxo-bridged species. It is the similarity of the Ru $3d_{5/2}$ binding energies in the present complexes containing $[Ru\text{–}O\text{–}Ru]^{4+}$ and $[Ru\text{–}S\text{–}S\text{–}Ru]^{4+}$ cores that lead us to the conclusion that in both instances a description as ruthenium(III) species is appropriate.

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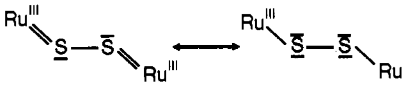
Table V. Comparison of Structural Data for (μ-Disulfido)ruthenium Complexes[a]

complex	d(S–S), Å	d(Ru–S), Å	dihedral angle Ru–S–S–Ru, deg		ref
$[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]^{4+}$	2.014(1)	2.191(1)	180	trans	7
		2.195(1)			
$[\{(\eta^5\text{-}Cp)Ru(PMe_3)_2\}_2(\mu\text{-}S_2)]^{2+}$	1.962(4)	2.208(3)	180	trans	3
$[\{Ru(PPh_3)\text{'}S\text{'}_4\}_2(\mu\text{-}S_2)]\cdot 2CS_2$	1.991(4)	2.245(3)	174.9	trans	5
		2.242(3)			
$[\{LRu(acac)\}_2(\mu\text{-}S_2)]^{2+}$	1.989(2)	2.202(2)		trans	this work
$[\{Ru(AN)_3(TMP)_2\}_2(\mu\text{-}S_2)]^{3+}$	1.995(3)	2.322(2)		trans	15

[a] Abbreviations: Cp = cyclopentadienylate, Me = methyl, Ph = phenyl, 'S_4' = 2,2′-(ethylenedithio)bis(thiophenolate)(2–), L = 1,4,7-trimethyl-1,4,7-triazacyclononane, acac = pentane-2,4-dionate, AN = acetonitrile, TMP = $P(OCH_3)_3$.

Crystal Structure Determination of 1. Figure 2 shows a perspective view of the dication in crystals of **1**, and Table IV summarizes selected bond distances and angles. The dication possesses crystallographically imposed centrosymmetry (C_i). This implies that the conformation of the three five-membered chelate rings Ru–N–C–C–N of the coordinated cyclic triamine is ($\lambda\lambda\lambda$) at one Ru ion and ($\delta\delta\delta$) at the other. Thus the "meso"-form crystallizes out. The other possible diastereomer with ($\lambda\lambda\lambda$) conformation at both Ru ions is not present (or ($\delta\delta\delta$) at both Ru atoms). Both ruthenium ions are in a pseudo-octahedral environment of a facially coordinated cyclic triamine, a bidentate chelating acac ligand, and a sulfur atom. The metrical details of the acac ligand are identical with those reported previously for $[\{LRu^{III}(acac)\}_2(\mu\text{-}O)](PF_6)_2$;[10] the average Ru–$O_{acac}$ distance in **1** is at 2.05 Å similar as in $Ru^{III}(acac)_3$[13] and $[Ru^{III}(acac)_2Cl_2]^-$.[14] The Ru–N distances of the triamine are not equivalent; the bond in trans position with respect to the sulfur atom is longer by 0.046 Å than the average of two corresponding Ru–N_{cis} distances. In the oxo-bridged dinuclear species the difference $\Delta[(Ru\text{–}N_{trans})\text{–}(Ru\text{–}N_{cis})]$ is very similar at 0.05 Å. This is taken as a clear indication for a structural trans influence of the S_2^{2-} bridge. The same effect has been observed for $[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]^{4+}$ with $\Delta = 0.058$ Å[7]. The trans effect is brought about by the relative short Ru–S bond with considerable double-bond character. From a comparison of structural data in Table V for other pertinent Ru-S-containing complexes this appears to be a general feature of all structurally characterized complexes containing the $[Ru\text{–}S\text{–}S\text{–}Ru]^{4+}$ core. It is revealing that one-electron reduction of this core causes an increase of the Ru–S distance whereas the S–S distance remains unchanged.[15] The S–S distance has been interpreted as intermediate between a S–S single and a double bond.[3,5,7]



In $[Ru_2(\mu\text{-}\eta^1,\eta^1\text{-}S_2)]^{4+}$ species this bond length varies between 1.962 and 2.014 Å. In $CH_3\text{–}S\text{–}S\text{–}CH_3$ the sulfur–sulfur distance is at 2.03 Å, which corresponds to a S–S single bond.[16] We feel that the S–S distance in these dinuclear ruthenium complexes is much closer to a single than a S=S double bond (1.887 Å in free S_2).

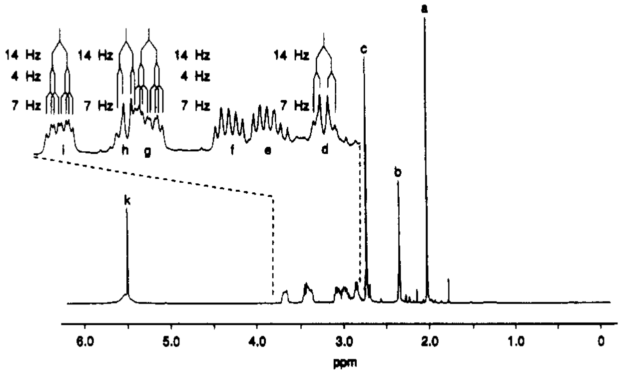


Figure 3. 400-MHz ^{1}NMR spectrum of **1** in pyridine-d_5 at ambient temperature. See Chart I and Table IV for proton assignments.

Table VI. 400-MHz ^{1}H and 100-MHz ^{13}C NMR Data for Complexes **1** and **2**

	^{1}H NMR[a]			^{13}C NMR[b]	
	δ, ppm	type, no. of H's	assgnt (label)[c]	δ, ppm	assgnt (label)[c]
complex *1*	1.98	s, 12	CCH_3 (a)	27.8	CCH_3 (A)
	2.32	s, 6	NCH_3 (b)	55.4	NCH_3 (B)
	2.70	s, 12	NCH_3 (c)	59.1	NCH_3 (C)
	2.83	q, 4	$\text{–}CHHCH_2$ (d)	62.9	CH_2 (D)
	3.45	q, 4	$\text{–}CHHCH_2$ (h)	66.7	CH_2 (D)
	2.7–3.7	m, 24	$\text{–}CH_2$ (d–i)	112.7	CH (E)
	5.48	s, 2	CH (k)	190.4	$C{=}O$ (F)
complex *2*	1.95	s, 6	NCH_3	27.6, 28.4	$C\text{-}CH_3$
	2.05	s, 12	CCH_3	47.9, 50.5	$N\text{-}CH_3$
	2.35	s, 4	$\text{–}CH_2\text{–}$	51.8, 55.9	$N\text{-}CH_3$
	3.10–3.20	m, 12	NCH_3	59.2, 59.4	$\text{–}CH_2\text{–}$
		s, 8	$\text{–}CH_2\text{–}$	61.0, 61.2	$\text{–}CH_2\text{–}$
	3.20–3.38	m, 8	$\text{–}CH_2\text{–}$	63.03, 63.3	$\text{–}CH_2\text{–}$
	3.62	m, 4	$\text{–}CH_2\text{–}$	99.4, 101.1	CH
	5.25	s, 2	CH	184.0, 190.4	$C{=}O$

[a] Measured in pyridine-d_5 at ambient temperature. [b] Measured in methanol-d_4 at ambient temperature; s = singlet; m = multiplet; q = quartet. [c] For the labeling, see Chart I.

^{1}H and ^{13}C NMR Spectra. The 400-MHz ^{1}H NMR spectrum of **1** in pyridine-d_5 at ambient temperature (Figure 3) shows signals for each methylene proton of the cyclic amine, two signals (ratio 2:1) for the methyl protons of *N*-methyl groups, and a single signal for the methyl protons of the coordinated acac ligand and only one signal for the methine protons of the two acac ligands. Table VI summarizes the data and in conjunction with Chart I gives the assignments. The assignments in Table VI were unambiguously established by the ^{13}C NMR spectrum, a ^{1}H–^{1}H correlation (Homo–COSY), and a series of NOE difference spectra. In crystals of **1** the centrosymmetric dication is present which implies that the three five-membered chelate rings Ru–N–C–C–N of the coordinated cyclic amine adopt ($\lambda\lambda\lambda$) at one ruthenium ion and ($\delta\delta\delta$) conformation at the second (meso-form). In order to assign the ^{1}H and ^{13}C signals, it suffices to consider half of the cation LRu(acac)S in an idealized C_s symmetry, where a mirror plane bisects the coordinated acac and amine ligand and atoms Ru and S and one N–CH_3 group (carbon atom B in Chart I) lie on this plane. Thus eight magnetically inequivalent carbon atoms are present which give rise to seven observed ^{13}C signals of which only two are due to methylene carbon atoms of the cyclic amine (in C_s symmetry three are expected). A more detailed assignment of these methylene carbon atoms (D) has not been possible.

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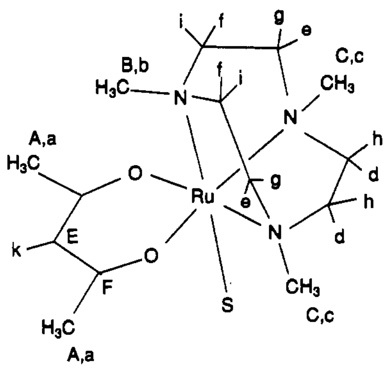
(14) Hasagawa, T.; Lau, T. C.; Taube, H.; Schaefer, W. P. *Inorg. Chem.* **1991**, *30*, 2921.

(15) Matsumoto, T.; Matsumoto, K. *Chem. Lett.* **1992**, 1539.

(16) Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655 and references therein.

Chart I [a]



[a] Proton labels a–k and carbon atom labels A–C; label D refers to methylene carbon atoms of the cyclic triamine for compound **1**.

The ^1H NMR spectrum of **2** in pyridine-d_5 is quite similar to that discussed above for **1**, but the ^{13}C NMR spectrum of **2** exhibits a remarkable difference. In the ^{13}C spectrum of **1** seven carbon resonances are observed, whereas the corresponding spectrum of **2** displays two sets of seven signals. Since we have not been able to grow single crystals of **2** and determine its crystal structure, we suggest that the precipitate of **2** contains the two possible diastereomers of the dication in equal amounts. In the meso-form the five-membered chelate rings of the coordinated amines have ($\lambda\lambda\lambda$) at one Ru ion and ($\delta\delta\delta$) conformation at the other, whereas the diastereomer would have ($\lambda\lambda\lambda$) conformation at both Ru centers (or ($\delta\delta\delta$) in its enantiomer). Due to the relative smaller absolute chemical shift in ^1H NMR experiments as compared to ^{13}C NMR spectroscopy, the small stereochemical difference between the two diastereomers is not detected in the ^1H NMR spectrum but is detected in the ^{13}C NMR spectrum.

Electrochemistry. Figure 4 shows the cyclic voltammogram of **1** in acetonitrile solution containing 0.10 M tetra-*n*-butylammonium hexafluorophosphate; that of **2** using the same experimental conditions is very similar. In the potential range +1.1 to −1.6 V vs Ag/AgCl (saturated LiCl in C_2H_5OH) a reversible one-electron oxidation wave at $E_{1/2} = 0.69$ V vs NHE and two quasi-reversible one-electron reduction waves at −0.73 and −1.51 V vs NHE are observed for **1**. Complex **2** displays also a reversible one-electron oxidation wave and two quasi-reversible one-electron reduction waves at +0.61, −0.57, and −1.30 V vs NHE, respectively.

Coulometric measurements at +1.30 V vs Ag/AgCl corroborate the one-electron oxidation of **1** ($n = 0.98 \pm 0.1$). We assign these processes as is indicated in eq 1, assuming metal-centered oxidation and reduction waves. It is conceivable that the one-electron oxidation corresponds to the oxidation of μ-disulfido (diselenido) to a coordinated μ-S_2^- (or μ-Se_2^-) radical ion, but the small potential difference of 0.08 V between **1** and **2** for these oxidation processes suggests to us that this is not the case. Attempts to isolate a chemically oxidized species from acetonitrile solution of **1** failed. Interestingly, for $[\{Ru(NH_3)_5\}(S_2)]^{4+}$ only an irreversible oxidation at 1.04 V vs NHE has been reported.[1] It is pertinent to these results that Matsumoto and Matsumoto[15] have recently isolated and structurally characterized the mixed-valent $Ru^{II}Ru^{III}$ μ-disulfido-bridged species $[\{Ru(AN)_3(TMP)_2\}_2(\mu\text{-}S_2)](PF_6)_3$, where AN is coordinated acetonitrile and TMP is $P(OMe)_3$. Rauchfuss et al.[3] have isolated salts of the $[\{CpRu(PPh_3)_2\}_2(\mu\text{-}S_2)]^+$ monocation which may also be reversibly oxidized to the dication and, subsequently, at +0.05 V vs NHE to the trication.

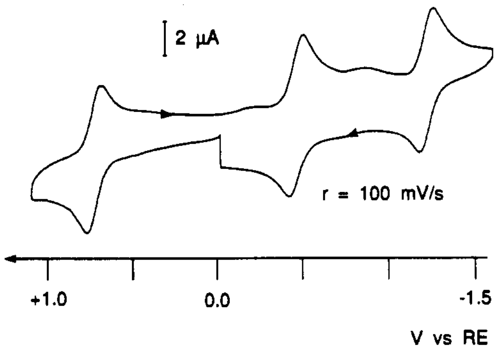


Figure 4. Cyclic voltammogram of **1** in acetonitrile (reference electrode (RE) Ag/AgCl (saturated $LiCl/C_2H_5OH$; 0.10 M $[TBA]PF_6$; glassy-carbon working electrode).

$$[Ru^{III}\text{-}X\text{-}X\text{-}Ru^{IV}]^{5+} + e^- \rightleftharpoons [Ru^{III}{}_2(\mu\text{-}X_2)]^{4+} + e^- \rightleftharpoons [Ru^{III}\text{-}X\text{-}X\text{-}Ru^{II}]^{3+} + e^- \rightleftharpoons [Ru^{II}\text{-}X\text{-}X\text{-}Ru^{II}]^{2+} \quad (1)$$

$$X = S, Se$$

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Supplementary Material Available: Tables giving crystal data and details of the structure determination of **1**, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates (6 pages). Order information is given on any current masthead page.