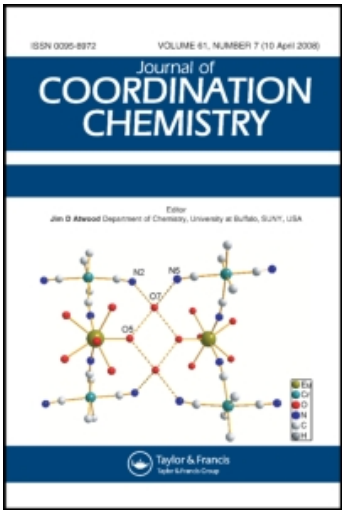

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Oxidation of Ru-bound thiolate thioether and its NS_4-ligand containing thiolate and thioether sulfur donors: synthesis, characterization, and X-ray structures

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Oxidation of Ru-bound thiolate thioether and its NS_4-ligand containing thiolate and thioether sulfur donors: synthesis, characterization, and X-ray structures§

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A ruthenium complex $[Ru(H_2O)\{Et_2NpyS_4(O_3)_2\}]\cdot$(**4**) containing sulfinates, sulfenates S-donors, and water as co-ligand has been synthesized from oxidation of hydrazine complex $[Ru(N_2H_4)(Et_2NpyS_4)]$ (**3**) and completely characterized with X-ray structural analysis [$Et_2NpyS_4^{-2}$ = 4-(diethylamino)-2,6-bis[(2-mercaptophenyl)thiomethyl]pyridine(2−)]. Complex **4** exhibits distorted octahedral coordination of the ruthenium center and the d[Ru–$S_{sulfinates}$] and d[Ru–$S_{sulfenates}$] are almost equivalent. The average d[S–$O_{sulfinate}$] at 148.0 pm is *ca* 10 pm longer than the average d[S–$O_{sulfenate}$] at 138.0 pm. The sulfinates IR(KBr) bands are located in the range 1132–1113 cm^{-1} as two band sets, $\nu(SO)_{asym}$ and $\nu(SO)_{sym}$, whereas the sulfenates show a single absorbance at approximately 882 cm^{-1}. The lower frequency of the ν(SO) stretches of the sulfenates as compared to that of their sulfinate rivals indicates a weaker S–O bond in the sulfenates and is consistent with X-ray crystal structure data (*vide infra*). Oxidation of the dithiol ligand Et_2NpyS_4–H_2 (**1**) under the same condition afforded the disulfide, in this case forming a macrocyclic ligand S,S-Et_2NpyS_4 (**2**) as is evidenced by an X-ray crystal structure determination. Thus, the oxidation of **3** involves activation of either the oxygen or thiolate by the ruthenium center.

Keywords: Sulfinates; Sulfenates; Ruthenium complexes; Sulfur oxidation; Disulfide; Macrocycle

1. Introduction

Redox chemistry of thiols plays a key role in many biological processes [1]. The important biochemical oxidation of cysteine includes its conversion to disulfides (cystine) and the formation of oxy acids, such as cysteine sulfenic acid, cysteine sulfinic acid (CSA), and hypotaurine (2-aminoethanesulfinic acid). The oxidation of cysteine residues in proteins and the role of metal ions in catalyzing these oxidations have been reviewed [2]. Cysteine oxygenates are the intermediates and products of the catabolism

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§Dedicated to Professor Rudi van Eldik on the occasion of his 65th birthday.
†Deceased.

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of cysteine [2a], and altered sulfur oxidation chemistry is associated with a number of diseases [3]. Disulfides play important structural and redox roles in proteins [4], and oxidation of cysteine sulfur is also believed to tune the properties of metalloenzyme active sites, such as in iron-containing nitrile hydratases [5], where cysteine is present in thiolate, sulfenate, and sulfinate redox states. Reactions involving sulfur oxidations have been extensively studied [6] and these reactions result in the oxidation of the sulfur centers. Reactions with O_2 are distinct from reactions with H_2O_2 in that the former can lead to products incorporating both atoms of O_2 (a four-electron, dioxygenase-like oxidation), whereas peroxide sequentially oxidizes sulfur by two electrons with the transfer of one oxygen. In a previous paper, we found that the iron thiolate can be converted to a S-bound sulfinato complex by the incorporation of dioxygen [7]. In this article we report an oxidation of a Ru(II) alkylthiolate hydrazine complex **3** upon reaction with H_2O_2 that also leads to ligand oxidation. The oxidation product of **3** with H_2O_2 is a ruthenium sulfinato sulfenato complex incorporating water as coligand. This Ru–SO_2–R complex is all S-bound and the oxygens are not removable by chemical agents. Hence, an S-bound sulfinate could represent an irreversibly oxygen-damaged enzyme. The resulting Ru(II) sulfinato sulfenato complex is a rare example of a structurally characterized product of thiolate oxidation. In contrast to this, one-electron oxidation of thiolate ligands under the same conditions results in the formation of disulfides, in this case forming a macrocyclic ligand **2** as obtained from the X-ray structure determination. Thus, the oxidation of **3** involves activation of either oxygen or thiolate by the ruthenium center.

2. Experimental

2.1. *General*

Et_2NpyS_4-H_2 and [Ru(N_2H_4)(Et_2NpyS_4)] were synthesized as described [7]. Hydrogen peroxide (30%) was purchased from Fischer Scientific Co. All manipulations were carried out in Schlenk lines and dry solvents were used. Spectra were recorded on the following instruments: IR (KBr discs), solvent bands were compensated: Perkin Elmer 983, 1620 FT IR, and 16PC FT-IR in the spectral range 4000–400 cm^{-1}; NMR: Jeol-JNM-GX 270, EX 270. Spectra were recorded at 25°C; mass spectra: Jeol MSTATION 700 spectrometers; elemental analyses (C, H, N, S): Carlo Erba EA 1106 or 1108 analyzer; cyclic voltammetry was performed with a Radiometer Copenhagen IMT 102 electrochemical interface using a three electrode cell with a glassy carbon (Radiometer Copenhagen EDI) working electrode and Pt reference and counter electrodes. Solutions were 10^{-3} M; NBu_4PF_6 (10^{-1} M) was used as the supporting electrolyte. Potentials were referenced to the normal hydrogen electrode (NHE) using Fc/Fc^+ as an internal standard $E(Fc/Fc^+) = +400$ mV *versus* NHE [8].

2.2. *Syntheses*

2.2.1. S,S-Et_2NpyS_4 · HCl (2). At 0°C, H_2O_2 (0.008 mL of 35% solution in H_2O) was added to a pale yellow solution **1** (35 mg, 0.07 mmol) in THF (10 mL). The mixture was

allowed to stand at room temperature for 1 h. The solvent was removed under vacuum and the residue was redissolved in $CHCl_3$. Slow evaporation of the $CHCl_3$ solution at room temperature led to the formation of crystals suitable for X-ray analysis (Yield 25 mg, 70%). Anal. Calcd for $C_{23}H_{25}ClN_2S_4$ (493.2) (%): C 56.01, H 5.11, N 5.68, S 26.01. Found (%): C 55.31, H 5.80, N 5.41, S 26.47.

2.2.2. [Ru(H$_2$O){Et$_2$NpyS$_4$–(O$_3$)$_2$}](4). At 0°C, H_2O_2 (0.008 mL of 35% solution in H_2O) was added to an orange suspension of **3** (40 mg, 0.07 mmol) in THF (10 mL). The mixture was allowed to stand at room temperature for 1 h, whereupon a microcrystalline solid was formed. The product was isolated *via* filtration, washed with MeOH and H_2O (10 mL each) and dried *in vacuo*. Yield 30 mg of **4**. ^{1}H-NMR (CD_2Cl_2, 269.60 MHz): $\delta = 0.86$–0.94 (t, 6H, $2CH_2CH_3$), 2.10 (b, 2H, H_2O), 3.01–3.09 (m, 4H, $2CH_2CH_3$), 4.20 (d, 2H, CH_2), 5.24 (d, 2H, CH_2), 6.12 (s, 2H, H_β pyridine), 7.14–7.82 (m, 8H, C_6H_4). IR (KBr): $\nu = 3450$ (b, O–H), 3070, 2966, 2930 (w, C–H), 1132, 1113, 882 (s, SO) cm^{-1}. MS (FD$^+$, CH_2Cl_2): $m/z = 652$ [Ru{*Et$_2$N*pyS$_4$-(O$_3$)$_2$}]$^+$. $C_{23}H_{26}N_2O_7RuS_4$ (671.79): Calcd (%) C 41.12, H 3.90, N 4.17; Found (%): C 41.19, H 4.29, N 5.47. Yellow single crystals of [Ru(H$_2$O){Et$_2$NpyS$_4$–(O$_3$)$_2$}]·3THF·2H$_2$O·MeOH (**4**·3THF·2H$_2$O·MeOH) were obtained from a saturated solution of **4** in a mixture of THF, H_2O, and MeOH at room temperature within 2 weeks.

2.3. *X-ray crystal structure determinations*

Suitable single crystals were embedded in protective perfluoropolyether oil; data were collected at 100 K on a Bruker-Nonius Kappa CCD diffractometer using Mo-Kα radiation ($\lambda = 71.073$ pm, graphite monochromator). Intensity data were corrected for Lorentz and polarization effects; a numerical absorption correction was applied in both cases. The structures were solved by direct methods and refined on F^2 using full-matrix least squares procedures (SHELXTL NT 6.12 [9]). The asymmetric unit of the crystal structure of **2** contains two independent molecules. With the exception of the water bound hydrogens in **2** and **4**, where the positions were derived from a difference Fourier synthesis, all hydrogens were placed in positions of optimized geometry. The isotropic displacement parameters of all hydrogens were tied to the equivalent isotropic displacement parameter of their carrier atoms by a factor of either 1.2 or 1.5. The selected crystallographic data, data collection, and structure refinement details are listed in Table 1.

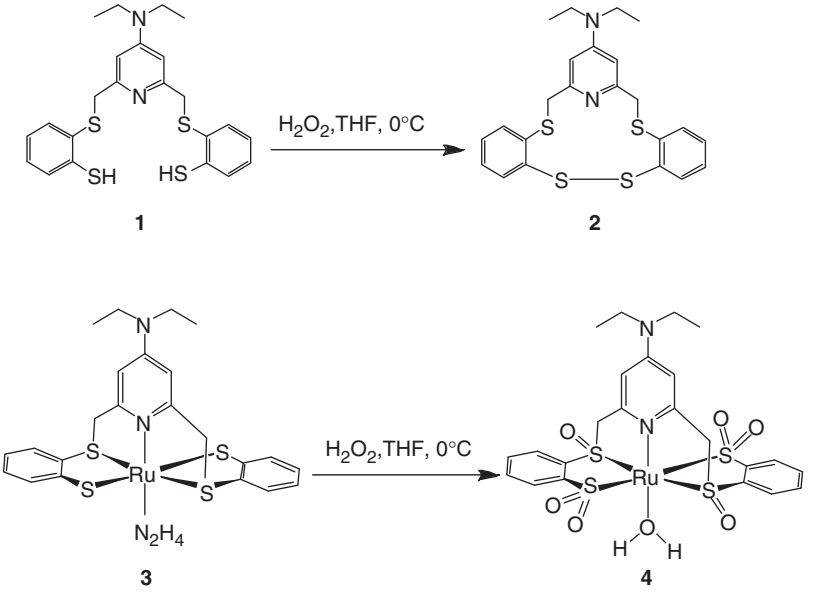
3. Results and discussion

3.1. *Synthesis and characterization*

The syntheses of **1** and **3** have been reported previously [7]. Reactions accomplished in this work are depicted in scheme 1. Complex **4** was obtained from the reaction of **3** with hydrogen peroxide as described in section 2. The yield was optimized by the variation of reaction stoichiometry, temperature, and dilution. The structure of **4** was fully

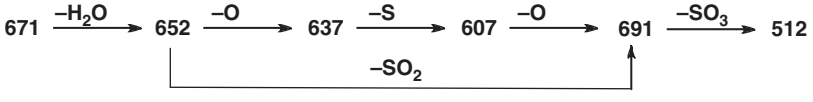
Table 1. Crystallographic data and structure refinement for **2** and **4**.

	2	**4**
Formula	$C_{23}H_{27}ClN_2OS_4$	$C_{36}H_{58}N_2O_{11.22}RuS_4$
M_r (g mol^{-1})	511.16	927.67
Crystal size (mm^3)	$0.43 \times 0.12 \times 0.07$	$0.33 \times 0.24 \times 0.24$
$F(000)$	2144	972
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P_{\bar{1}}$
Unit cell dimention (Å, °)		
a	1857.8(2)	1190.5(6)
b	913.2(1)	1278.5(8)
c	2888.3(2)	1423.1(7)
α	90	94.078(4)
β	101.538(4)	102.915(4)
γ	90	103.581(5)
V (nm^3)	4.8011(8)	2.0347(2)
Z	8	2
ρ_{calc} (g cm^{-3})	1.414	1.514
μ (mm^{-1})	0.526	0.651
T (K)	100	100
θ range (°)	3.34–25.68	3.43–27.10
Measured reflection	32442	36531
Unique reflection	9075	8929
R_{int}	0.0645	0.0489
Observed reflection	5569	6749
σ-criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_1 [$I > 2\sigma(I)$]	0.0645	0.0489
wR_2 (all data)	0.1240	0.1142
Absorption correction T_{min}/T_{max}	0.864/0.974	0.861/0.920



Scheme 1. Oxidation of the dithiol ligand **1** and the hydrazine complex **3**.

supported by its mass spectrum and the results of an elemental analysis, both of which indicate the presence of the water co-ligand and sulfur oxidation. This was further confirmed by an X-ray crystal structure determination. The IR spectrum of **4** is consistent with its structure. The sulfinates show a two band set, $\nu(SO)_{asym}$ and $\nu(SO)_{sym}$ in the range 1132–1113 cm^{-1}, whereas the sulfenates show a single absorbance at lower wavenumber at 882 cm^{-1} [10]. The lower frequency of the $\nu(SO)$ stretches of the sulfenates as compared to that of their sulfinates indicates a weaker S–O bond in the sulfenates and is consistent with X-ray crystal structure data, *vide infra*. The water coligand appears as a very sharp band at 3421 cm^{-1}. Complex **4** was examined also by FD MS in CH_2Cl_2. The spectrum shows the presence of a stable fragment ion assignable to the parent complex without the water coligand. Additionally, **4** loses SO_2, showing a signal at $m/z = 591$ whose high intensity suggests direct production from the parent ion rather than stepwise loss of two O and one S atom. The loss of SO_2 is followed by removing SO_3 showing a strong signal at $m/z = 512$ as shown in the following equation:



Characterization of **4** by NMR spectroscopy finds the methylene bridge of the ^1H NMR spectrum particularly diagnostic. The C_2 symmetry around ruthenium dictates the number of methylene resonances observed. The two methylene groups are chemically and magnetically equivalent and appear as a doublet of doublets at 4.20 and 5.24 ppm accountable to the fact that the two protons in each methylene group are not magnetically equivalent. The hydrazine NH signals could not be seen in the ^1H-NMR spectrum of **4**, instead, a new signal at 2.10 ppm appears (exchanged by D_2O) which was assigned to the protons of the H_2O co-ligand. Oxidation of sulfur and consequent exchange of the co-ligand N_2H_4 by H_2O is an interesting phenomenon in relation to hydrogen bonding. The exchange of N_2H_4 by H_2O may happen due to the fact that the N_2H_4 co-ligand is stable only in the presence of hydrogen bonding as reported earlier [7]. Oxidation of the sulfur donors damages the hydrogen bonding and as a result the N_2H_4 decoordinates to leave a free coordination site. In this case the free coordination site may be blocked by either water or by coupling with another molecule *via* sulfide linkage. However, the second possibility is excluded here because of the thiolate oxidation.

The oxidation of **3** was achieved electrochemically by cyclic voltammetry. The cyclic voltammogram of **3** in CH_2Cl_2 is shown in figure 1. Only one irreversible oxidation wave at $E_{1/2} = +935$ mV was observed within the solvent limits which could be assigned to the redox couple **3**/[**3**]$^+$. A high potential value reflects the observed difficult chemical oxidation. Also, one reduction wave at $E_{1/2} = -203$ mV was observed which could be assigned to the redox couple **3**/[**3**]$^-$.

Complex **4** is stable, once bound; the dioxygen cannot be displaced by bubbling N_2 through the mixture, indicating that the reaction is irreversible. In order to investigate whether the ruthenium is an essential component in the sulfur oxidation, the ligand itself was subjected to oxidation under the same condition as for **4**. The ligand is easily oxidized at the thiolate groups, leading to the connection of two of the dianions **1** via

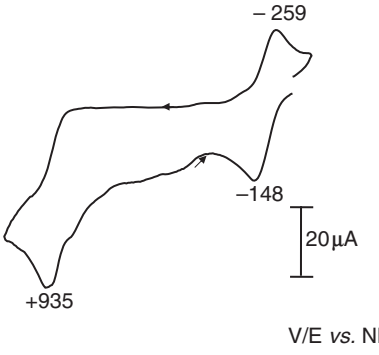


Figure 1. Cyclic voltammogram of **3** in CH_2Cl_2 (10^{-3} M, 10^{-1} NBu_4PF_6, $v = 50\,mV\,s^{-1}$, potentials given in millivolt).

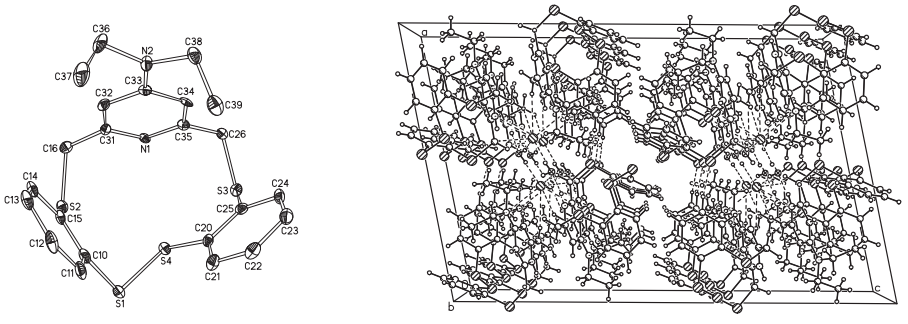


Figure 2. Molecular structure (left, ellipsoids are drawn at the 50% probability level; chloride anion, solvate molecules, and H atoms omitted for clarity) and crystal packing (right) of the disulfide **2**.

disulfide bridges to form a macrocycle ligand S,S′-Et_2NpyS_4 (**2**). This oxidation hence corresponds to the enzymatic and nonenzymatic oxidation of thiols (cysteine residues) to disulfides (cystine bridges) in biological systems. Thus, the oxidation reaction of **3** involves either activation of oxygen or of the thiolate ligand by the ruthenium center.

3.2. *Crystal structures of 2 and 4*

The macrocyclic disulfide S,S-$Et_2NpyS_4 \cdot HCl \cdot H_2O$(**2** $\cdot H_2O$) and the [Ru(H_2O) {Et_2NpyS_4–$(O_3)_2$}] $\cdot$ 3THF $\cdot$ $2H_2O$ $\cdot$ MeOH (**4** $\cdot$ 3THF $\cdot$ $2H_2O$ $\cdot$ MeOH) were characterized by X-ray diffraction analysis. Yellow single crystals of **2** were obtained from a saturated $CHCl_3$ solution at room temperature in the course of 1 week whereas yellow single crystals of **4** were obtained from a saturated solution of **4** in a mixture of THF, H_2O, and MeOH at room temperature within 2 weeks. The ORTEP diagrams of the macrocyclic ligand **2** and the neutral complex **4** are shown in figures 2 and 3, respectively. Crystal data, data collection parameters, and refinement details are listed in table 1; selected interatomic distances and bond angles are compiled in tables 2 and 3.

The disulfide ligand **2** $\cdot H_2O$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) and contains two independent molecules in its asymmetric unit which show almost

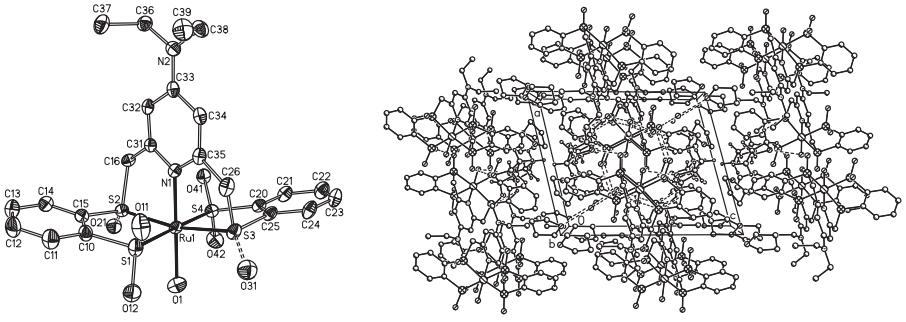


Figure 3. Molecular structure (left, ellipsoids are drawn at the 50% probability level; solvate molecules and H atoms omitted for clarity) and crystal packing (right) of **4**.

Table 2. Selected bond lengths (Å) and angles (°) for $\mathbf{2} \cdot H_2O$.

S(1)–S(4)	205.3(2)	S(1)–C(10)	179.8(4)
S(2)–C(15)	178.4(4)	S(2)–C(16)	184.2(4)
S(3)–C(25)	178.4(4)	S(3)–C(26)	182.7(4)
S(4)–C(20)	177.4(4)		
C(10)–S(1)–S(4)	103.9(2)	C(20)–C(25)–S(3)	117.0(3)
C(15)–S(2)–C(16)	102.2(2)	C(20)–S(4)–S(1)	105.1(2)
C(25)–S(3)–C(26)	101.9(2)	C(15)–C(10)–S(1)	123.5(3)
C(31)–C(16)–S(2)	111.1(3)	C(10)–C(15)–S(2)	120.3(3)
C(35)–C(26)–S(3)	113.9(3)		

Table 3. Selected bond distances (Å) and angles (°) for $\mathbf{4} \cdot 3THF \cdot 2H_2O \cdot MeOH$.

Ru(1)–N(1)	205.4(3)	Ru(1)–O(1)	214.0(3)
Ru(1)–S(4)	230.1(1)	Ru(1)–S(1)	230.2(1)
Ru(1)–S(3)	231.1(1)	Ru(1)–S(2)	231.2(1)
S(1)–O(11)	147.9(3)	S(1)–O(12)	148.3(3)
S(1)–O(12)	148.3(3)	S(4)–O(41)	147.2(3)
S(4)–O(42)	148.0(3)	S(4)–O(42)	148.0(3)
N(1)–Ru(1)–O(1)	179.1(2)	N(1)–Ru(1)–S(4)	91.00(8)
O(1)–Ru(1)–S(4)	89.76(9)	N(1)–Ru(1)–S(1)	90.54(8)
O(1)–Ru(1)–S(1)	88.70(9)	S(4)–Ru(1)–S(1)	178.45(4)
N(1)–Ru(1)–S(3)	83.91(8)	O(1)–Ru(1)–S(3)	95.70(9)
S(4)–Ru(1)–S(3)	87.71(3)	S(1)–Ru(1)–S(3)	92.60(3)
N(1)–Ru(1)–S(2)	83.82(8)	O(1)–Ru(1)–S(2)	96.58(9)
S(4)–Ru(1)–S(2)	91.94(3)	S(3)–Ru(1)–S(2)	167.71(4)
S(1)–Ru(1)–S(2)	83.08(3)		

identical conformations. The *d*(S–S) in **2** is slightly shorter than in disulfides in general (av. 207.2 ± 0.08 pm) [11] and other cyclo-bis(disulfides), such as tetrathia-cyclo-eicosanes in particular (208.3(1) pm) [12] and at the same time slightly longer than in the cyclo-hexaeicosane (203.9(3) pm) [13]. The S(1), S(4), S(2), and S(3) sulfurs form a well-approximated plane (the largest deviation from the corresponding least squares plane is observed for S4 and amounts to 13.1(3) pm) and the two phenyl rings as well as the pyridine ring lie all on the same side of this plane. The S–S–C angles in **2** fall within the range of the average S−S−C angles in related neutral cyclo-disulfides (≈104.5(3) pm) [13]. The structure of **3** has been reported previously [7] but its character will be discussed in comparison with **4**. For **4**, the thiolate sulfur donors were oxidized to the sulfinates $-SO_2-$, whereas the thioether sulfur donors were oxidized only partially (S2 by 8(2)% and S3 by 14(2)%) to the sulfenates –SO−. The Et_2NpyS_4 ligand is a square-pyramidal coordination cap and the overall geometry around the ruthenium center is pseudo-octahedral. The pyridine N1 donor and the water coligand, as well as the two sulfinates and the two sulfenate donors of Et_2NpyS_4^{-2}, occupy pairwise *trans*-positions and thus prove the sterical rigidity of the py$(CH_2)_2$ backbone. A comparison of **3** and **4** demonstrates that the Ru–donor distances in all cases lie in the range observed for [$RuNS_4$] cores [7, 14]. In **4**, the *d*[Ru–$S_{sulfenate}$] and *d*[Fe–N] remain practically unchanged whereas *d*[Ru–$S_{sulfinate}$] exhibit shortening by about 7.2 pm (237.3 pm for **3** *vsrsus* 230.1 pm for **4)**, in agreement with previous studies which conclude that *d*[Ru–S] was governed by three factors: (i) the σ-donor ability, expected to be best in the thiolate which decreases with increasing oxygenation, (ii) a contraction in the size of sulfurs as formal oxidation state of the sulfur change from −2 for Ru–$S_{thiolate}$ in **3**, 0 for Ru–$S_{sulfenate}$, and to +2 for Ru–$S_{sulfinate}$ in **4**, and (iii) destabilization of the Ru−S bond due to the repulsive interaction between the filled *d* orbital of the metal and two lone pairs of the thiolate sulfurs [10]. The *d*[Ru−$S_{(av)}$] bond distances of SO_2 (≈230.1(2)) and SO (≈231.1(1)) are almost equivalent. The average *d*[S−$O_{sulfinate}$] at 148.0 pm is *ca* 10 pm longer than the average *d*[S−$O_{sulfenate}$] at 138.0 pm. There is an extensive hydrogen bonding network involving the aqua co-ligand and the solvent of crystallization (THF and H_2O, figure 3).

4. Conclusion

The present work demonstrates that oxidation of the Ru(II) alkylthiolate hydrazine complex leads to a ruthenium–sulfinato–sulfenato complex incorporating water as co-ligand. Such Ru(II)–sulfinato–sulfenato complex bearing water as co-ligand is a rare example of a structurally characterized product of thiolate oxidation. In contrast to this, oxidation of the thiolate ligand under the same conditions results in the formation of disulfides, forming a macrocyclic ligand. This indicates that the ruthenium center is an essential component and the reaction involves activation of either the oxygen or the thiolate ligand by the ruthenium center.

Supplementary material

Crystallographic data for the X-ray crystal structure analyses have been deposited with the Cambridge Crystallographic Data Centre as supplementary Publications

CCDC-765957 (**2**) and CCDC-765958 (**4**), respectively. Copies of this information can be obtained free of charge from The Director. Postal Address: CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, telephone: (44) 01223 762910; Facsimile: (44) 01223 336033 (E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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