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Influence of the diamine on the reactivity of thiosulfonato ruthenium complexes with hydrosulfide (HS^-)†

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We have recently reported that cationic thiosulfonato ruthenium complexes [(*p*-cymene)Ru(bipy)-(SSO_2Ar)]$^+$ (bipy: 2-2′-bipyridine, Ar: phenyl or *p*-tolyl) react with thiolates (RS^-, R = alkyl or aryl) by cleavage of the S–SO_2 bond and formation of a new S–S bond. In this work, we report that the outcome of the reaction is different if the hydrosulfide anion (R = H) is used, the product obtained being the hydrogen(sulfido) derivative [(*p*-cymene)Ru(bipy)(SH)]$^+$. The bipy ligand is crucial in this result, and its replacement by ethylenediamine leads to a different product, the trisulfido-bridged dinuclear complex [[(*p*-cymene)Ru(en)(S)]$_2$S]$^{2+}$. These two new species have been fully characterized, including by X-ray diffraction studies, and the two different mechanisms leading to their formation are discussed.

Introduction

Sulfur-containing ligands play a major role in coordination chemistry. This rich chemistry relies on several synthetic pathways for the formation of the metal–sulfur bond, the most versatile for anionic ligands being the reaction between a metal complex and a sulfur-containing molecule in the presence of a base. However, this procedure is limited by the stability of the sulfur species under basic conditions, and a number of ligands, like for instance the sulfonato or disulfanido ligands, are not accessible using this strategy. We have recently reported an original route towards these disulfanido complexes by nucleophilic attack of thiolates on ruthenium-bound thiosulfonato ligands.[1] In this reaction, the ruthenium(II) centre is crucial, as its kinetic inertness drives the reaction towards the S–SO_2 bond rather than towards the metal centre, resulting in the cleavage of the thiosulfonate and the formation of a new S–S bond. Here, we report the study of this reaction carried out with the hydrosulfide anion (HS^-). The nature of the chelating diamine is crucial to the outcome of the reaction, with either a hydrogen(sulfido) complex or a trisulfido-bridged dinuclear species being isolated. While hydrogen(sulfido) species[2] are well documented in ruthenium chemistry, with for example the numerous reactions involving the cyclopentadienyl derivatives,[3] cationic polysulfide derivatives are scarce in the literature.

Experimental section

Physical measurements

^{1}H NMR spectra were recorded at 300 K on a Bruker ARX-250 spectrometer or at 500 MHz on a Bruker AVANCE II-500 spectrometer, and the chemical shifts are calibrated on the residual solvent peak.[4] Fluorescence studies were carried out on a Hitachi F7000 spectrometer. Elemental analyses were carried out by the microanalysis service at Gif-sur-Yvette CNRS. ^{34}S (90%) was purchased from Icon Isotopes.

Materials

Solvents were distilled using standard techniques and treated under argon prior to use when necessary. Chemicals were purchased from Aldrich or Thermo-Fischer and used as received. [(*p*-Cymene)Ru(bipy)Cl]·PF_6 and [(*p*-cymene)Ru(en)Cl]·PF_6 were prepared from the corresponding chloro derivatives by anion exchange with NH_4PF_6 in methanol.[1,5] The isotopically labeled ^{34}S phenylthiosulfonate was synthesized by the reaction of the sodium salt of phenylsulfinic acid with elemental sulfur (resp. ^{34}S) in pyridine.[6]

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Synthesis and characterization of the thiosulfonato complexes 1a–b and 1′a–b. All the complexes were synthesized following this general procedure: a mixture of complex [(*p*-cymene)Ru(diamine)Cl]·PF_6 (0.5 mmol) and silver nitrate (0.5 mmol) was refluxed under an inert atmosphere in 10 mL of degassed methanol for 1 h, filtered, and the thiosulfonate salt (0.55 mmol) added. The reaction mixture was stirred for an additional 1 h, and the yellow powder filtered and dried under vacuum (**1a–b**) or the solvent removed and the residue purified by chromatography (Sephadex LH-20, methanol, **1′a–b**). Complex **1′a** was crystallized as its BPh_4 salt by slow diffusion of benzene in a saturated dichloromethane solution of complex **1′a**, to give yellow crystals suitable for XRD studies.

[(*p*-Cymene)Ru(en)(SSO_2(*p*-tolyl))]·BPh_4 (1′a·BPh_4). Yield: 61%. Anal. calc. (found) for $C_{43}H_{49}BN_2O_2RuS_2$: C, 64.41 (64.29); H, 6.16 (6.12); N, 3.49 (3.44). ^{1}H NMR (δ, DMSO-d_6): 7.78 (d, 2H, J_{H-H} = 8.3 Hz), 7.43 (d, 2H, J_{H-H} = 8.3 Hz), 7.18 (m, 8H), 6.93 (t, 8H, J_{H-H} = 8.1 Hz), 6.80 (m, 4H), 6.13 (br, 2H), 5.42 (s, 4H), 4.68 (br, 2H), 2.71 (st, 1H, J_{H-H} = 6.8 Hz), 2.47 (m, 2H), 2.45 (m, 2H), 2.42 (s, 3H), 2.11 (s, 3H), 1.11 (d, 6H, J_{H-H} = 6.8 Hz).

[(*p*-Cymene)Ru(en)(SSBz)]·PF_6 (2′·PF_6). 50 mg of complex **1′a**·PF_6 (0.08 mmol) were dissolved in 3 mL of methanol, and a solution of sodium benzyl thiolate (prepared by mixing 10 μL of benzylthiol and 80 μL of a 1.0 M solution of sodium methoxide in methanol) added. The yellow solution turned orange, and was then stirred at r.t. for 1 h. The solvent was then removed, and the crude product dissolved in a minimum amount of acetone, filtered, and concentrated to give **2′**·PF_6 as an orange powder (26 mg, 51%). Anal. calc. (found) for $C_{19}H_{29}F_6N_2PRuS_2$: C, 38.31 (38.31); H, 4.91 (4.86); N, 4.70 (4.68). ESI^+-MS (*m*/*z*): 451 (100%, **2′**). ^{1}H NMR (δ, DMSO-d_6): 7.34 (m, 5H), 6.30 (br, 2H), 5.51 (d, 2H, J_{H-H} = 5.6 Hz), 5.40 (d, 2H, J_{H-H} = 5.6 Hz), 3.57 (s, 2H), 3.50 (br, 2H), 2.89 (st, 1H, J_{H-H} = 6.6 Hz), 2.34 (m, 4H), 2.17 (s, 3H), 1.17 (d, 6H, J_{H-H} = 6.6 Hz).

[(*p*-Cymene)Ru(bipy)(SH)]·BPh_4 (3·BPh_4). Method A: 50 mg of complex **1a**·PF_6 (0.07 mmol) were dissolved in 1 mL of dimethylsulfoxide, and sodium hydrosulfide added (5 mg, 0.07 mmol). After stirring for 15 min, the solvent was removed, and the residue dissolved in 2 mL of methanol. A solution of 27 mg (0.08 mmol) of sodium tetraphenylborate in 0.5 mL of methanol was then added to yield an orange precipitate. After filtration, it was dissolved in dichloromethane and the solution was layered with benzene, to give orange crystals of **3·BPh_4**. Method B: 200 mg of complex [(*p*-cymene)Ru(bipy)Cl]·PF_6 (0.35 mmol) and 59 mg (0.35 mmol) of silver nitrate were dissolved under argon in 15 mL of methanol, and refluxed for 1 h. After filtration, sodium hydrosulfide (20 mg, 0.35 mmol) was added to the orange solution, which became brown. After stirring for 1 h, a solution of 123 mg of sodium tetraphenylborate (0.38 mmol) in 1 mL of methanol was added to precipitate **3·BPh_4** as an orange solid (146 mg, 56%). Anal. calc. (found) for $C_{44}H_{43}BN_2RuS{\cdot}0.7H_2O$: C, 69.87 (69.90); H, 5.92 (5.96); N, 3.70 (3.56). ESI^+-MS (*m*/*z*): 425 (100%, **3**). ^{1}H NMR (δ, DMSO-d_6): 9.26 (d, 2H, J_{H-H} = 5.5 Hz), 8.66 (d, 2H, J_{H-H} = 8.0 Hz), 8.25 (t, 2H, J_{H-H} = 8.1 Hz), 7.72 (t, 2H, J_{H-H} = 5.6 Hz), 7.18 (m, 8H), 6.93 (t, 8H, J_{H-H} = 7.2 Hz), 6.80 (m, 4H), 6.04 (d, 2H, J_{H-H} = 6.2 Hz), 5.78 (d, 2H, J_{H-H} = 6.2 Hz), 2.62 (st, 1H, J_{H-H} = 6.8 Hz), 2.23 (s, 3H), 0.94 (d, 6H, J_{H-H} = 6.8 Hz), −2.51 (s, 1H).

[(*p*-Cymene)Ru(en)(S)]$_2$S·(BPh_4)$_2$ (4′·(BPh_4)$_2$). 100 mg of complex **1′a**·PF_6 (0.16 mmol) was dissolved under argon in 2.5 mL of dimethylsulfoxide, and sodium hydrosulfide added (9 mg, 0.16 mmol). After stirring for 10 min, the solution was slowly added to cold diethyl ether to give an oily residue, which was redissolved in 5 mL of methanol and precipitated by addition of 51 mg of sodium tetraphenylborate. After filtration, 38 mg of **4′·(BPh_4)$_2$** was obtained as a yellow powder (38 mg, 36%). Crystals suitable for XRD studies were obtained by layering a concentrated solution of **4′·(BPh_4)$_2$** in dichloromethane with benzene. Anal. calc. (found) for $C_{72}H_{84}B_2N_4Ru_2S_3{\cdot}H_2O$: C, 64.37 (64.49); H, 6.45 (6.59); N, 4.17 (4.15). ESI^+-MS (*m*/*z*): 1006 and 1007 (100%, **4′**). ^{1}H NMR (δ, DMSO-d_6): 7.18 (m, 8H), 6.93 (t, 8H, J_{H-H} = 7.2 Hz), 6.80 (m, 4H), 6.07 (br, 2H), 5.58 (d, 2H, J_{H-H} = 6.0 Hz), 5.50 (d, 2H, J_{H-H} = 6.0 Hz), 3.84 (br, 2H), 2.83 (st, 1H, J_{H-H} = 6.9 Hz), 2.57 (m, 2H), 2.42 (m, 2H), 2.17 (s, 3H), 1.18 (d, 6H, J_{H-H} = 6.9 Hz).

Single-crystal X-ray diffraction

Crystal data and experimental conditions are listed in Table 1. Data were collected with a Bruker SMART APEX CCD diffractometer (Mo-Kα radiation graphite-monochromated radiation, λ = 0.71073 Å) controlled by the APEX2 software package.[7] Data integration and global cell refinement were performed with the program SAINT.[8] Data were corrected for absorption by the multiscan semiempirical method implemented in SADABS.[9] The structure was solved by direct methods using SHELXS 97.[10] Refinement, based on F^2, was carried out by full matrix least squares with SHELXL-97 software.[11] Non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were placed in their geometrically generated positions and allowed to ride on their parent atoms with an isotropic thermal parameter 20% higher than that of the atom of attachment. For complex **3**, the hydrogen atom attached to S1 was deduced from a difference Fourier map and refined with an isotropic temperature factor. The drawings of the molecules were realized with ORTEP III.[12]

Results and discussion

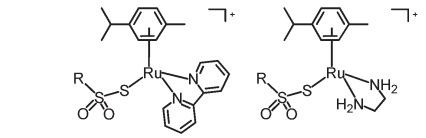
Synthesis and characterization of the thiosulfonato complexes 1 and 1′

For our studies, we used complexes (see Scheme 1) based on 2-2′-bipyridine (bipy),[1] as well as new complexes based on ethylenediamine (en).

We have already reported the crystal structure of [(*p*-cymene)Ru(bipy)(SSO_2Ph)]$^+$ **1b** in our preliminary report. The crystal structure of **1′a** (see Table 1 for crystal data and structure refinements), isolated as its BPh_4^- salt, is displayed in Fig. 1. A list of bond distances and angles is given in Table 2. The ruthenium–sulfur bond is slightly longer than in the

Table 1 Crystal data and refinement details for **1′a·BPh$_4$**, **3·BPh$_4$** and **4′·(BPh$_4$)$_2$**

	1′a·BPh$_4$	**3·BPh$_4$**	**4′·(BPh$_4$)$_2$**
Empirical formula	$C_{43}H_{49}BN_2O_2RuS_2$	$C_{50}H_{49}BN_2RuS$	$C_{72}H_{84}B_2N_4Ru_2S_3$
Formula weight	801.84	821.86	1325.37
Temperature (K)	100(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P21/c$	$P21/c$
a (Å)	9.0834(4)	12.8455(18)	11.221(3)
b (Å)	11.4504(4)	15.144(2)	61.115(17)
c (Å)	19.9443(4)	22.259(3)	10.502(3)
α (°)	94.078(2)	90.00	90.00
β (°)	97.236(2)	95.330(3)	115.227(5)
γ (°)	105.574(2)	90.00	90.00
Volume (Å^3)	1970.32(12)	4311.4	6515(3)
Z	2	4	4
μ (mm^{-1})	0.542	0.447	0.605
Reflections collected	67 976	44 712	92 977
Ind. reflections	13 099	9951	14 527
R(int)	0.057	0.045	0.043
Final R indices	0.0373	0.0517	0.0507
R indices (all data)	0.0547	0.0641	0.0706



Scheme 1 Thiosulfonato complexes used in this study.

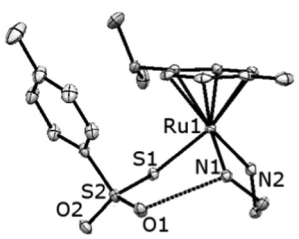


Fig. 1 ORTEP view of complex **1′a·BPh$_4$** showing thermal ellipsoids at 50% probability, atom labelling and the hydrogen-bond between O1 and N1. Hydrogen atoms and the BPh$_4$ anion are omitted for clarity.

related[13] thiolato or sulfonato derivatives [(*p*-cymene)Ru(en)(SPh)]$^+$ and [(*p*-cymene)Ru(en)(S(O)iPr)]$^+$ (0.019 and 0.034 Å, respectively) but within the range of that observed in the parent bipyridine complex **1b**.[1] The difference of electronic properties between the pure σ-donor ethylenediamine and the π-acceptor 2-2′-bipyridine in **1b**, which can compete with the arene for the ruthenium electronic density, is illustrated by the slightly longer ruthenium–arene centroid ring distance in the former than in the latter (Δ = 0.012 Å).

The crystal structure also confirms that the ethylenediamine ligand can act as a hydrogen-bond donor in arene–ruthenium complexes,[13,14] with an N1–H1B···O1–S1 interaction indicated by the N1–O1 distance of 2.880 Å, which correlates with a longer S1–O1 than an S1–O2 bond.

Table 2 Selected bond distances (Å) and angles (°) for complexes **1′a·BPh$_4$**, **3·BPh$_4$** and **4′·(BPh$_4$)$_2$**

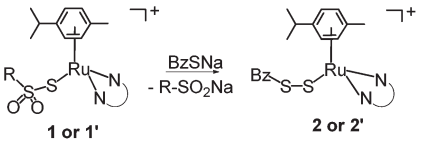
	1′a·BPh$_4$	**3·BPh$_4$**	**4′·(BPh$_4$)$_2$**
Ru1–S1	2.4129(5)	2.3774(1)	2.3952(12)
Ru1–N1	2.1330(2)	2.074(2)	2.137(3)
Ru1–N2	2.1386(2)	2.084(3)	2.131(3)
Ru1–C (average)	2.207	2.210	2.266
Ru2–C (average)	—		2.193
Ru2–N3	—	—	2.128(4)
Ru2–N4	—	—	2.110(3)
Ru2–S3	—	—	2.334(2)
	—	—	2.598(7)
S1–S2	2.0284(7)	—	2.0608(17)
S2–S3	—	—	1.690(7)
	—	—	2.196(3)
N1–Ru1–S1	89.07(5)	84.66(8)	86.54(9)
N2–Ru1–S1	83.55(5)	84.58(9)	85.88(10)
N1–Ru1–N2	79.31(7)	76.74(10)	79.23(12)
N3–Ru2–N4	—	—	78.22(16)
N3–Ru2–S3	—	—	94.6(2)
			84.53(16)
N4–Ru2–S3	—	—	81.75(18)
			95.04(11)

Reactivity of complexes 1 and 1′ with thiolates

As anticipated, the thiosulfonato complexes **1** or **1′** react with thiolates,[1] to quantitatively yield the corresponding disulfanido derivatives **2** or **2′**, as illustrated in Scheme 2.

Reactivity of complexes 1 and 1′ with hydrosulfide

Complexes **1a** and **1′a** both instantaneously react with one equivalent of sodium hydrosulfide in DMSO or DMF. However, the outcome of the reaction is strongly dependent on the diamine ligand. The product isolated from the reaction with **1a** after precipitation with sodium tetraphenylborate shows a strongly shielded signal at −2.51 ppm in ^{1}H NMR integrating for one proton (Fig. S1†). It also gives an ion at m/z = 425 (100%) by ESI$^+$-MS, these data being in agreement with its



Scheme 2 Reaction of complex **1** or **1′** with sodium benzyl thiolate.

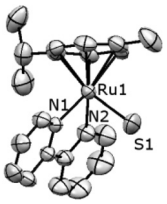


Fig. 2 ORTEP view of complex **3·BPh$_4$** showing thermal ellipsoids at 50% probability and atom labelling. Hydrogen atoms and the BPh_4 anion are omitted for clarity.

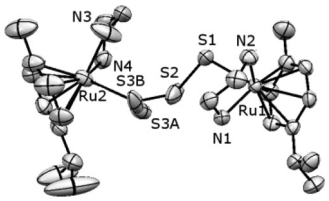
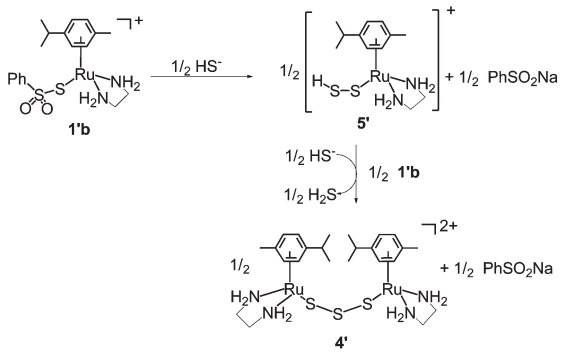


Fig. 3 ORTEP view of complex **4′·(BPh$_4$)$_2$** showing thermal ellipsoids at 50% probability and atom labelling. Hydrogen atoms, the co-crystallized benzene molecule, and the BPh_4 anions are omitted for clarity. The two occupation sites for S3 are displayed.

formulation as the hydrogen(sulfido) complex [(*p*-cymene)Ru(bipy)(SH)]$^+$ (**3**). This formulation was confirmed by the synthesis of an authentic sample of **3** from [(*p*-cymene)Ru(bipy)(Cl)]$^+$ and NaSH (see the Experimental section), which shows the same spectroscopic properties, and by its X-ray structure, displayed in Fig. 2.

The Ru–S bond distance (2.377 Å) compares well with those already reported for other monomeric hydrogen(sulfido) Ru(II) complexes[3d,15] or [(*p*-cymene)Ru(bipy)(SSBz)]$^+$.[1] It must be noted that the crude reaction mixture before precipitation with sodium tetraphenylborate contains **3** as major species (Fig. S1′†). In contrast, the reaction of the thiosulfonate complex **1′a** with one equivalent of sodium hydrosulfide leads to a product lacking the typical strongly shifted signal corresponding to the coordination of an SH group in ^{1}H NMR (Fig. S2†). This new complex, **4′**, isolated as its tetraphenylborate salt, shows an ion in the ESI$^+$-MS spectrum at m/z = 1006 (100%), and its elemental analysis is in accordance with the formation of the trisulfido-bridged dinuclear complex [[(*p*-cymene)Ru(en)(S)]$_2$S·(BPh$_4$)]$^+$. This is further confirmed by its X-ray structure displayed in Fig. 3.

Structures of transition metal complexes with a single μ-trisulfido bridge are scarce in the literature,[16] and none involves a ruthenium centre. Indeed, with ruthenium, only μ-trisulfido moieties which are part of a cyclic core of general formula



Scheme 3 Favored mechanism for the formation of **4′** from **1′b**.

Ru_2S_x (x = 5, 6) have been reported.[17] The structure of **4′** is best refined with two occupation sites for S3. Bond distances and angles (Table 2) are fairly conventional, with nevertheless two intramolecular hydrogen-bonds detected between the ethylenediamine ligand nitrogens N1 and N4 and the central sulfur atom S2 (N1–S2 and N4–S2 distances are 3.394 and 3.299 Å, respectively and N1–H1A–S2 and N4–H4–S2 angles are 133.50 and 142.44°, respectively).

The striking difference in the reactivity of complexes **1a** and **1′a** prompted us to further investigate the mechanisms leading to the two different products **3** and **4′**. Although we had never observed a direct attack of the sulfur-based nucleophiles onto the ruthenium centre in our previous studies with thiolates, this mechanism is however the simplest to explain the formation of complex **3** from **1a**. To unambiguously discriminate between this mechanism and other more complex reaction pathways, we used the ^{34}S isotopically labeled thiosulfonate $PhSO_2{}^{34}S^-$ as a ligand (complex **1b**). As expected, the molecular ion in the ESI$^+$-MS spectra of **1b** displays an additional +2 Da (m/z = 567 (100%)), confirming the incorporation of the labeled sulfur in the complex. The ESI$^+$-MS spectrum of complex **3** obtained after the reaction of ^{34}S-labeled **1b** with sodium hydrosulfide is shown in Fig. S3.† It corresponds to a hydrogen(sulfido) derivative in which the sulfur is a ^{32}S and not a ^{34}S, indicating a direct substitution of HS^- at the metal centre. This proposition is further supported by the presence as major species of $PhSO_2{}^{34}S^-$ (m/z = 175 (100%)) in the ESI$^-$-MS spectra. Starting from the corresponding isotopically enriched complex **1′b**, the μ-trisulfido dinuclear complex **4′** is obtained, its mass spectrum (Fig. S4†) indicating the presence of two ^{34}S. This is in accordance with a mechanism in which the hydrosulfide reacts on the S–S(O)$_2$ bond (Scheme 3) rather than at the metal centre. The breaking of this bond would result in the formation of the hydrogen(disulfanido) complex **5′**, which could then either react with the starting complex **1b′** to give the trisulfido compound **4′**, or directly yield **4′** and H_2S by disproportionation. Deprotonation of **5′** by the hydrosulfide anion could account for the faster reaction of the electrophilic **1b′** with **5′**, rather than with the anionic HS^-.

Thus, the nature of the chelating diamine is a determining factor in the reaction between thiosulfonato ruthenium

complexes and hydrosulfide, while it shows no importance in their reaction with thiolates. Extensive studies have been carried out on complexes $[(\eta^6\text{-arene})Ru(diamine)(Z)]^{n+}$ ((Z) being an anionic or neutral ligand) since the discovery of their anticancer properties,[18] the rationalization of these data is not straightforward, and electronic as well as steric factors of each of the three building blocks η^6-arene, diamine or Z must be taken into account. Here, we propose that the more electropositive and less sterically crowded metal centre in complexes **1** than in complexes **1′** is at the basis of this switch of reactivity.

Conclusions

The reaction between the anion HS^- and thiosulfonato ruthenium complexes, although sensitive to the nature of the metal coordination sphere, offers a new rational access to rare trisulfido-bridged dinuclear derivatives.

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