Synthesis, Spectroscopic and Structural Characterization of New Ru^{II} and Ru^{III} Complexes Containing Triazole- and Thiadiazole-Type Ligands

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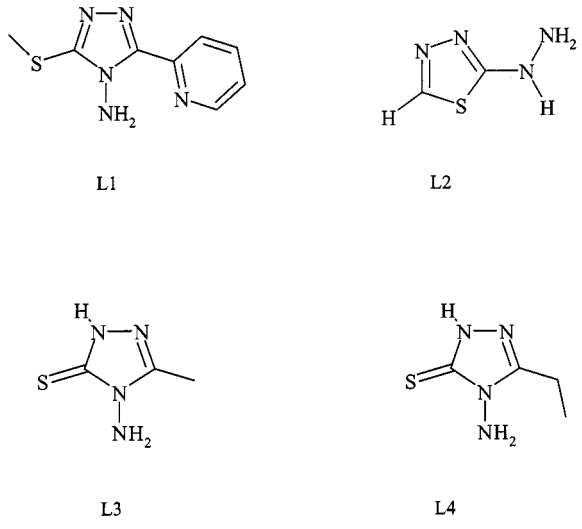
The chemical behavior of triazole, thiadiazole, and triazoline derivatives of thiocarbonohydrazide towards *cis*-$[RuCl_2(DMSO)_4]$ (**2**) was studied. Reaction of 4-amino-5-methylthio-3-(2-pyridyl)-1,2,4-triazole (L1) with **2** gave two diastereomeric complexes, *trans,cis*-$[RuCl_2(DMSO)_2(L1)]$ (**3**) and chiral *cis,cis*-$[RuCl_2(DMSO)_2(L1)]$ (**4**). Reaction of **2** with 2-(2-formylhydrazino)-1,3,4-thiadiazole in MeOH gave the complex *trans,cis*-$[RuCl_2(DMSO)_2(L2)]$ (**5**) with concomitant deformylation of the starting ligand. The process was catalyzed by Ru^{II} in very low yield. Synthesis of the Ru complexes of 4-amino-3-methyl-1,2,4-Δ^2-triazoline-5-thione (L3) and 4-amino-3-ethyl-1,2,4-Δ^2-triazoline-5-thione (L4) resulted in an interesting oxidation of the metal promoted by DMSO. Reaction of **2** with these ligands in a 6 N HCl solution led to the isolation of the complexes *mer*-$[RuCl_3(DMSO)(L3)]\cdot 1/2\ H_2O$ (**6**) and *mer*-$[RuCl_3(DMSO)(L4)]\cdot 1/2\ H_2O$ (**7**). The complex *mer*-$[RuCl_3(DMSO)(L4)]\cdot CH_3COOH\cdot H_2O$ (**7'**) was obtained by recrystallization of **7** from ethyl acetate. The complexes **6**, **7**, and **7'** were highly stable in HCl solutions and acetone but not in neutral aqueous solution. To the best of our knowledge this is the first report of Ru^{III} complexes with an N–N–C–S chelating system.

Introduction

Cyclic derivatives of thiocarbonohydrazide and carbonohydrazide are a class of compounds rarely investigated from a structural point of view. They can exhibit analgesic properties[1] and some transition metal complexes have been studied for their pharmacological properties (such as fungicides, acaricides, insecticides, nematicides).[2] The 4-amino-5-thioxo-*s*-triazoline derivatives are known for their capability of complexing a number of soft metal ions.[3] They are also used in fixer compositions for silver halide photographic materials, as corrosion inhibitors, for rapid gravimetric determination of copper, and selective microevaluation of Au^{III}, Tl^{I}, and Ag^{I}.[4] We have previously prepared and structurally characterized complexes of Cu^{II}, Cu^{I}, $Cu^{II/I}$, and Au^{I} with 4-amino-3-methyl-1,2,4-Δ^2-triazoline-5-thione, which may be considered a good stabilizing agent of the low oxidation state.[3,5] This ligand is a weak monoprotic acid which exhibits thione-thiol tautomerism[5] in solution and undergoes an interesting desulfuration reaction promoted by copper(II).[6] In this paper we report our studies on the complexing capability of these ligands towards Ru^{II} and Ru^{III} ions.

Werner-type complexes of ruthenium with cyclic derivatives of thiocarbonohydrazide are a new class of compounds that are of interest for the development of transition metal coordination chemistry. The chloride–dimethyl sulfoxide–ruthenium derivatives containing a nitrogen ligand are of great interest for their potential as non-platinum inorganic antitumor drugs.[7] Moreover the N–N–C–S chelating system is similar to that of thiosemicarbazides and thiosemicarbazones, which constitute an important class of *N,S* donor ligands due to their interesting biological properties.[8] The ligands that we have considered are depicted in Scheme 1. In this report we describe the synthesis and the single-crystal X-ray structures of L1 **1**, L1·HCl **1'**, *trans,cis*-$[RuCl_2(DMSO)_2(L1)]$ (**3**), *cis,cis*-$[RuCl_2(DMSO)_2(L1)]$ (**4**), *trans,cis*-$[RuCl_2(DMSO)_2(L2)]$ (**5**), *mer*-$[RuCl_3(DMSO)(L3)]\cdot 1/2H_2O$ (**6**), *mer*-$[RuCl_3(DMSO)(L4)]\cdot 1/2H_2O$ (**7**) and *mer*-$[RuCl_3(DMSO)(L4)]\cdot CH_3COOH\cdot H_2O$ (**7'**).



Scheme 1. Structures of the ligands

Results and Discussion

Synthesis and Characterization

All complexing reactions were studied using *cis*-$[RuCl_2(DMSO)_4]$ (**2**). The ligands we have considered can

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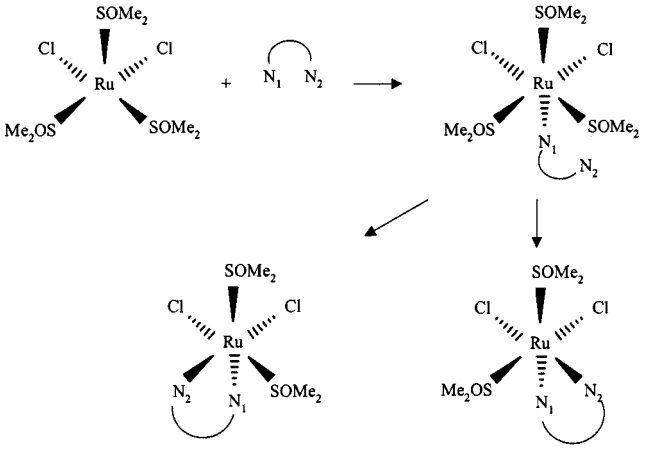
act as monodentate or bidentate *N,N* (L1, L2) or *N,S* (L3, L4) chelating agents; moreover they can interact with the metals through other donating atoms to form polymeric species.[3,5] In L1 the triazole and pyridine fragments are coplanar and can adopt two conformations with the pyridine nitrogen atom on the same side of the exocyclic amine nitrogen atom (**1**) or on the opposite side, as found in **1'**.

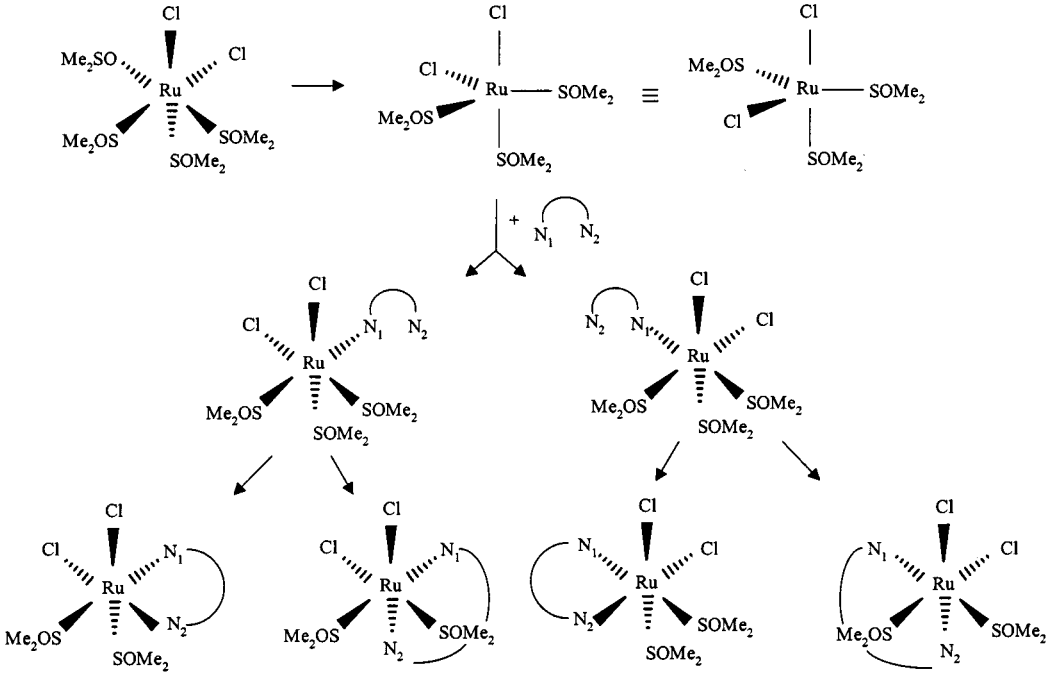
Reaction of **2** with L1 in MeOH produces two diastereomeric complexes, *trans,cis*-[$RuCl_2(DMSO)_2(L1)$] (**3**) and *cis,cis*-[$RuCl_2(DMSO)_2(L1)$] (**4**). The reaction conditions leading to **4** are probably governed by kinetic factors; in fact the complex was obtained only once despite many attempts that led invariably to the formation of **3**. It is well-known that Ru^{II}, a low spin d^6 system, undergoes substitution by a dissociative mechanism.[9] The leaving group in complex **2** is the *O*-coordinated DMSO molecule that lies *trans* to *S*-coordinated DMSO.[10] For steric reasons the trigonal bipyramidal intermediate (TBP) (Scheme 2) will lead to the formation of 100% *cis* isomer **4**, as is also the case of a square pyramid intermediate (SP) (Scheme 3). To explain the formation of **3** we hypothesize a rearrangement of the intermediates TBP or SP to the more stable TBP with three DMSO ligands in equatorial positions, leading to 100% of the *trans*-isomer **3** (Scheme 4). To correctly explain the formation of **4** it is necessary to hypothesize that the first binding of the ligand L1 proceeds through the pyridine nitrogen atom, due to the greater basicity of this atom than that of the triazole [see structure of L1·HCl (**1'**)] even if basicity and nucleophilicity are not equivalent concepts.

Reaction of **2** with 2-(2-formylhydrazino)-1,3,4-thiadiazole in MeOH forms the complex *trans,cis*-[$RuCl_2(DMSO)_2(L2)$] (**5**) in which the ligand is deformylated. This process is catalyzed by Ru^{II} and the yield is very low. A similar deformylation process of [2-(2-formylhydrazino)-1,3,4-thiadiazole] occurs in a 12 M solution of NH_4OH only if Zn^{2+} is added. In an acidic medium rearrangement of the ligand to form 4-amino-1,2,4-Δ^2-triazoline-5-thione was observed. The *trans,cis* isomer may arise through the same mechanism proposed for **3**. In all three complexes **3**, **4**, **5** the *S*-coordinated DMSO molecules are oriented in the same manner with the oxygen atoms lying on an equatorial plane.

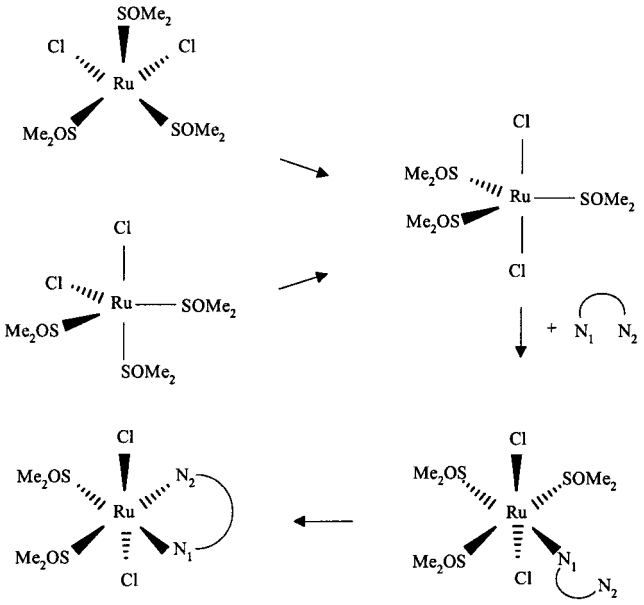
The synthesis of the Ru complexes with L3 and L4 as ligands revealed an interesting oxidative process of the metal. In fact upon treatment of **2** with these ligands in a 6 N HCl solution, Ru^{III} complexes were obtained. This mech-



Scheme 3. Proposed formation pathway of **4** via the SP intermediate



Scheme 2. Proposed formation pathway of **4** via the TBP intermediate



Scheme 4. Proposed formation pathway of **3**

anism does not involve molecular oxygen, as the reaction also proceeds under nitrogen atmosphere. It is well-known that L3 and L4 can act as reducing agents, so the oxidative process has to be due to the presence of DMSO. The oxidizing properties of DMSO in acidic solutions were tested in the presence of Ru^{II}, leading us to hypothesize an equilibrium:

$$2\,Ru^{II} + (CH_3)_2SO + 2\,H^+ \rightleftarrows 2\,Ru^{III} + (CH_3)_2S + H_2O$$

Dimethylsulfide complexes have been synthesized from acidic DMSO solutions,[11] and a similar equilibrium is probably involved in our reaction. In order to detect the dimethylsulfide produced from the reduction of DMSO in our system, the gases evolved during the reaction were allowed to flow through ethylene glycol for 8 h. This solution was analyzed by gas chromatography, showing an appropriate amount of $(CH_3)_2S$. The mechanism we propose involves the formation of a complex having formula $[RuCl_2(DMSO)_2(L)]$ (L = L3 or L4) in which the metal atom undergoes an oxidation process as shown in Scheme 5.

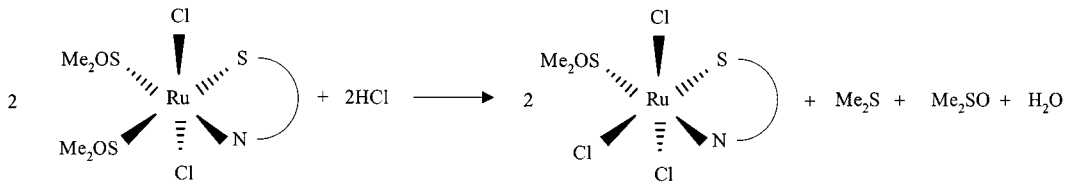
It is probable that during the oxidation, a DMSO molecule coordinated to one ruthenium atom can act as an *S,O* bridging ligand to a second Ru^{II} complex. A simultaneous inner sphere electron transfer mechanism of one electron from each Ru^{II} atom to the bridging DMSO can then occur. The complexes **6**, **7**, and **7'** are not stable in neutral aqueous solutions, whereas they are highly stable in HCl solutions and acetone. Conductivity experiments performed in acetone did not show any increase in molar conductivity, but when a small amount of water was added, the molar conductivity increased dramatically over three hours.

All three complexes synthesized and structurally characterized show a *mer* configuration and to the best of our knowledge this is the first report of Ru^{III} complexes with an N–N–C–S chelating system.

Spectroscopic Investigations

The ^{1}H-NMR spectrum of the complex **3** shows the CH_3 signal of L1 at $\delta = 2.75$, whereas the methyl groups of the two coordinated DMSO ligands give a signal at $\delta = 3.17$. This is in accordance with the assignments for free L1, and of DMSO coordinated to Ru^{II}.[10] The aromatic region shows three multiplets integrating for 1 H in the range $\delta = 7.73$–8.75. The mean shift of these signals with respect to free L1 is about 0.5 ppm, with the exception of the hydrogen atom *ortho* to the pyridine nitrogen atom which gives a signal at $\delta = 10.48$ as compared to $\delta = 8.70$ in free L1. The exocyclic amino group gives signal at $\delta = 6.84$ showing a shift towards higher field of about 0.3 ppm.

Several spectra of the paramagnetic complexes **6** and **7** were collected in different solvents in order to assign the signals and collect data regarding substitution of the DMSO ligand. A spectrum of both complexes in $[D_6]$acetone/$[D_6]$DMSO was collected between $\delta = +50$ and -50 although all the signals were observed between $\delta = +10$ and -12. In some ruthenium(III) complexes,[7] the signal of the methyl groups of the sulfur-coordinated DMSO is observed around $\delta = -14$ as a broad peak. A similar signal near $\delta = -11$ is present in the spectra of **6** and **7**. The signals of the hydrogen atoms of the coordinated amino groups were not located. This is probably due to both the paramagnetic shift and line broadening caused by the presence of the nearby paramagnetic centre. In the complex **6** the signal of the methyl group of L3 was observed as a broad peak at around $\delta = 6.4$. After 14 days this signal became narrower and shifted to $\delta = 5.64$; in the free ligand L3 the methyl group gives a signal at $\delta = 2.23$. In a freshly prepared sample of the analogous complex **7** the signal of the methylene group was observed at $\delta = 5.01$ and neither a shift nor a narrowing of the peak were observed after 16 days, while the signal of the methyl group was observed at $\delta = -0.12$. The signals of these two groups in free L4 are at $\delta = 2.63$ and $\delta = 1.17$, respectively. We have no explanation for the shift of the methyl group signal in the spectrum of **6**, but another important feature arises from these spectra. As the



Scheme 5

distance between the alkyl group and the triazole ring increases, the chemical shifts of the alkyl groups become more similar to those observed in the free ligand. This is probably due to the presence of a non-zero spin density on the triazole ring as a result of back-bonding from the metal to the sulfurous ligand.[12] This may also be the reason why the thioamide hydrogen atom cannot be located between δ = +50 and –50. It should be noted that in the case of the complex **6** the solvent used was a mixture of acetone and DMSO. After 14 days at nearly 300 K no substitution of the coordinated DMSO was observed, strongly suggesting that the ruthenium complex is substitutionally inert. To identify the signal of the acidic thioamide hydrogen atom, a small portion of D_2O was added to the sample of **6** and a spectrum was collected immediately but no change was observed. A week after the addition of D_2O to the sample, the colour of the solution had changed from green to pale yellow. A new spectrum was collected between δ = +50 and –50 but no paramagnetic peaks were observed.

Conductivity Measurements

The complexes **6** and **7** were synthesized in aqueous solution, with the pH maintained around 0 using highly concentrated hydrochloric acid. NMR experiments revealed that when dissolved in anhydrous solvents such as acetone or DMSO, the complex is quite stable for several days. On addition of small portions of water, a dramatic change in the nature of the complex occurs (Figure 1).

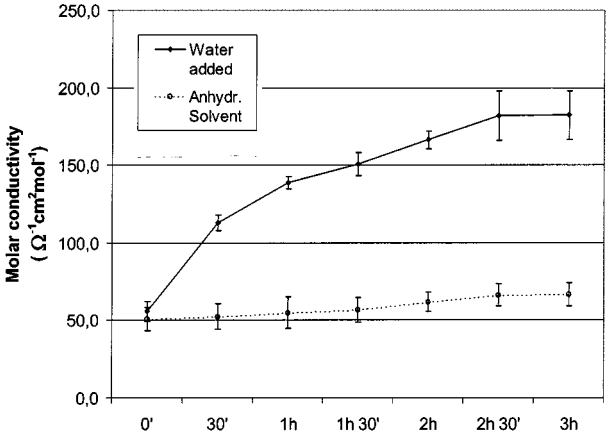


Figure 1. Conductivity measurements of **6**; measurements were made using a $1.016 \cdot 10^{-4}$ M solution of $[RuCl_3(DMSO)(L3)] \cdot 1/2\ H_2O$ in acetone; to follow the reaction, water (0.2 mL) was added to the complex solution (2 mL)

X-ray Structure Analysis

The crystal structures of the ligand L1 (**1**) and of its hydrochloride derivative **1'** are depicted in Figure 2 and Figure 3, respectively. Selected bond lengths and angles are provided in Table 1. The triazole and pyridine rings are essentially coplanar in both compounds {τ[N(1)–C(2)–C(3)–N(5)] = 169.3(2)° for **1** and –0.1(5)° for **1'**} but the molec-

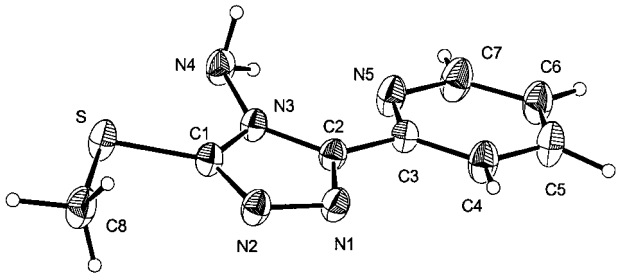


Figure 2. Molecular structure and numbering scheme of compound **1**; thermal ellipsoids are drawn at the 30% probability level

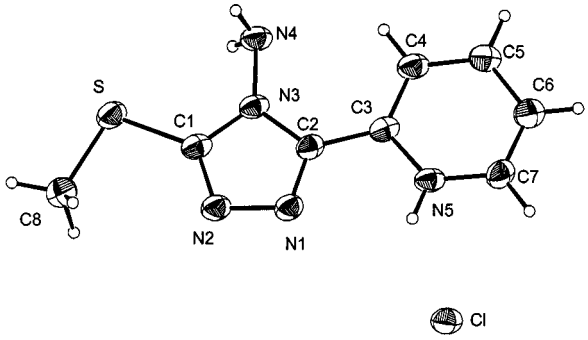


Figure 3. Molecular structure and numbering scheme of compound **1'**; thermal ellipsoids are drawn at the 30% probability level

Table 1. Selected bond lengths [Å] and angles [°] for **1**, **1'**, **3**, and **4**

	1	**1'**	**3**	**4**
Ru–N(1)			2.066(5)	2.032(4)
Ru–N(5)			2.163(6)	2.135(4)
Ru–S(3)			2.257(2)	2.260(1)
Ru–S(2)			2.270(2)	2.243(1)
Ru–Cl(2)			2.390(2)	2.412(1)
Ru–Cl(1)			2.413(2)	2.454(1)
S–C(1)	1.744(3)	1.735(3)	1.726(8)	1.735(5)
S–C(8)	1.798(4)	1.797(3)	1.804(9)	1.756(9)
N(1)–C(2)	1.308(3)	1.312(4)	1.326(8)	1.314(6)
N(1)–N(2)	1.395(3)	1.395(3)	1.400(7)	1.391(6)
N(2)–C(1)	1.310(4)	1.316(4)	1.310(8)	1.310(7)
N(3)–C(1)	1.352(3)	1.367(4)	1.378(8)	1.375(7)
N(3)–C(2)	1.370(3)	1.368(4)	1.372(8)	1.356(6)
N(3)–N(4)	1.411(3)	1.413(4)	1.411(7)	1.412(6)
N(5)–C(7)	1.324(4)	1.326(4)	1.324(8)	1.347(6)
N(5)–C(3)	1.330(5)	1.369(4)	1.360(8)	1.356(6)
N(1)–Ru–N(5)			75.8(2)	76.71(16)
N(1)–Ru–S(3)			92.59(17)	95.60(12)
N(5)–Ru–S(3)			166.50(16)	170.71(11)
N(1)–Ru–S(2)			172.86(16)	92.81(13)
N(5)–Ru–S(2)			99.46(17)	91.08(11)
N(1)–Ru–Cl(2)			93.46(15)	170.74(12)
N(5)–Ru–Cl(2)			84.82(16)	94.07(11)
N(1)–Ru–Cl(1)			85.34(15)	89.49(13)
N(5)–Ru–Cl(1)			89.14(15)	85.60(11)
C(2)–N(1)–N(2)	107.8(2)	107.9(3)	109.7(6)	109.4(4)
C(1)–N(2)–N(1)	106.5(2)	106.5(2)	105.9(6)	105.4(4)
C(1)–N(3)–C(2)	105.5(2)	105.1(3)	106.8(6)	105.6(4)
C(1)–N(3)–N(4)	123.2(2)	128.3(3)	121.3(7)	128.6(4)
C(2)–N(3)–N(4)	131.2(2)	126.6(3)	131.9(7)	125.7(4)
C(3)–N(5)–C(7)	117.7(2)	123.8(3)	116.7(7)	117.8(4)

ules are in different conformations. In both compounds the methyl carbon atoms are synperiplanar with respect to the imine nitrogen atom N(2) (τ[N(2)–C(1)–S–C(8)] = –1.8(2) and –4.2(3)° for **1** and **1'**, respectively). The pyramidal exocyclic amine nitrogen atom N(4) shows the lone pair oriented towards the sulfur atom in **1** and towards the hydrogen atom of the pyridine C(4) atom in **1'**. The most significant differences concerning the bond angles are the C(2)–N(3)–N(4) [131.2(2) and 126.6(3)° for **1** and **1'**, respectively] and the C(2)–C(3)–C(4) [119.1(3)° (**1**), 128.5(3)° (**1'**)] angles, probably due to the different conformations of the amine hydrogen atoms. The larger endocyclic N(5) angle in **1'** is due to the protonation of the pyridine nitrogen atom [123.8(3)° (**1'**), 117.7(2)° (**1**)].

The two Ru^{II} octahedral constitutional isomers *trans*,*cis*-(**3**) and *cis*,*cis*-[$RuCl_2(DMSO)_2$(L1)] (**4**) are shown in Figure 4 and Figure 5, respectively. Selected bond lengths and angles are reported in Table 1. In both complexes the ligand, with N(1) and N(5) synperiplanar, acts as *N*,*N* chelating agent. The torsion angles τ[N(1)–C(2)–C(3)–N(5)] [–8.6(8) and –6.6(8)° for **3** and **4**, respectively] are slightly larger than in **1'**; the S–C_{Me} bond lies on the triazole ring plane in **3** whereas it is out of the plane in **4** due to intramolecular steric hindrance {τ[N(2)–C(1)–S(1)–C(8)] = –2.2(8) and –26.6(7)°}. The conformation of the N(4) amine nitrogen atom in **3** is similar to that found in **1** while in **4** it is similar to that found in **1'**, with the same interaction C(4)–H···N(4) and same trend in the C(2)–N(3)–N(4) bond angles [131.9(7)° (**3**) and 125.7(4)° (**4**)]. In both diastereomeric complexes the DMSO molecules show S=O bonds oriented in the same direction and lying roughly on a coordination plane [N(1)N(5)S(2)S(3)Ru (**3**), N(5)S(2)S(3)-Cl(1)Ru (**4**)] which consequently nearly bisects the C–S–C DMSO bond angles. The *cis*,*cis* isomer is chiral but owing to the centrosymmetric space group both enantiomers are present in the crystal. The OC-6–32-*C* enantiomer is depicted in Figure 5. In both complexes the Ru–N(1) bond lengths involving the imine triazole nitrogen atoms are shorter than the Ru–N(5) ones involving the pyridine N atoms [2.066(5), 2.163(6) Å for **3** and 2.032(4), 2.135(4) Å for **4**, respectively]. The distance Ru–N(1) is longer in **3** than in **4** due to the *trans* influence of the DMSO–*S* ligand.

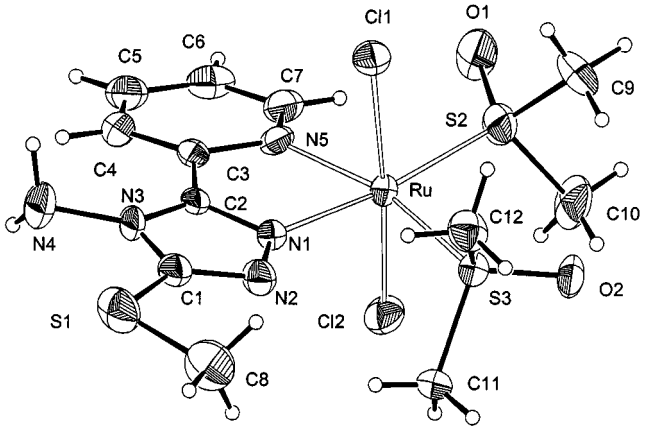


Figure 4. Molecular structure and numbering scheme of complex**3**; thermal ellipsoids are drawn at the 30% probability level

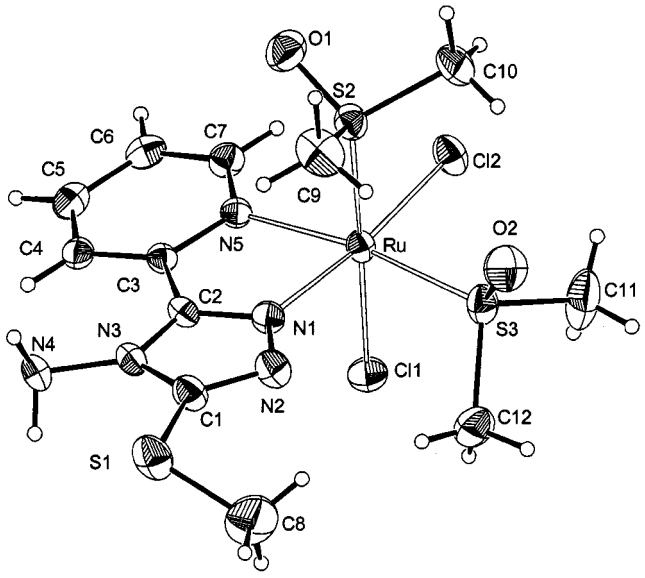


Figure 5. Molecular structure and numbering scheme of complex **4**; thermal ellipsoids are drawn at the 30% probability level

In the octahedral Ru^{II} complex *trans*,*cis*-[$RuCl_2$-$(DMSO)_2$(L2)] (**5**) (Figure 6) the 2-hydrazino-1,3,4-thiadiazole ligand L2 binds via the amine N(4) and the imine N(2) nitrogen atoms. The organic moiety and the ruthenium, sulfur, and oxygen atoms of the two DMSO ligands lie on a crystallographic mirror plane, so that the S=O bonds are oriented in exactly the same direction. The Ru–N(4) bond length involving the amine nitrogen atom is slightly longer than the Ru–N(2) one involving the imine N atom [2.130(6), 2.096(7) Å]. In this case the bite angle [79.3(3)°] is larger than in **3** [75.8(2)°] and **4** [76.7(2)°]. In the coordinated organic ligand the N(3)–C(1) bond length [1.315(12) Å] reveals a high degree of conjugation of the N(3) π orbitals with the heterocyclic ring and consequently a decrease of the double-bond character of the C(1)–N(2) [1.354(11) Å] bond.

In the complexes of Ru^{III} *mer*-[$RuCl_3$(DMSO)-(L3)]·1/2 H_2O (**6**), *mer*-[$RuCl_3$(DMSO)(L4)]·1/2 H_2O (**7**), and *mer*-[$RuCl_3$(DMSO)(L4)]·CH_3COOH·H_2O (**7'**) the 3-substituted 4-amino-Δ^{2-}1,2,4-triazoline-5-thione molecules act as *N*,*S* chelating ligands and the DMSO ligands are *trans* to the amine nitrogen atoms with the S=O bonds in the plane of the chelating ligands and oriented towards the thione S atoms. All complexes show a pseudo-C_s symmetry (Figure 7, Figure 8) except for the C(4) methyl carbon atoms of the ethyl groups in **7** and **7'**. In the three Ru^{III} complexes the Ru–$S(2)_{DMSO}$ bond lengths are ca. 0.05 Å shorter than the Ru–S(1) ones and the Ru–N(4) bond lengths *trans* to S(2) are equivalent (Table 2). The equatorial Ru–Cl(3) bonds are longer than the axial Ru–Cl ones due to the S-*trans* influence of the thione groups. The Ru–S(1) bond length in the three complexes shows some variability but as the bond strength increases a lengthening of the *trans* Ru–Cl(3) bond is observed [Ru–S(1) = 2.326(3) Å (**7**), 2.319(1) Å (**6**), 2.309(1) Å (**7'**), Ru–Cl(3) = 2.375(3) Å (**7**),

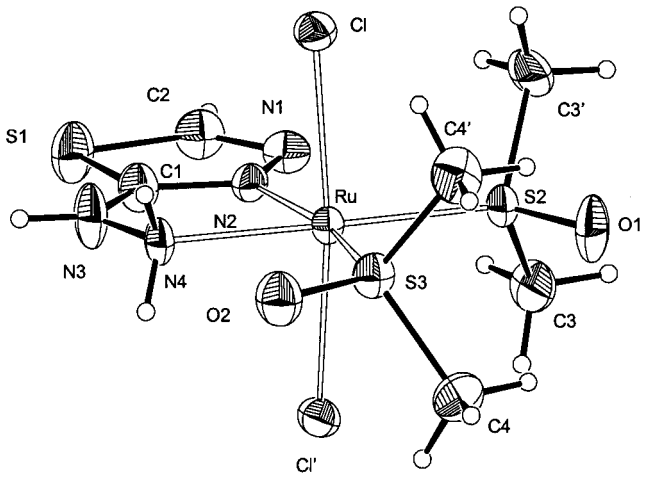


Figure 6. Molecular structure and numbering scheme of complex **5**; thermal ellipsoids are drawn at the 30% probability level; selected bond lengths [Å] and angles [°]: Ru–N(2) 2.096(7), Ru–N(4) 2.130(6), Ru–S(2) 2.242(2), Ru–S(3) 2.253(2), Ru–Cl 2.400(2), S(1)–C(2) 1.702(11), S(1)–C(1) 1.731(11), N(1)–C(2) 1.312(12), N(1)–N(2) 1.355(10), N(2)–C(1) 1.354(11), N(3)–C(1) 1.315(12), N(3)–N(4) 1.413(11); N(2)–Ru–N(4) 79.3(3), N(2)–Ru–S(2) 97.6(2), N(4)–Ru–S(3) 88.3(2), N(2)–Ru–Cl 87.46(4), N(4)–Ru–Cl 87.36(4), C(2)–S(1)–C(1) 86.9(4), C(2)–N(1)–N(2) 109.3(8), C(1)–N(2)–N(1) 114.9(7), C(1)–N(2)–Ru 110.7(6), N(1)–N(2)–Ru 134.4(6), C(1)–N(3)–N(4) 117.1(7), N(3)–N(4)–Ru 110.2(5), N(3)–C(1)–N(2) 122.8(9), N(3)–C(1)–S(1) 125.8(7), N(2)–C(1)–S(1) 111.4(7), N(1)–C(2)–S(1) 117.5(7)

2.386(1) Å (**6**), 2.395(1) Å (**7'**)]. A lengthening of the C(1)–S(1) bonds for the three complexes with respect to the free ligand L3[6] is observed [C(1)–S(1) = 1.705(11), 1.720(6), 1.716(3) and 1.674(6) Å for **7**, **6**, **7'** and L3 respectively]. The coordination alters significantly the double-bond character of the C–S group as is observed to a smaller extent in the copper complexes[3,6] $[CuCl_2(L3)] \cdot H_2O$ [1.693(6), 1.687(6) Å], $[Cu_2Cl_4(L3)]_n \cdot nH_2O$ [1.697(12) Å] and $[Cu_3Cl_5(OH_2)(L3)_2]_n \cdot 2nH_2O$ [1.699(5), 1.694(5) Å].

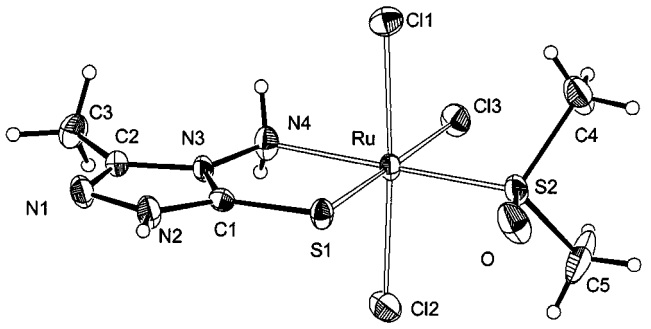


Figure 7. Molecular structure and numbering scheme of complex **6**; the H_2O molecule is omitted for clarity; thermal ellipsoids are drawn at the 30% probability level

To the best of our knowledge the only ruthenium complexes with a neutral ligand and a similar N–N–C–S chelating system are $[(\eta^6\text{-}p\text{-cymene})RuCl(taz)]PF_6$ (taz = 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine),[13] $[Ru(HL)(PPh_3)_2Cl]Cl \cdot CH_2Cl_2$ and $[Ru(HL)(PPh_3)(mpi)]Cl_2 \cdot CH_2Cl_2 \cdot 3H_2O$ [HL = methyl 2-pyridyl ketone 4-(4-tolyl)thiosemicarbazone, mpi = methyl(2-pyridyl)methyleneimine],[14] in which the metal has an oxidation state of +2. In the taz complex the C–S distance [1.687(3) Å] supports the double-bond character of the 3-thioxo group[15] and the C–S group is not significantly altered by coordination. In the two HL complexes the C–S bonds, 1.707(6), 1.698(7) Å, are similar to those found in **6**, **7**, and **7'**. In these Ru^{II} cationic complexes the Ru–S bond lengths [2.354(1) Å,[13] 2.386(2), 2.358(2) Å,[14]] are greater than those found in our Ru^{III} complexes, due to the lower oxidation state of the metal.

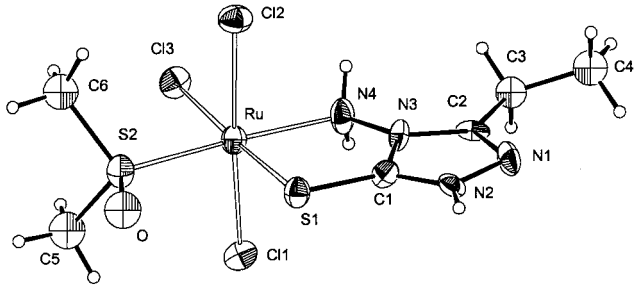


Figure 8. Molecular structure and numbering scheme of complex **7**; the H_2O molecule is omitted for clarity; thermal ellipsoids are drawn at the 30% probability level

Table 2. Selected bond lengths [Å] and angles [°] for **6**, **7**, and **7'**

	6	**7**	**7'**
Ru–N(4)	2.158(5)	2.157(8)	2.162(2)
Ru–S(2)	2.256(1)	2.268(3)	2.267(1)
Ru–S(1)	2.319(1)	2.326(3)	2.309(1)
Ru–Cl(2)	2.353(2)	2.363(3)	2.355(1)
Ru–Cl(1)	2.370(2)	2.368(3)	2.369(1)
Ru–Cl(3)	2.386(1)	2.375(3)	2.395(1)
S(1)–C(1)	1.720(6)	1.705(11)	1.716(3)
N(1)–C(2)	1.287(8)	1.355(11)	1.299(4)
N(1)–N(2)	1.381(7)	1.355(10)	1.381(3)
N(2)–C(1)	1.313(7)	1.313(12)	1.321(4)
N(3)–C(1)	1.334(7)	1.359(12)	1.344(4)
N(3)–C(2)	1.382(10)	1.336(11)	1.392(3)
N(3)–N(4)	1.405(7)	1.411(10)	1.418(3)
N(4)–Ru–S(1)	85.8(1)	86.7(2)	86.96(7)
S(2)–Ru–S(1)	91.09(5)	91.9(1)	90.43(4)
N(4)–Ru–Cl(2)	89.6(2)	89.7(3)	87.14(7)
S(1)–Ru–Cl(2)	90.58(5)	90.4(1)	89.77(3)
N(4)–Ru–Cl(1)	84.9(2)	85.0(3)	88.99(7)
S(1)–Ru–Cl(1)	92.88(5)	91.9(1)	91.04(3)
N(4)–Ru–Cl(3)	92.2(1)	90.5(2)	88.86(7)
C(1)–S(1)–Ru	96.2(2)	96.4(4)	95.8(1)
C(2)–N(1)–N(2)	104.9(5)	103.1(8)	105.3(2)
C(1)–N(2)–N(1)	112.1(5)	114.3(9)	112.2(3)
C(1)–N(3)–C(2)	108.7(5)	109.7(9)	108.7(2)
C(1)–N(3)–N(4)	121.4(5)	123.0(8)	121.6(2)
C(2)–N(3)–N(4)	129.8(5)	126.4(8)	129.6(2)
N(3)–N(4)–Ru	111.9(3)	110.0(5)	110.5(2)

Water molecules of solvation are present in the three Ru^{III} complexes, while in **7'** a free molecule of ethanoic acid cocrystallizes. A broad network of hydrogen bonds is present in every compound structurally characterized.

All Ru complexes display a distorted octahedral coordination and in the *trans*–Cl complexes the axial Cl–Ru–Cl angles [173.95(7)° (**3**), 173.28(9)° (**5**), 173.35(6)° (**6**), 174.13(11)° (**7**), 176.00(3)° (**7'**)] show a significant deviation from linearity forced by the steric hindrance of the DMSO methyl groups. The *trans* Ru–Cl bond lengths in the Ru^{II}

complexes [2.390(2)–2.413(2) Å] compare well with the values found in other *trans*-Cl DMSO Ru^{II} complexes[10,16–21] [2.397(1)–2.432(1) Å]. The lengthening of the Ru–Cl(1) in **4** [2.454(1) Å] reflects the strong *trans* influence of the DMSO ligand, whereas the Ru–Cl(2) bond [2.412(1) Å] *trans* to N(1) agrees with the value found in *cis*,*cis*,*cis*-$[RuCl_2(Me_2SO)_2(py)(Me_3Bzm)]$[22] [2.4148(7) Å] ($Me_3Bzm$ = 1,5,6-trimethylbenzimidazole, py = pyridine). In the Ru^{III} complexes **6**, **7**, **7'**, the *trans* Ru–Cl bond lengths [2.353(2)–2.370(2) Å] are close to the upper limit of the range [2.308(2)–2.366(4) Å] found in other DMSO Ru^{III} complexes.[7,16,23]

Experimental Section

Materials and Instrumentation: Thiocarbonohydrazide, iodomethane, and ruthenium trichloride hydrate were purchased from Aldrich and Fluka. Unless otherwise specified, all reagents and solvents were AR grade and used without further purification. The syntheses of 4-amino-3-methyl-1,2,4-Δ^2-triazoline-5-thione,[24] 4-amino-3-ethyl-1,2,4-Δ^2-triazoline-5-thione,[25] 2-(2-formylhydrazino)-1,3,4-thiadiazole,[25] 4-amino-3-(2-pyridyl)-1,2,4-Δ^2-triazoline-5-thione,[25] and *cis*-dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) [10] (**2**) were performed following reported procedures. – IR spectra were collected on an FT-IR Nicolet 5PC spectrometer using KBr pellets. – ^1H NMR spectra were collected on Bruker WM 300 MHz, AC 300 MHz or AC 100 MHz spectrometers. – Mass spectra were collected on a Finnigan 1020 spectrometer equipped with a MATSSQ 710 quadrupole revealer. – GC analyses were performed with a Carlo Erba MFC 500 equipped with a FID revealer and a CPSIL5CB 100% polysiloxane column (10 m × 0.32 mm, 1.20 μm) (Chrompack, Middleburg, Holland). Helium (purity 99,9%) was used as the carrier gas with a flow rate of 10 mL/min under isothermal conditions (40° C). Elemental analyses were performed using a Carlo Erba Elemental Analyzer EA 1108. – Conductivity measurements were performed using a CRISON microCM 2202 conductimeter equipped with a temperature probe. – Melting points were collected on a Gallenkamp apparatus.

4-Amino-5-methylthio-3-(2-pyridyl)-1,2,4-triazole (1): In a double necked 100 mL round bottomed flask equipped with a condenser NaOH (0.208 g, 5.2 mmol) was dissolved in DMSO (2 mL). A warm solution of 4-amino-3-(2-pyridyl)-1,2,4-Δ^2-triazoline-5-thione (1 g, 5.17 mmol) in DMSO (5 mL) was added dropwise into the flask while stirring. Iodomethane (0.65 mL, 1.48 g, 10.4 mmol) was added dropwise into the flask while stirring and the solution obtained stirred at room temperature for 1.5 h (exothermicity is observed). The solution was added dropwise into water (50 mL) at 0–5 °C. The product was extracted with CH_2Cl_2 (5 × 15 mL), the organic phase washed with water (2 × 15 mL), dried (Na_2SO_4), and concentrated to 1/3 volume under reduced pressure. White crystals of **1** were collected by slow evaporation; the product can also be recrystallized from ethanol. Yield 0.641 g (60%). – m.p. 108–109 °C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3260 (NH_2 asym. str.), 3171 (NH_2 sym. str.), 2923, 1659, 1463, 1420, 1416 (S–CH_3 asym. def.), 1011, 786 (CH_{py} oop def.). – ^1H NMR ([D$_6$]DMSO): δ = 8.70 (1 H, CH_{py}), 8.07 (1 H, CH_{py}), 8.00 (1 H, CH_{py}), 7.53 (1 H, CH_{py}), 6.55 (2 H, NH_2), 2.65 (3 H, CH_3). – $C_8H_9N_5S$ (207.26): calcd. C 46.36, H 4.38, N 33.79, S 15.47; found C 46.26, H 3.87, N 32.40, S 16.20.

4-Amino-5-methylthio-3-(2-pyridinium)-1,2,4-triazole Chloride (1'): The compound was synthesized by dissolving L1 (0.5 g 2.41 mmol) in a minimum amount of a water:ethanol (1:1) solution. The pH was lowered to ca. 3 by the addition of several drops of ca. 1 N HCl solution. L1' is easily crystallizable as white needles. Yield 0.410 g (70%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3187 (NH_2 str.), 3114 (CH_{py} str.), 1617 (triazole ring def.), 1603, 1541 (NH_2 def.), 1295 (S–CH_3 sym. def.), 1223, 1084, 797 (CH_{py} oop def.), 676 (CH_{py} oop def.), 506. – ^1H NMR ([D$_6$]DMSO): δ = 8.75 (1 H, CH_{py}), 8.16 (1 H, CH_{py}), 8.03 (1 H, CH_{py}), 7.61 (1 H, CH_{py}), 4.39 (3 H, NH_2 and NH_{py} mediated peak), 2.66 (3 H, CH_3). – $C_8H_{10}ClN_5S$ (297.16): calcd. C 39.42, H 4.16, N 28.73, S 13.15; found C 39.06, H 3.97, N 29.16, S 13.21.

***trans,cis*- (3) and *cis,cis*-Dichlorobis(dimethyl sulfoxide-*S*)(4-amino-5-methylthio-3-(2-pyridyl)-1,2,4-triazole-*N,N'*)ruthenium(II) (4):** The synthesis was performed under nitrogen atmosphere in a three necked 250 mL round bottomed flask equipped with a condenser. **1** (0.064 g, 0.31 mmol) was dissolved in dry methanol (5 mL) and the solution was heated slightly while stirring. A solution of **2** (0.15 g, 0.31 mmol) in dry methanol (10 mL) was added dropwise into the flask and the solution was heated at reflux for 1.5 h. The red-orange solution obtained was poured in a crystallizer and orange crystals of product were collected by slow evaporation. Yield of **3** 0.101 g (60%). – *trans,cis* isomer: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3273 (NH_2 asym. str.), 3167 (NH_2 sym. str.), 2922 (CH_3 str.), 1620, 1451, 1418 (S–CH_3 asym. def.), 1384, 1092 (S–O DMSO *S*-coord),1069, 1015 (CH_3 DMSO rock),781, 679 (C–S_{DMSO} str.), 426 (Ru–S str.). – ^1H NMR ([D$_6$]DMSO): δ = 10.48 (1 H, CH_{py}), 8.75 (1 H, CH_{py}), 8.20 (1 H, CH_{py}), 7.73 (1 H, CH_{py}), 6.84 (2 H, NH_2), 3.17 (CH_3 DMSO *S*-coord), 2.75 (3 H, CH_3). – $C_{12}H_{21}Cl_2N_5O_2RuS_3$ (535.49): calcd. C 26.92, H 3.95, N 13.08, S 17.96; found C 27.62, H 4.70, N 12.61, S 17.48. – *cis,cis* isomer: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3270 (NH_2 asym. str.), 3159 (NH_2 sym. str.), 2919 (CH_3 str.), 1635, 1450, 1411 (S–CH_3 asym. def.), 1096 (S–O DMSO *S*-coord), 1066, 1013 (CH_3 DMSO rock), 780, 678 (C–S_{DMSO} str.), 425 (Ru–S str.). – $C_{12}H_{21}Cl_2N_5O_2RuS_3$ (535.49): calcd. C 26.92, H 3.95, N 13.08, S 17.96; found C 27.37, H 4.24, N 12.76, S 17.63.

***trans,cis*-Dichlorobis(dimethyl sulfoxide-*S*)(2-hydrazino-1,3,4-thiadiazole-*N,N'*)ruthenium(II) (5):** The synthesis was performed under nitrogen atmosphere in a three necked 250 mL round bottomed flask equipped with a condenser. **2** (0.07 g, 0.14 mmol) and 2-(2-formylhydrazino)-1,3,4-thiadiazole (0.041 g, 0.28 mmol) were dissolved in methanol (15 mL) and the solution was heated at reflux while stirring for 1.5 h. The red-orange solution obtained was poured into a crystallizer and red crystals of the product were collected by slow evaporation. Yield 0.012 g (20%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3239 (NH str.), 3180 (NH_2 asym. str.), 3149 (NH_2 sym. str.), 1619 (NH_2 def.), 1216, 1095 (S–O DMSO *S*-coord), 1069, 1013, 687 (C–S_{DMSO} str.), 429 (Ru–S str.). – $C_6H_{16}Cl_2N_4O_2RuS_3$ (444.38): calcd. C 16.21, H 3.62, N 12.60, S 21.64; found C 16.04, H 3.83, N 12.76, S 21.58.

***mer*-Trichloro(dimethyl sulfoxide-*S*)(4-amino-3-methyl-1,2,4-Δ^2-triazoline-5-thione-*N,S*)ruthenium(III) Hemihydrate (6):** In a 100 mL round-bottomed flask, **2** (0.15 g, 0.31 mmol) was added to a suspension of L3 (0.04 g, 0.31 mmol) and HCl (ca. 6 N, 20 mL) while stirring. The mixture was stirred for 0.5 h at room temperature, then the mixture was warmed on a heating plate for 1 h. The green solution obtained was poured into a crystallizer. Dark-green crystals of the product were obtained by slow evaporation. Yield 0.059 g (45%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3449 (OH str.), 3197 (NH str.), 3102 (NH_2 str.), 1610, 1505 (Thioam I), 1124, 1089 (S–O DMSO *S*-coord), 1024, 688 (C–S_{DMSO} str.), 433 (Ru–S str.). – ^1H NMR ([D$_6$]acetone): δ = 6.4 (br, CH_3), –10.42 (br, CH_3 DMSO *S*-

coord). – $C_5H_{13}Cl_3N_4O_{1.5}RuS_2$ (424.73): calcd. C 14.14, H 3.08, N 13.19, S 15.10; found C 14.32, H 2.83, N 12.83, S 15.30.

***mer*-Trichloro(dimethyl sulfoxide-*S*)(4-amino-3-ethyl-1,2,4-Δ²-triazoline-5-thione-*N,S*)ruthenium(III) Hemihydrate (7):** The procedure was the same as for the synthesis of the previous complex, but using L4 (0.045 g, 0.31 mmol). Green crystals of the product were obtained. Yield 0.061 g (45%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3441 (OH str.), 3194 (NH_2 str.), 1608, 1498 (Thioam I), 1386 (CH_3 rock), 1124 (S–O DMSO *S*-coord), 1029, 684 (C–S_{DMSO} str.), 434 (Ru–S str.) – ^{1}H NMR ([D_6]acetone): δ = 5.01 (br 2 H, CH_2), –0.12 (3 H, CH_3), –11.15 (br, CH_3 DMSO *S*-coord). – $C_6H_{15}Cl_3N_4O_{1.5}RuS_2$ (438.76): calcd. C 16.43, H 3.45, N 12.77, S 14.61; found C 17.16, H 3.34, N 12.22, S 13.88.

***mer*-Trichloro(dimethyl sulfoxide-*S*)(4-amino-3-methyl-1,2,4-Δ²-triazoline-5-thione-*N,S*)ruthenium(III) Hydrate Acetic Acid Solvate (7'):** In a 100 mL round-bottomed flask **2** (0.15 g, 0.31 mmol) was added to a suspension of L4 (0.045 g, 0.31 mmol) and HCl (ca. 6 N, 20 mL) while stirring. The mixture was stirred for 0.5 h at room temperature, then warmed on a heating plate for 1 h and the green solution obtained was poured in a crystallizer for 24 h. The product was then extracted into ethyl acetate (several portions of 5–10 mL until the organic layer was no longer green). Green crystals of the product

Table 3. Crystallographic data of **1**, **1'**, **3**, and **4** and details of the structure solution and refinement procedures

	1	**1'**	**3**	**4**
Empirical formula	$C_8H_9N_5S$	$C_8H_{10}ClN_5S$	$C_{12}H_{21}Cl_2N_5O_2RuS_3$	$C_{12}H_{21}Cl_2N_5O_2RuS_3$
Formula weight	207.26	243.72	535.49	535.49
Wavelength [Å]	1.54184	0.71073	0.71073	1.54184
Crystal system, space group	Monoclinic, *Cc*	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions *a* [Å]	8.553(2)	7.754(3)	8.668(3)	11.828(5)
b [Å]	15.830(6)	16.822(7)	12.203(6)	8.314(2)
c [Å]	7.702(2)	8.180(4)	19.632(7)	20.877(9)
β [°]	113.49(2)	91.96(2)	97.27(2)	90.45(2)
Volume [Å³]	956.4(5)	1066.4(8)	2059.9(14)	2052.9(13)
Z, Calculated density [Mg m^{-3}]	4, 1.439	4, 1.518	4, 1.727	4, 1.733
Absorption coefficient [mm^{-1}]	2.744	0.527	1.341	11.584
F(000)	432	504	1080	1080
Crystal size [mm]	0.15 × 0.18 × 0.28	0.22 × 0.31 × 0.40	0.25 × 0.31 × 0.48	0.21 × 0.21 × 0.38
φ range for data collection [°]	5.59 to 69.88	3.48 to 25.01	3.18 to 24.00	3.74 to 69.96
Index ranges	$-8 \le h \le 10$, $-16 \le k \le 19$, $-7 \le l \le 9$	$-9 \le h \le 9$, $0 \le k \le 19$, $0 \le l \le 9$	$-9 \le h \le 9$, $0 \le k \le 13$, $0 \le l \le 22$	$-14 \le h \le 14$, $-5 \le k \le 10$, $-2 \le l \le 25$
Reflections collected/unique, *R*(int)	976/925, 0.0186	2001/1873, 0.1149	3315/3220, 0.0468	3990/3888, 0.0443
Data/restraints/parameters	925/2/158	1873/0/154	3220/0/231	3888/0/238
Goodness-of-fit on F^2[a]	1.103	0.823	0.835	0.970
Final *R* indices [$I > 2\sigma(I)$] (*R*1, *wR*2)	0.0247, 0.0682	0.0376, 0.0623	0.0407, 0.0741	0.0433, 0.1110
R indices (all data) (*R*1, *wR*2)	0.0249, 0.0685	0.1009, 0.0760	0.1095, 0.0903	0.0586, 0.1190
Extinction coefficient	0.0045(6)			
Largest diff. peak and hole [eÅ^{-3}]	0.163 and –0.177	0.290 and –0.248	0.654 and –0.395	0.849 and –1.008

[a] GOOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$, $R1 = \Sigma \parallel Fo \mid - \mid Fc \parallel / \Sigma \mid Fo \mid$, $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 4. Crystallographic data of **5**, **6**, **7**, and **7'** and details of the structure solution and refinement procedures

	5	**6**	**7**	**7'**
Empirical formula	$C_6H_{16}Cl_2N_4O_2RuS_3$	$C_5H_{13}Cl_3N_4O_{1.5}RuS_2$	$C_6H_{15}Cl_3N_4O_{1.5}RuS_2$	$C_8H_{20}Cl_3N_4O_4RuS_2$
Formula weight	444.38	424.73	438.76	507.82
Wavelength [Å]	1.54184	1.54184	0.71073	0.71073
Crystal system, space group	Tetragonal, $P4_2/mbc$	Orthorhombic, *Pcca*	Orthorhombic, *Pccn*	Monoclinic, $P2_1/n$
Unit cell dimensions *a* [Å]	17.597(7)	22.130(7)	23.010(9)	11.029(4)
b [Å]	17.597(7)	10.331(3)	10.542(5)	14.450(6)
c [Å]	9.857(4)	12.290(4)	12.046(6)	12.608(5)
β [°]				110.67(2)
Volume [Å³]	3052(2)	2809.8(15)	2922(2)	1880.0(13)
Z, Calculated density [Mg m^{-3}]	8, 1.934	8, 2.008	4, 1.794	8, 1.995
Absorption coefficient [mm^{-1}]	15.396	17.016	1.901	1.500
F(000)	1776	1680	1744	1020
Crystal size [mm]	0.20 × 0.32 × 0.41	0.21 × 0.21 × 0.45	0.25 × 0.31 × 0.40	0.25 × 0.25 × 0.45
φ range for data collection [°]	5.03 to 69.92	4.28 to 70.02	3.12 to 27.04	3.05 to 30.00
Index ranges	$0 \le h \le 21$, $0 \le k \le 21$, $0 \le l \le 12$	$-13 \le h \le 26$, $-7 \le k \le 12$, $-14 \le l \le 1$	$-29 \le h \le 27$, $-5 \le k \le 13$, $-15 \le l \le 15$	$-15 \le h \le 14$, $0 \le k \le 20$, $0 \le l \le 17$
Reflections collected/unique, *R*(int)	2990/1535, 0.0404	2677/2677, 0.0000	3202/3202, 0.0000	5685/5471, 0.0386
Data/restraints/parameters	1535/0/104	2677/0/158	3202/0/134	5471/0/217
Goodness-of-fit on F^2[a]	1.019	1.024	0.648	0.852
Final *R* indices [$I > 2\sigma(I)$] (*R*1, *wR*2)	0.0483, 0.1230	0.0622, 0.1804	0.0586, 0.1348	0.0304, 0.0589
R indices (all data) (*R*1, *wR*2)	0.0643, 0.1314	0.0679, 0.1882	0.2016, 0.1624	0.0726, 0.0672
Largest diff. peak and hole [eÅ^{-3}]	2.143 and –0.898	1.565 and –2.173	1.638 and –0.740	0.766 and –0.733

[a] GOOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, $R1 = \Sigma \parallel Fo \mid - \mid Fc \parallel / \Sigma \mid Fo \mid$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

were obtained by slow evaporation. Yield 0.063 g (40%). – IR (KBr, cm^{-1}). $\tilde{\nu}$ = 3470 (OH str.), 3158 (NH_2 asym. str.), 3045 (NH_2 sym. str.), 2925, 1722 (COOH), 1616, 1521 (Thioam I), 1384 (CH_3 rock), 1204, 1081 (S–O DMSO *S*-coord), 1028, 686 (C–S_{DMSO} str.), 605, 432 (Ru–S str.). – $C_8H_{20}Cl_3N_4O_4RuS_2$ (507.82): calcd. C 18.92, H 3.97, N 11.03, S 12.63; found C 18.78, H 4.05, N 10.96, S 12.68.

Experimental Procedure for Conductivity Measurements: Four samples of a solution of **7** in dry acetone (1.016 10^{-4} M, 2 mL) were prepared. Distilled water (0.2 mL) was added to two of the four samples, and seven measurements were made (every 30 min), the first immediately after the addition of water. The colour of the samples to which water was added changed from green to pale yellow in 3 h.

X-ray Crystal Structure Determinations: Diffraction data were recorded at 293(2) K with the φ/2φ technique on a Siemens AED (**1**, **5**, **7**), a Philips PW 1100 (**1'**, **3**, **7'**), and an Enraf–Nonius CAD4 diffractometer (**4**, **6**). The individual profiles were analyzed following the method of Lehmann and Larsen.[26] Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods [SIR92][27] and refined by full-matrix least-squares methods based on F^2 using the SHELXL-97[28] program. All the non-hydrogen atoms were refined anisotropically except the ethyl carbon atoms and the oxygen and the methyl carbon atoms of the DMSO ligand in compound **7**. In **1** the hydrogen atoms, taken from a difference Fourier map, were refined freely. In the other compounds, the hydrogen atoms were placed in calculated positions and refined with a riding model, except those of the non-coordinated amine groups, the solvated water hydrogens and the carboxylic hydrogen atoms which were freely refined for the most part. Empirical absorption corrections were applied for compounds **4**, **5**, and **6**.[29] Crystal data and some details of the structure determinations are listed in Table 3 and Table 4. Further details of the crystal structures (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, and can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England [Fax: (internat.) +44 (0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk] on quoting the reference number CCDC-121951–121958, the names of the authors, and the full journal citation. All calculations were carried out on the DIGITAL AlphaStation 255 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma. The programs PARST[30] and ORTEP[31] were also used.

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