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A new class of triazepine–ruthenium(II) complexes: synthesis, crystal structure and NMR spectroscopic properties

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Abstract

Two unprecedented three-dimensional ruthenium(II) complexes **I** and **II** derived from 2-methyl-5-oxo-7-phenyl-3-thioxo-3,4,5,6-tetrahydro-2*H*-1,2,4-triazepine (HTAZO) and 2-methyl-7-phenyl-3,5-dithioxo-3,4,5,6-tetrahydro-2*H*-1,2,4-triazepine (H_2TAZS) have been prepared by the reaction of these triazepines with [Ru(*p*-cymene)Cl_2]$_2$ in the presence of triethylamine. NMR spectroscopic and X-ray diffraction studies of the structures of the resulting complexes reveal different behavior of HTAZO and H_2TAZS in the coordination process.

Keywords: Heterocycles; Triazepine; Ruthenium(II); X-ray analyses; NMR

1. Introduction

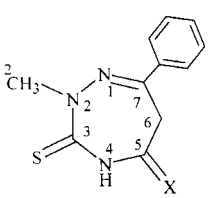
In recent years, heterocyclic systems have found wide application in organometallic chemistry. Thus a large number of complexes with heterocyclic molecules as ligands have been prepared [1–4]. These kinds of compounds act predominantly as chelates, giving versatile mono, bi or polynuclear complexes [5–8] having broad applicability in a wide range of reactions in organic synthesis [2,5b,6,7,8]. In spite of the frequent use of heterocyclic compounds as ligands, mainly with transition metals, complexes containing 1,2,4-triazepines are not known. This type of chelate which presents different coordination sites, could provide efficient catalysts with great conformational rigidity (Scheme 1).

2. Results and discussion

As part of our work in this field [9], we have prepared two unprecedented 1,2,4-triazepine-ruthenium(II) complexes by reacting [Ru(*p*-cymene)Cl_2]$_2$ with HTAZO [10,11] (four equivalents) and H_2TAZS [10,11] (four equivalents) respectively, in the presence of an excess of triethylamine under 2-propanol reflux conditions.

We have found that, when HTAZO reacts with [Ru(*p*-cymene)Cl_2]$_2$, only one chlorine atom is removed leading productively and cleanly to formation of the mononuclear complex [RuCl(*p*-cymene)TAZO] (**I**) [12]. However, with H_2TAZS, the two chlorine atoms are displaced from the complex precursor to afford readily a good yield of binuclear [Ru(*p*-cymene)TAZS]$_2$ (**II**).

The NMR spectroscopic data (Table 1) of these complexes suggest that both triazepines HTAZO and H_2TAZS were transformed before complexation, into the respective triazepinate ligands $TAZO^-$ and



X= O HTAZO
X= S H_2TAZS

Scheme 1.

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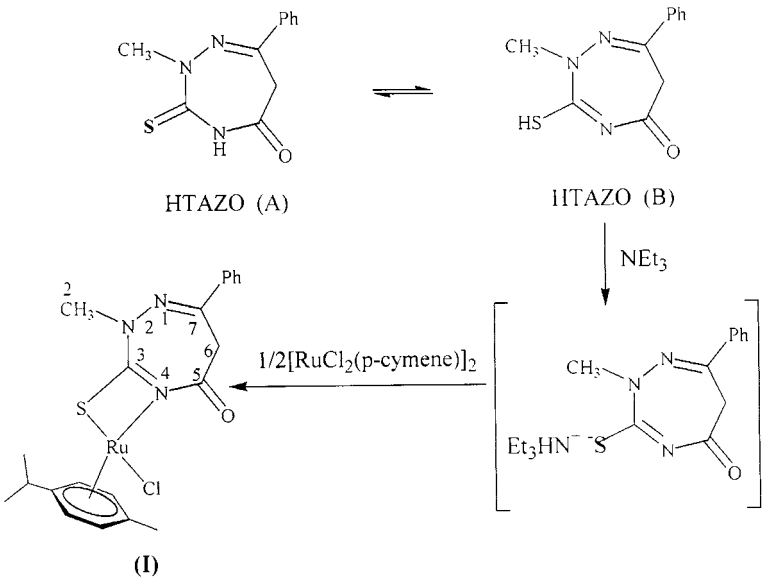
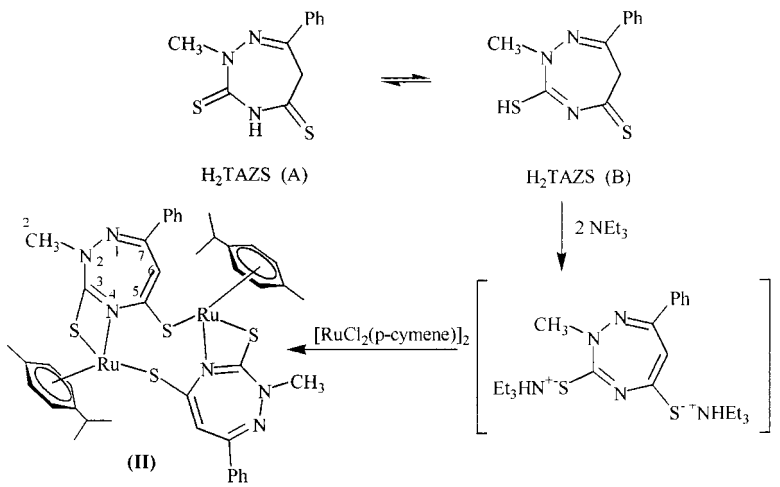
Table 1
Some pertinent ^{1}H (300 MHz) and ^{13}C-NMR (75 MHz) assignments (TMS standard, $CDCl_3$ solvent, δ in ppm) of HTAZO, H_2TAZS and the corresponding complexes

	HTAZO	Ru-TAZO (**I**)	H_2TAZS	Ru-TAZS (**II**)
H–S	8.62, br s, 1H		10.01, br s, 1H	
H–C(6)	4.02, s, 2H	3.82, d 12.5 Hz, 1H 3.48, d 12.5 Hz, 1H	4.28, s, 2H	7.04, s, 1H
H–CN(2)	3.75, s, 3H	3.52, s, 3H	3.81, s, 3H	3.13, s, 3H
C(3)	173.78	180.55	172.59	178.86
C(5)	163.74	164.73	195.28	170.64
C(6)	39.62	41.31	46.45	120.11
C(7)	159.47	154.66	160.99	160.40
C–N(2)	46.17	43.66	47.66	38.72



Scheme 2.



Scheme 3.

$TAZS^{2-}$ via the pathways shown in Schemes 2 and 3. This behavior is similar to that we described for the alkylation of these trazepines with mono and dihaloalkanes [11].

The ^{1}H-NMR spectra of HTAZO and H_2TAZS show respectively a broad singlet at 8.62 ppm and 10.01 ppm corresponding to the SH group. Signals for the H_2C(6) methylene group at 4.02 ppm (for HTAZO) and 4.28 ppm (for H_2TAZS) are also observed (Table 1). This reveals that both HTAZO and H_2TAZS exist in solution as the tautomeric form B (in solid state form A has been demonstrated [10]) (Schemes 2 and 3).

Upon binding of HTAZO to the metal, a typical AB system and a geminal coupling are observed in the ^{1}H-NMR spectrum for the H_2C(6) group (Table 1). This indicates a rigid structure of the Ru-TAZO complex with less conformational flexibility compared to the free HTAZO triazepine (Table 1).

On the other hand, comparison of ^{1}H-NMR spectra of HTAZO, H_2TAZS and their corresponding ruthenium complexes shows that coordination led to deprotonation of the ligands, as indicated by loss of the SH signal. Moreover, we observed for the complex **II** the disappearance of the H_2C(6) methylene group signal and the appearance of a singlet at 7.04 ppm due to an ethylenic proton. This shows an additional deprotonation of the H_2TAZS triazepine leading to a coordination of the other sulfur atom in position 5 (Schemes 2 and 3).

In the ^{13}C-NMR, participation of both triazepines S–C(3)–N(4) moiety is shown furthermore by downfield shift (average $\Delta\delta \sim 6$ ppm) of the C(3) carbon atom. A shielding of C(7) and C(2) carbon atoms is also observed (Table 1).

After coordination of HTAZO, the changes in chemical shift of C(5) and C(6) carbon atoms are less pronounced ($\Delta\delta \sim 1$–4 ppm). Remarkably, the H_2TAZS C(5) carbon atom is hardly shielded by about 24.64 ppm, while the C(6) signal is observed in the H–Csp^2 area ($\delta = 120.11$ ppm). These data reveal great modification in the electronic charge distribution of the H_2TAZS S–C(5)–C(6) fragment which evolute from S=C(5)–C(6) towards S–C(5)=C(6) configuration. This is confirmed by the X-ray structural analyses: the S(5)–C(5) bond length is 1.748(7) Å (1.753(6) for molecule b) and the C(5)–C(6) bond length is 1.377(9) Å (1.354(9) for molecule b). Moreover the angles around C(5) are close to 120°: S(5)–C(5)–C(6) 121.7(5)° (120.8(5)°), S(5)–C(5)–N(4) 117.3(5)° (117.8(5)°), C(6)–C(5)–N(4) 120.4(6)° (121.0(6)°).

In view of all these facts, we can state that while both sulfur atoms of H_2TAZS at C(3) and C(5) positions are coordinated to the metal, only that of HTAZO at C(3) position participates in the coordination. It is noteworthy to emphasize that the HTAZO C(5) oxo group is not involved.

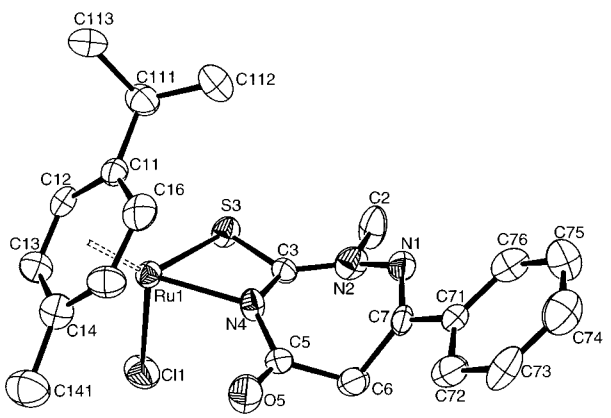


Fig. 1. Molecular structure of the dinuclear complex (Ru-TAZS)$_2$ with atom labeling. Ellipsoids represent 50% probability.

3. Description of the structure

For the Ru-TAZS complex, the asymmetric unit is built up from two halves of the molecule and a $CHCl_3$ solvent molecule. Each half is linked through the S(5) (or S(105)) atom to its related centrosymmetry counterpart thus resulting in the occurrence of two dinuclear complexes in the unit cell. The molecular structure of one of these dinuclear ruthenium complexes is shown with atoms labeling scheme in Fig. 1. Important bond lengths and angles are reported in Table 2. The $TAZS^{2-}$ ligand exhibits an unprecedented μ-κS, κ^2N,S coordination mode: the two sulfur atoms S(3) and S(5) and the nitrogen N(4) are indeed engaged in coordination with the Ru atoms. The nitrogen and S(3) form a four-membered chelate ring containing the ruthenium Ru(1) whereas the second sulfur atom S(5) is coordinated to the centrosymmetric related Ru(1)′. The μ-κS, κ^2N,S coordination mode has been previously observed in some di- and trinuclear (η^6-arene)ruthenium(II) complexes containing bridging heterocyclic thioamide [13] and in the polymeric cadmium(II) complex [Cd(mbt^2]n [14]. However, in these cases, the three donating N,S,S atoms belong to two different ligands whereas in the title complex the two sulfur and the nitrogen atoms arise from the same $TAZS^{2-}$ ligand. The bridging sulfur atoms (S(5) or S(105)) lead to the formation of an eight-membered ring Ru(1)–N(4)–C(5)–S(5)–Ru(1)′–N(4)′–C(5)′–S(5)′ which has a chair conformation (or a step like structure). It is indeed formed of three planes Ru(1)–S(5)–S(5)′–Ru(1)′, Ru(1)–N(4)–C(5)–S(5) and its centrosymmetric related one, with dihedral angle between them of 79.6(2)°. Although, such eight-membered (M–N–C–S–M–N–C–S) rings are rather commonly observed with chelating N,S containing ligands [15], the preferred conformation is boat-shaped. To the best of our knowledge, only one example of a chair conformation for such a ring has been reported for bis(benzoylmethylthiopyridinium)-bis(triphenylphosphine)-di-silver(I) [16].

Table 2
Important bond lengths (Å) and angles (°); e.s.d.s in parentheses refer to the last significant digit

Molecule a		Molecule b	
Ru(1)–N(4)	2.112(5)	Ru(2)–N(104)	2.116(5)
Ru(1)–C(12)	2.177(6)	Ru(2)–C(22)	2.179(7)
Ru(1)–C(13)	2.177(8)	Ru(2)–C(23)	2.182(7)
Ru(1)–C(15)	2.189(7)	Ru(2)–C(25)	2.179(8)
Ru(1)–C(16)	2.193(7)	Ru(2)–C(26)	2.162(7)
Ru(1)–C(11)	2.206(7)	Ru(2)–C(21)	2.203(7)
Ru(1)–C(14)	2.208(7)	Ru(2)–C(24)	2.198(7)
Ru(1)–S(5) # 1 [a]	2.402(2)	Ru(2)–S(105) # 2	2.400(2)
Ru(1)–S(3)	2.4343(19)	Ru(2)–S(103)	2.4227(19)
S(3)–C(3)	1.722(6)	S(103)–C(103)	1.705(7)
S(5)–C(5)	1.748(7)	S(105)–C(105)	1.753(6)
S(5)–Ru(1) # 1	2.402(2)	S(105)–Ru(2) # 2	2.400(2)
N(1)–C(7)	1.303(9)	N(101)–C(107)	1.278(9)
N(1)–N(2)	1.464(8)	N(101)–N(102)	1.458(8)
N(2)–C(3)	1.414(8)	N(102)–C(103)	1.421(8)
N(2)–C(2)	1.438(9)	N(102)–C(102)	1.446(9)
N(4)–C(3)	1.307(8)	N(104)–C(103)	1.298(8)
N(4)–C(5)	1.403(8)	N(104)–C(105)	1.413(8)
C(5)–C(6)	1.377(9)	C(105)–C(106)	1.354(9)
C(6)–C(7)	1.427(10)	C(106)–C(107)	1.462(10)
C(7)–C(71)	1.507(10)	C(107)–C(171)	1.498(11)
N(4)–Ru(1)–S(5) # 1	89.11(16)	N(104)–Ru(2)–S(105) # 2	87.03(16)
N(4)–Ru(1)–S(3)	66.88(16)	N(104)–Ru(2)–S(103)	66.48(16)
S(5) # 1–Ru(1)–S(3)	81.05(7)	S(105) # 2–Ru(2)–S(103)	82.57(7)
C(3)–S(3)–Ru(1)	79.2(2)	C(103)–S(103)–Ru(2)	79.6(2)
C(5)–S(5)–Ru(1) # 1	107.4(2)	C(105)–S(105)–Ru(2) # 2	107.4(2)
C(7)–N(1)–N(2)	113.4(6)	C(107)–N(101)–N(102)	114.4(6)
C(3)–N(2)–C(2)	115.4(5)	C(103)–N(102)–C(102)	114.0(6)
C(3)–N(2)–N(1)	108.0(5)	C(103)–N(102)–N(101)	110.2(5)
C(2)–N(2)–N(1)	108.7(5)	C(102)–N(102)–N(101)	107.9(6)
C(3)–N(4)–C(5)	122.9(5)	C(103)–N(104)–C(105)	125.3(5)
C(3)–N(4)–Ru(1)	102.0(4)	C(103)–N(104)–Ru(2)	101.8(4)
C(5)–N(4)–Ru(1)	134.2(4)	C(105)–N(104)–Ru(2)	132.5(4)
N(4)–C(3)–N(2)	121.5(6)	N(104)–C(103)–N(102)	121.8(6)
N(4)–C(3)–S(3)	111.9(5)	N(104)–C(103)–S(103)	112.1(5)
N(2)–C(3)–S(3)	126.6(5)	N(102)–C(103)–S(103)	126.1(5)
C(6)–C(5)–N(4)	120.4(6)	C(106)–C(105)–N(104)	121.0(6)
C(6)–C(5)–S(5)	121.7(5)	C(106)–C(105)–S(105)	120.8(5)
N(4)–C(5)–S(5)	117.3(5)	N(104)–C(105)–S(105)	117.8(5)
C(5)–C(6)–C(7)	125.8(6)	C(105)–C(106)–C(107)	125.6(6)
N(1)–C(7)–C(6)	127.1(7)	N(101)–C(107)–C(106)	127.9(7)
N(1)–C(7)–C(71)	114.3(6)	N(101)–C(107)–C(171)	117.3(6)
C(6)–C(7)–C(71)	118.6(6)	C(106)–C(107)–C(171)	114.7(7)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x, -y, -z+1$; # 2 $-x+1, -y+1, -z+1$.

The geometry observed for the four-membered chelate ring compares well with the similar ring in the Ru-TZAO mononuclear complex (Fig. 2) and in some other related κ^2N,S ruthenium chelates (Table 3). It is worth pointing out that the triazepine rings in complexes **I** and **II** present different conformations as shown by comparison of their torsional angles and bond distances (Table 4). The C(5)–C(6) and C(6)–C(7) bond lengths of 1.522 and 1.491 Å respectively, clearly indicate that the C(6) atom remains a methylene group as suggested by the NMR studies.

4. Experimental

2-Propanol (Aldrich) was distilled over magnesium under nitrogen atmosphere, triethylamine (Aldrich) was distilled over molecular sieve (4 Å). $[Ru(p\text{-cymene})Cl_2]_2$ complex was prepared according to literature procedures [17]. Elemental analyses were performed by Laure Donnadieu-Noé on a Perkin–Elmer 2400 série II in the Laboratoire de Chimie de Coordination. HTAZO and H_2TAZS triazepines were synthesized by published methods [10,18].

4.1. HTAZO

M.p. 177–178°C (ethanol). ^{1}H-NMR ($CDCl_3$): $\delta =$ 8.62 [s, 1H, SH], 7.54–7.82 [m, 5H, C_6H_5], 4.02 [s, 2H, $H_2C(6)$], 3.75 [s, 3H, $H_3CN(2)$]. ^{13}C-NMR ($CDCl_3$): $\delta = 173.78$ [C(3)], 163.74 [C(5)], 159.47 [C(7)], 132.84, 132.02, 129.19 and 127.34 [C–Ar], 46.17 [C–N(2)], 39.62 [C(6)]. Anal. Found (calc. for $C_{11}H_{11}N_3OS$): H 4.54 (calc. 4.6), C 56.63 (calc. 56.6), N 18.08 (calc. 18.08).

4.2. H_2TAZS

M.p. 180–181°C (ethanol). ^{1}H-NMR ($CDCl_3$): $\delta =$ 10.01 [br s, 1H, SH], 7.94–7.43 [m, 5H, C_6H_5], 4.28 [s, 2H, $H_2C(6)$], 3.81 [s, 3H, $H_3CN(2)$]. ^{13}C-NMR ($CDCl_3$): $\delta = 195.28$ [C(5)], 172.59 [C(3)], 160.99 [C(7)], 132.44, 132.12, 129.00 and 127.32 [C–Ar], 47.66 [C–N(2)], 46.45 [C(6)]. Anal. Found (Calc. for $C_{11}H_{11}N_3S_2$): H 3.74 (calc. 4.4), C 53.01 (calc. 53.0), N 16.85 (calc. 16.8).

4.3. General procedure for the synthesis of [Ru–triazepine] complexes

A mixture of $[Ru(p\text{-cymene})Cl_2]_2$, 1,2,4-triazepine and triethylamine (molar ratio 1:4:8) in 2-propanol was heated at 80°C for 1 h under nitrogen atmosphere using standard Schlenk-type glassware. The orange–red solution was then concentrated to dryness and the resulting solid was treated with absolute ethanol. After filtration, from the resulting solution crystals of the product were obtained. X-ray measurements and NMR spectral data were performed on the crystalline product so obtained.

4.4. [RuCl(p-cymene)TAZO] (I)

70% yield. ^{1}H-NMR ($CDCl_3$): $\delta = 7.34$–7.85 [m, 5H, C_6H_5 triazepine], 5.58 [d 6.1 Hz, 1H, C_6H_4 *p*-cymene], 5.55 [d 6.1 Hz, 1H, C_6H_4–*p*-cymene], 5.40 [d 6.2 Hz, 1H, C_6H_4–*p*-cymene], 5.19 [d 6.2 Hz, 1H, C_6H_4–*p*-cymene], 3.82 [d 12.5 Hz, 1H, H–C(6)], 3.48 [d 12.5 Hz, 1H, H–C(6)], 3.52 [s, 3H, $H_3CN(2)$], 2.83 [m, 1H, H–C *p*-cymene], 2.21 [s, 3H, H_3C *p*-cymene], 1.22 [d 7.1 Hz,

3H, H_3C *p*-cymene], 1.18 [d 7.0 Hz, 3H, H_3C *p*-cymene]. ^{13}C-NMR ($CDCl_3$): $\delta = 180.55$ [C(3)], 164.73 [C(5)], 154.66 [C(7)], 133.67, 131.25, 128.81 and 127.32 [C–Ar triazepine], 102.68, 97.65, 81.89, 81.45, 80.81 and 80.14 [C–Ar *p*-cymene], 43.66 [C–N(2)], 41.31 [C(6)], 31.62 [C–Me_2 *p*-cymene], 22.54, 22.31 and 19.21 [H_3C *p*-cymene]. Anal. Found (calc. for $C_{21}H_{24}ClN_3ORuS$): H 4.74 (calc. 4.8), C 50.01 (calc. 50.1), N 8.26 (calc. 8.4).

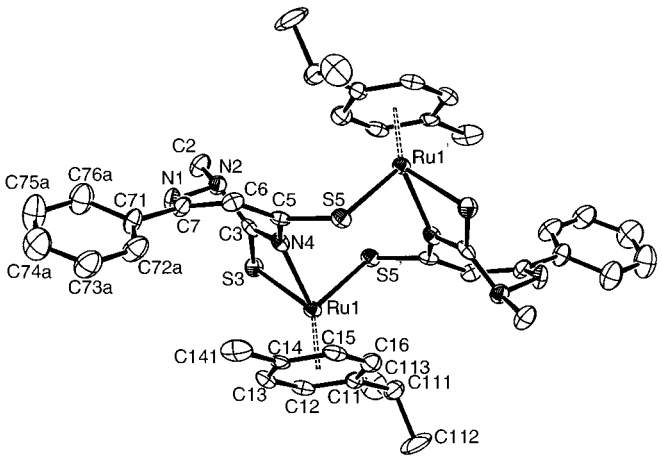


Fig. 2. Molecular structure of the mononuclear complex (Ru-TAZO) with atom labeling.Ellipsoids represent 50% probability.

Table 3
Comparison of geometry for different κ^2N,S ruthenium chelate rings

	Ru-TAZO	$(Ru\text{-}TAZS)_2$	[13]
Ru–S	2.446(3) (2.429(3))	2.434(2) (2.423(2))	2.427(3)
Ru–N	2.099(8) (2.095(8))	2.112(5) (2.116(5))	2.090(11)
S–C	1.731(10) (1.724(10))	1.722(6) (1.705(7))	1.772(12)
N–C	1.342(13) (1.310(13))	1.307(8) (1.298(8))	1.280(15)
S–Ru–N	66.5(2) (67.2(2))	66.9(2) (66.5(2))	66.9(3)
Ru–S–C	80.2(3) (79.0(3))	79.2(2) (79.6(2)	78.7(4)
S–C–N	108.9(7) (111.5(7))	111.9(5) (112.1(5))	109.2(10)
Ru–N–C	103.8(6) (102.3(6))	102.0(4) (101.8(4))	104.5(8)

Table 4
Comparison of the torsional angles (°) and bond distances (Å) within the triazepine rings for complexes **I** and **II**

	II (Ru-TAZS)	**I** (Ru-TAZO)
N1–N2–C3–N4	−76.77	−25.325
N2–C3–N4–C5	4.67	−26.030
C3–N4–C5–C6	37.81	0.647
N4–C5–C6–C7	−1.51	62.909
C5–C6–C7–N1	−38.09	−75.192
C6–C7–N1–N2	−2.47	4.914
C7–N1–N2–C3	71.11	53.584
N(1)–C(7)	1.303(9)	1.257(12)
N(1)–N(2)	1.464(8)	1.406(12)
N(2)–C(3)	1.414(8)	1.354(14)
N(4)–C(3)	1.307(8)	1.342(13)
N(4)–C(5)	1.403(8)	1.364(12)
C(5)–C(6)	1.377(9)	1.522(14)
C(6)–C(7)	1.427(10)	1.492(14)

4.5. *[Ru(p-cymene)TAZS]$_2$ (II)*

85% yield. ^{1}H-NMR ($CDCl_3$): $\delta = 7.35$–7.77 [m, 5H, C_6H_5 triazepine], 7.04 [s, 1H, H–C(6)], 5.60 [d 5.8 Hz, 1H, C_6H_4 *p*-cymene], 5.35 [d 5.8 Hz, 1H, C_6H_4–*p*-cymene], 5.31 [d 5.9 Hz, 1H, C_6H_4–*p*-cymene], 5.27 [d 5.9 Hz, 1H, C_6H_4–*p*-cymene], 3.13 [s, 3H, H_3CN(2)], 2.85 [m, 1H, H–C *p*-cymene], 2.19 [s, 3H, H_3C *p*-cymene], 1.18 [d 6.9 Hz, 3H, H_3C *p*-cymene], 1.05 [d 6.8 Hz, 3H, H_3C *p*-cymene]. ^{13}C-NMR ($CDCl_3$): $\delta =$ 178.86 [C(3)], 170.64 [C(5)], 160.40 [C(7)], 136.16, 129.87, 128.43 and 128.10 [C–Ar triazepine], 120.11 [C(6)], 102.05, 95.54, 88.45, 87.86, 82.84 and 82.53 [C–Ar *p*-cymene], 38.72 [C–N(2)], 30.57 [C–Me_2 *p*-cymene], 23.20, 22.52 and 17.94 [H_3C *p*-cymene]. Anal. Found (calc. for $C_{43}H_{47}Cl_3N_6Ru_2S_4$): H 3.15 (calc. 4.5), C 45.26 (calc. 47.8), N 8.12 (calc. 7.7).

4.6. *X-ray crystallographic study*

Suitable crystals were obtained by slow diffusion in a mixture of $CHCl_3$–EtOH. Data were collected on a Stoe IPDS diffractometer. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

The structure was solved by direct methods (SIR97 [19]) and refined by least-squares procedures on F^2. All H atoms attached to carbon were introduced in calculations in idealized positions [d(CH) = 0.96 Å] and treated as riding models. One of the phenyl rings is disordered, the ring is oscillating between two positions roughly distributed around the axis going through C(71) to C(74). This disordered ring was treated using the available tools in SHELXL-97 [20]. Least-squares refinements were carried out by minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$, having values listed in Table 5.

The calculations were carried out with the SHELXL-97 program [20] using the integrated system WINGX(1.63) [21]. Molecular views were realized with the help of ORTEP [22]

Table 5
Crystal data and structure refinement for Ru-TAZS

Empirical formula	$C_{42}H_{46}N_6Ru_2S_4{\cdot}CHCl_3$
Formula weight	1084.60
Temperature (K)	160(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.742(2)
b (Å)	14.595(3)
c (Å)	14.842(3)
α (°)	99.88(3)
β (°)	96.48(3)
γ (°)	90.97(3)
Volume (Å^3)	2276.2(8)
Z	2
Crystal size (mm^3)	$0.15\times0.16\times0.08$
θ range for data collection (°)	1.81–24.22
Index ranges	$-12\le h\le12$, $-16\le k\le16$, $-17\le l\le17$
Reflections collected	18423
Independent reflections	6794 [$R_{int}=0.1097$]
Completeness to $\theta=24.22°$ (%)	92.7
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6794/414/576
Goodness-of-fit on F^2	0.850
Final R indices [$I>2\sigma(I)$]	$R_1=0.0457$, $wR_2=0.0752$
R indices (all data)	$R_1=0.1077$, $wR_2=0.0889$
Largest difference peak and hole (e Å^{-3})	0.653 and -0.796

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147735. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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