



Reactions of ruthenium(II) with thiamacrocycles: structures of *trans*-dichlorido-1,4,7,10,13,16-hexathiacyclooctadecane-ruthenium(II), bis-(dichloro-dimethylsulfoxide-ruthenium(II)) 1,4,7,10,13-pentathiacyclopentadecane, and *cis*-dichlorido-1,4,8,11-tetrathiacyclotetradecane-ruthenium(II)

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Abstract

The straightforward reaction of thiamacrocycles (1,4,7,10,13,16-hexathiacyclooctadecane ([18]aneS₆), 1,4,7,10,13-pentathiacyclopentadecane ([15]aneS₅), 1,4,8,11-tetrathiacyclotetradecane ([14]aneS₄), and 1,4,7-trithiacyclononane ([9]aneS₃)) with RuCl₂(dmsO)₄ in CHCl₃ or CH₂Cl₂ has produced several crystalline compounds which have been structurally characterized. X-ray crystallographic analysis reveals the following complexes: [*trans*-RuCl₂([18]aneS₆)] (**1**), [(RuCl₂(dmsO))₂[15]aneS₅] (**2**), [*cis*-RuCl₂([14]aneS₄)] (**3**), and [RuCl₂([9]aneS₃)(dmsO)] (**4**). As anticipated all low-spin Ru(II) ions have distorted octahedral environment. Unforeseen was the formation of a dinuclear compound, with one sulfur atom of [15]aneS₅ forming a bridge between two *cis*-RuCl₂ moieties. For all these structures, the Ru–S separations range from 2.29 to 2.36 Å (thiaether) with much larger values for Ru–S–Ru bridge (2.509 (3) and 2.499 (3) Å), and 2.24–2.25 Å (dimethyl sulfoxide). The crystallographic parameters at –100 °C are as follows: **1**: monoclinic, space group *P*2₁/*c*; *a*, *b*, *c* (Å): 8.8975 (3), 11.9747 (5), 9.5666 (4); β = 109.923 (1)°. *V* = 958.27 (7) Å³, *Z* = 2; **2**: monoclinic, space group *P*2₁/*c*; *a*, *b*, *c* (Å): 23.029 (5), 8.3909 (19), 14.220 (3); β = 102.118 (6)°. *V* = 2686.6 (10) Å³, *Z* = 4; **3**: monoclinic, space group *P*2₁/*n*; *a*, *b*, *c* (Å): 8.5071 (12), 14.272 (2), 12.9361 (18), β = 93.566 (4)°. *V* = 1567.6 (4) Å³, *Z* = 4; **4**: monoclinic, space group *P*2₁/*c*; *a*, *b*, *c* (Å): 8.2424 (5), 12.4688 (7), 14.8408 (10), β = 104.546 (2). *V* = 1476.34 (16) Å³, *Z* = 4 (the last structure is practically identical to already measured at different temperature).

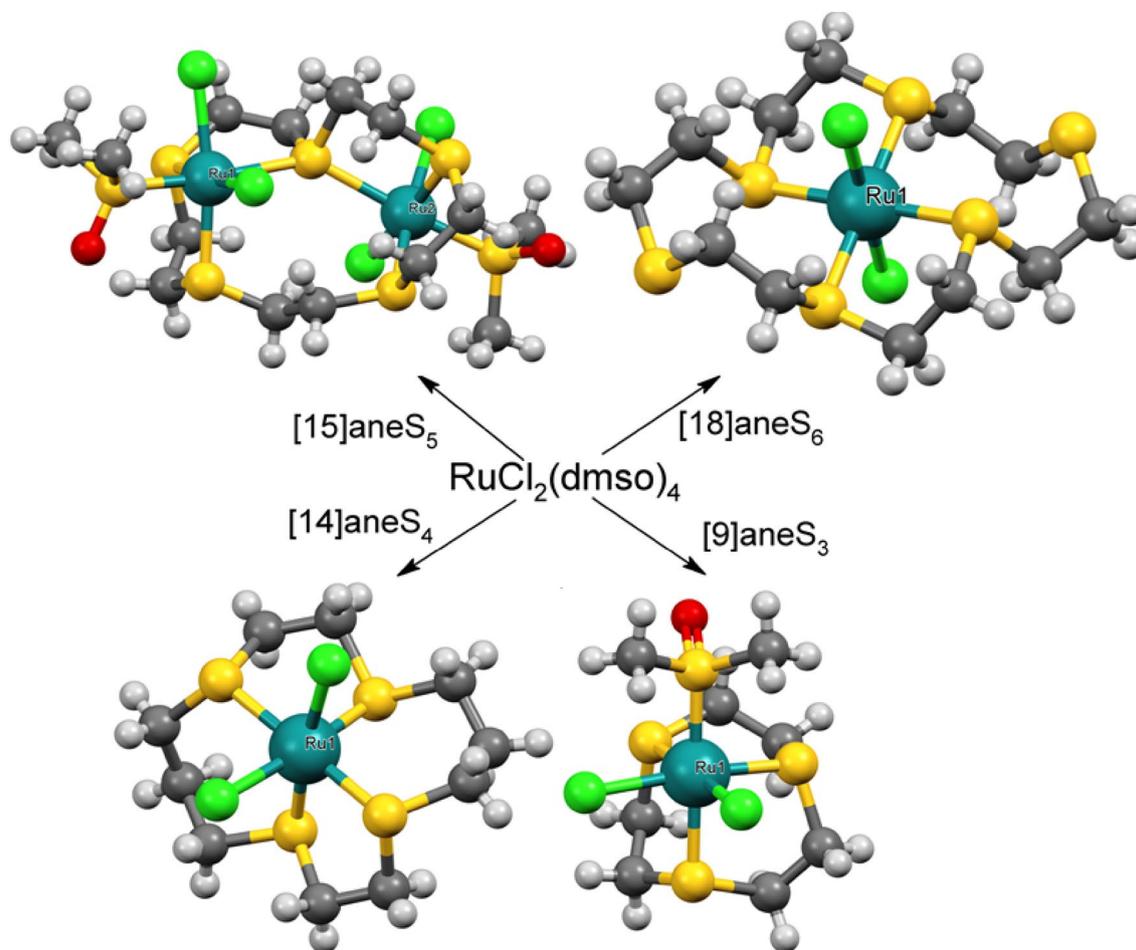
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Graphical Abstract



Keywords Ruthenium(II) · Macrocyclic thiaether · 1,4,7,10,13,16-Hexathiacyclooctadecane · 1,4,7,10,13-Pentathiacyclopentadecane · Crystal structure

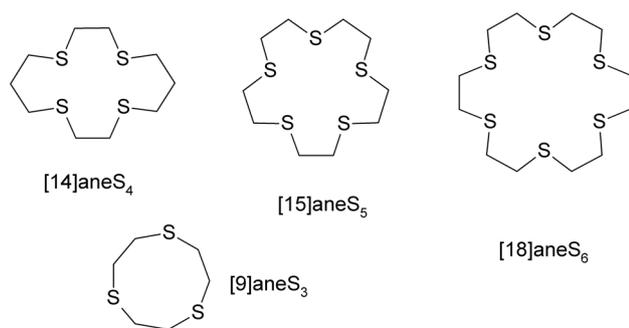
Introduction

In an important research field of metal anticancer complexes, ruthenium attracted nearly as much attention as platinum. Ruthenium compounds have shown broad diversity, in terms of activity, toxicity, and mechanisms of anticancer action [1, 2]. Some of promising compounds and/or precursors are ruthenium thiamacrocyclic complexes [3]. A number of other noteworthy research directions include Creutz–Taube electron transfer processes [4] and molecular cage formation [5]. All these accomplishments explain continuing interest in studying new ruthenium compounds with sulfur-containing macrocycles [6] (Scheme 1).

Synthetic studies in ruthenium thiamacrocyclic compounds have 40 years of history. A large number of ruthenium complexes with small [9]aneS₃ macrocycle were

investigated: Cambridge Structure Database [7] reported 140 crystal structures of such compounds in year 2017. Complexes with larger macrocycles are less researched. Crystal structures of two compounds with [15]aneS₅, [Ru(PPh₃)([15]aneS₅)](BPh₄)₂ [8] and [Ru([15]aneS₅)Cl](PF₆) [9], and one cationic complex with [18]aneS₆, [Ru([18]aneS₆)](BPh₄)₂ [10] are reported. In all cases, an auxiliary bulky anion, PF₆[−] or BPh₄[−], was added to precipitate the macrocyclic complex cation from the solution in a polar solvent.

It is obviously helpful to have a general approach applicable to a broad range of ligands. In this project, we employed RuCl₂(dmsO)₄ as a starting material, taking advantage of solubility of this molecular complex in aprotic solvents such as dichloromethane and chloroform, in which thiamacrocycles are also soluble. A simple preparation procedure of dichlorotetrakis(dimethyl sulfoxide)ruthenium(II)



Scheme 1 Formulas of macrocyclic thiaethers

is given in [11, 12]; its use as a source material for new ruthenium(II) complexes was suggested [12]. Several isomers of $\text{RuCl}_2(\text{dmsO})_4$ were isolated [12, 13], the most common are *cis, fac*- $\text{RuCl}_2(\text{dmsO-S})_3(\text{dmsO-O})$ and *trans, mer*- $\text{RuCl}_2(\text{dmsO-S})_4$. The *trans, mer*-configuration is kinetically favored, but thermodynamically unstable with respect to the *cis* isomer. *Trans*- isomer preparation is described in [14]. While the *cis*- isomers are thermodynamically more stable than the *trans*- species, a photochemically driven *cis* to *trans* isomerization reaction is observed in dimethyl sulfoxide solution [13].

All known ruthenium(II) complexes with thiaethers are low-spin and therefore are diamagnetic. Their ^1H NMR spectra are easily measurable: however, because all hydrogen atoms belong to methylene CH_2 groups, it is difficult to obtain meaningful structural information from these data. Early researches tried to assign *cis*- and *trans*- isomers of ruthenium(II) thiaether complexes from vibrational spectroscopy data. In general, it looks attractive, because $\nu_{\text{S=O}}$ vibration bands are strong in IR and ν_{CS} bands are strong in Raman spectra [15]. However, later structural studies revealed the wrong isomer assignment [16]. These considerations make X-ray diffractometry uniquely suitable for identification of all components of our reactions. Because of this, diffraction data were widely employed in this study for identification of both reactants and products. New crystal structures obtained are discussed in more detail.

Experimental

All necessary chemicals, such as RuCl_3 , thiamacrocycles, and organic solvents were obtained from commercial sources (Aldrich) and used without further purification. The synthesized complexes were characterized by ^1H NMR spectroscopy (solutions in CDCl_3 ; TMS was an internal standard; Bruker Avance 300 MHz spectrometer). Raman spectra were recorded in the range of $150\text{--}2800\text{ cm}^{-1}$ using R-2001 spectrometer (Raman Systems Inc). Thermo LTQ

mass spectrometer with ESI ionization was employed for solutions in acetonitrile.

Single-crystal X-ray data were collected on a Bruker VENTURE Photon-100 CMOS diffractometer at 173 K with APEX 2 software suite; absorption correction was applied using SADABS [17], the structures were solved by the direct methods using SHELXT [18] and was refined using the SHELXL-2014 [19] program package. In crystal structures reported in this work, all non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined with riding coordinates with $U_{\text{iso}} = 1.5 U_{\text{iso}}(\text{C})$ for methyl groups and $U_{\text{iso}} = 1.2 U_{\text{iso}}(\text{C})$ for methylene groups.

Cis-form of $\text{RuCl}_2(\text{dmsO})_4$ was synthesized from commercial RuCl_3 using standard procedure [10]. Its identity was confirmed using vibrational spectroscopy [$\delta_{\text{CH}_3, \text{asym}}$ and ($\delta_{\text{CH}_3, \text{sym}}$), 1108, 938 ($\nu_{\text{S=O}}$), 710, 692 ($\nu_{\text{CS, asym}}$ and $\nu_{\text{CS, sym}}$), 270 (ν_{RuS}) cm^{-1}] [13, 15] followed by X-ray diffractometry (known structure [13]). Slow re-crystallization from ethanol yielded some crystals of *trans*-isomer, identified by X-ray diffractometry as another known structure [14].

Synthesis of $[\text{Ru}([\text{18]aneS}_6)\text{Cl}_2] (\text{1})$

48.5 mg $\text{RuCl}_2(\text{dmsO})_4$ dissolved in 5 mL CHCl_3 was mixed with 36 mg [18]aneS₆ dissolved in 5 mL of CHCl_3 at room temperature. The color turned from pale to bright yellow at gentle heating. Overnight standing followed by slow evaporation yielded around 20 mg of yellow solid; additional material was recovered by reducing volume to 2–3 mL. Resulting material is stable in air. Raman spectrum: 680 and 623 cm^{-1} ($\nu_{\text{CS, asym}}$ and $\nu_{\text{CS, sym}}$); ^1H NMR (CDCl_3 , 25 °C): 2.8–3.5 (m, CH_2); no peaks of S-coordinated dimethyl sulfoxide. MS-ESI spectrum shows a group of peaks characteristic to RuCl isotope composition with highest on at $m/z = 575$ which corresponds to $[\text{102Ru}^{35}\text{Cl}(\text{18aneS}_6)(\text{dmsO})]^+$. Crystals grown from dichloromethane or chloroform were too small for X-ray data collection; however, slow evaporation of solution in acetone yielded satisfactory crystals.

Single-crystal structure determination of $[\text{Ru}([\text{18]aneS}_6)\text{Cl}_2]$

A yellow block ($0.42 \times 0.27 \times 0.15$ mm) was obtained from acetone solution and was mounted using Mitigen loop (see Fig. S1 in Supplementary as an example).

Crystal data $\text{C}_{12}\text{H}_{24}\text{Cl}_2\text{RuS}_6$, $M = 532.64$, monoclinic, space group $P2_1/c$; a, b, c (Å): 8.8975 (3), 11.9747 (5), 9.5666 (4); $\beta = 109.923$ (1)°. $V = 958.27$ (7) Å³, $Z = 2$ (implying that each Ru atom lies on a crystallographic inversion centre). 19,490 measured, 3186 independent and 2949 observed [$I > 2\sigma(I)$] reflections, 97 parameters, $(\sin \theta/\lambda)_{\text{max}}$

(\AA^{-1}) = 0.735. $R[F^2 > 2\sigma(F^2)] = 0.019$, $wR(F^2) = 0.049$, $S = 1.07$.

Synthesis of $[(cis\text{-RuCl}_2(\text{dmsO}))_2[15]\text{aneS}_5]$ (**2**)

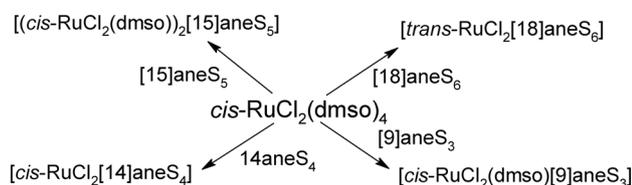
240 mg $\text{RuCl}_2(\text{dmsO})_4$ dissolved in 15 mL CHCl_3 was mixed with 150 mg $[15]\text{aneS}_5$ at room temperature. Overnight standing followed by slow evaporation yielded around 40 mg of yellow solid; additional material was recovered by reducing volume to 2–3 mL. Resulting material is air-stable. Raman spectrum (see Fig. S2 in Supplementary): 715, 674 and 634 cm^{-1} ($\nu_{\text{CS,asym}}$ and $\nu_{\text{CS,sym}}$); 270 (ν_{RuS}); FTIR (Fig. S2) show similar overlapping bands at 718, 700, 680 and 633 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 25 °C, see Fig. S3 in Supplementary): 2.8–3.6 (m, CH_2), with sharp peaks of S-coordinated dimethyl sulfoxide at 3.4. MS-ESI spectrum shows a group of peaks characteristic to RuCl isotope composition with highest on at $m/z = 437$ which corresponds to $[^{102}\text{Ru}^{35}\text{Cl}([15]\text{aneS}_5)]^+$. This synthetic procedure was repeated multiple times using CHCl_3 and CH_2Cl_2 as solvents, all resulting in the same crystalline product. X-ray powder diffraction diagrams of bulk polycrystalline material (Supplementary Fig. S3) is consistent with simulated diffractogram of $[(\text{RuCl}_2(\text{dmsO}))_2[15]\text{aneS}_5]$ (this study). In some cases, crystals were large enough to attempt single-crystal X-ray investigation.

Single-crystal structure determination of $[(cis\text{-RuCl}_2(\text{dmsO}))_2[15]\text{aneS}_5]$

X-ray investigation of this compound shows significant twinning; solution of the twinned structure always produced the same binuclear structure. Here we report the best of these experiments. A yellow plate ($0.19 \times 0.14 \times 0.04\text{ mm}$) was obtained from dichloromethane solution and was mounted using Mitigen loop.

Crystal data $\text{C}_{14}\text{H}_{32}\text{Cl}_4\text{O}_2\text{Ru}_2\text{S}_7$, $M = 800.75$, monoclinic, space group $P2_1/c$; a, b, c (\AA): 23.029 (5), 8.3909 (19), 14.220 (3); $\beta = 102.118$ (6)°. $V = 2686.6$ (10) \AA^3 , $Z = 4$. 4821 independent and 3018 observed [$I > 2\sigma(I)$] reflections, 267 parameters, $(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1}) = 0.603. $R[F^2 > 2\sigma(F^2)] = 0.072$, $wR(F^2) = 0.16$, $S = 1.04$ (Scheme 2).

Similar synthetic approach using $[14]\text{aneS}_4$ and $[9]\text{aneS}_3$ yielded $[cis\text{-RuCl}_2([14]\text{aneS}_4)]$ (**3**) and $[cis\text{-RuCl}_2([9]\text{aneS}_3)]$



Scheme 2 Reaction of thiamacrocycles with $cis\text{-RuCl}_2(\text{dmsO})_4$

(dmsO) (**4**) respectively. Crystal structure of dihydrate $[cis\text{-RuCl}_2([14]\text{aneS}_4)] \cdot 2\text{H}_2\text{O}$ is known [16]. Our product was anhydrous complex with very similar but not identical structure.

Single-crystal structure determination of $[cis\text{-RuCl}_2([14]\text{aneS}_4)]$

Several twinned crystals were tested, all yielding the same structure; we report the best result. A yellow twinned block ($0.21 \times 0.20 \times 0.19\text{ mm}$) was mounted using Mitigen loop.

Crystal data $\text{C}_{10}\text{H}_{20}\text{Cl}_2\text{RuS}_4$, $M = 440.47$, monoclinic, space group $P2_1/n$; a, b, c (\AA): 8.5071 (12), 14.272 (2), 12.9361 (18), $\beta = 93.566$ (4)°, $V = 1567.6$ (4) \AA^3 , $Z = 4$. 3007 independent and 2319 observed [$I > 2\sigma(I)$] reflections, 155 parameters, $(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1}) = 0.603. $R[F^2 > 2\sigma(F^2)] = 0.088$, $wR(F^2) = 0.23$, $S = 1.08$.

Single-crystal structure determination of $[cis\text{-RuCl}_2([9]\text{aneS}_3)(\text{dmsO})]$

Crystal data $\text{C}_8\text{H}_{18}\text{Cl}_2\text{ORuS}_4$, $M = 430.43$, monoclinic, space group $P2_1/c$; a, b, c (\AA): 8.2424 (5), 12.4688 (7), 14.8408 (10), $\beta = 104.546$ (2)°, $V = 1476.34$ (16) \AA^3 , $Z = 4$. 5391 independent and 4303 observed [$I > 2\sigma(I)$] reflections, 147 parameters, $(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1}) = 0.758. $R[F^2 > 2\sigma(F^2)] = 0.028$, $wR(F^2) = 0.064$, $S = 1.06$. This structure is practically identical to obtained before by different route and measured at -173° [20]; because of that it is not discussed further.

For the structures listed above the deposition numbers at the Cambridge Crystallographic Data Centre are CCDC 1,589,088–1,589,091.

Results and discussion

Molecular structure of (**1**)

The single crystal X-ray structure of $[\text{Ru}([18]\text{aneS}_6)\text{Cl}_2]$ shows a centrosymmetric complex with the Ru atom lying on an inversion center. Four macrocyclic thiaether donor atoms of the thiamacrocyclic are bound to the distorted octahedral ruthenium(II) center, $\text{Ru-S1} = 2.3639$ (3) and $\text{Ru-S3} = 2.3440$ (3) \AA . The S donors are bound at four equatorial sites while two apical positions are occupied by chloride ions, $\text{Ru-Cl1} = 2.4331$ (3) \AA . The angles around the central ruthenium(II) which involve chloride ions deviate significantly from ideal octahedron values: $\text{S1-Ru-Cl1} = 82.573$ (10) and $\text{S3-Ru-Cl1} = 83.596$ (11)°, while $\text{S3-Ru-S1} = 91.614$ (9) is close to 90°. The bond lengths and angles of Ru–S bonds in $[\text{Ru}([18]\text{aneS}_6)\text{Cl}_2]$ are very similar to those reported [9] for $[\text{Ru}([18]\text{aneS}_6)]^{2+}$

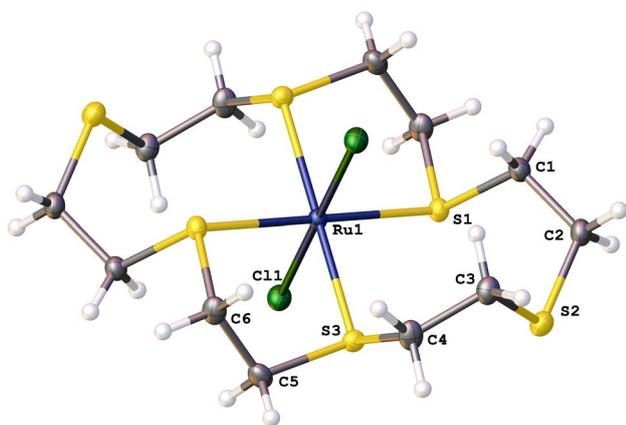


Fig. 1 Molecular structure of $[\text{Ru}([\text{18}]\text{aneS}_6)\text{Cl}_2]$ (**1**) with thermal ellipsoids drawn at 50% probability

showing that in both cases ruthenium(II) ion fits $[\text{18}]\text{aneS}_6$ without any apparent deformation of metal coordination or ligand geometry. However, in our case a strong Ru–Cl interaction favors coordination of chloride ion instead of the available thiaether donor atom S2 of the macrocycle (Fig. 1).

In $[\text{Ru}([\text{18}]\text{aneS}_6)\text{Cl}_2]$, all C–C torsion angles are *gauche* with values with absolute values from 48° to 56° ; C–S bonds are *gauche*, *anti* or *trans*, making the conformation sequence $(\text{A}^-\text{G}^-\text{G}^-)(\text{AG}^-\text{T})(\text{GGG})(\text{AGG})(\text{A}^-\text{GT})(\text{G}^-\text{G}^-\text{G}^-)$ which reflects the presence of inversion center in the structure. There are two potential intramolecular hydrogen bonds C1–H1b \cdots Cl1 and C3–H3b \cdots Cl1 (H1b–Cl1 and H3b–Cl1 separations are 2.71 and 2.59 Å

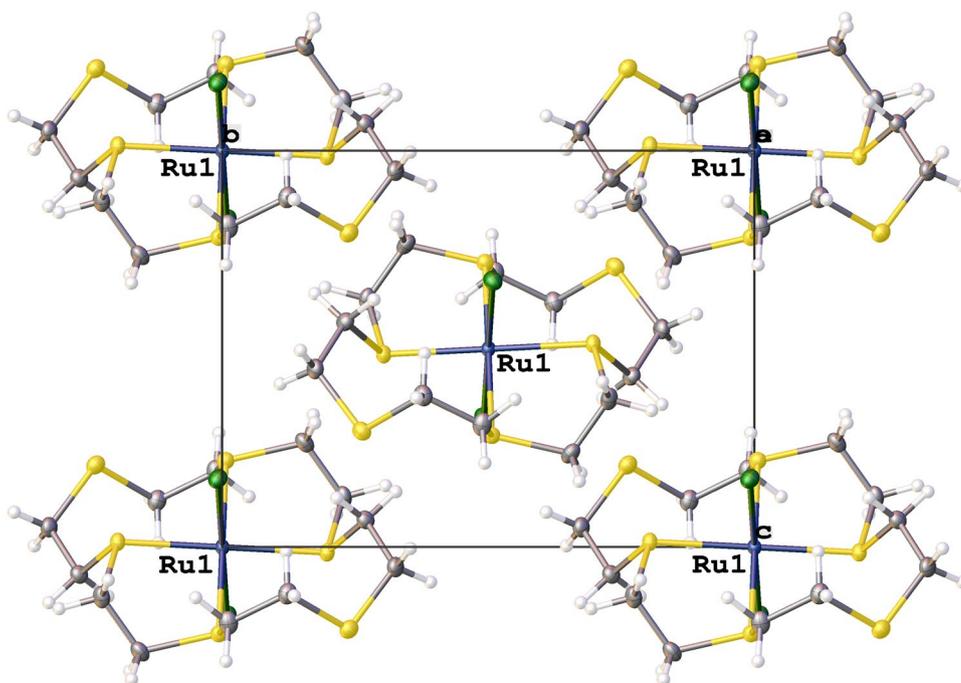
respectively) that stabilize the conformation. Two identical five-membered cycles show twisted on C5–C6 conformation. In $[\text{Ru}([\text{18}]\text{aneS}_6)]^{2+}$, all macrocyclic torsion angles are \pm *gauche*, with absolute values of $41^\circ \pm 1^\circ$ for C–C bonds and $79^\circ \pm 5^\circ$ for C–S bonds [10]. Overall conformation of the macrocycle molecule in the cationic complex is $[(\text{GGG})(\text{G}^-\text{G}^-\text{G}^-)]_3$. It reflects high flexibility of macrocyclic thiaethers molecule, enabling it to easily change conformation in order to fit the coordination environment of central Ru(II) ion.

Molecules of (**1**) are kept together with the help of several very weak C–H \cdots Cl and C–H \cdots S contacts, all of the H \cdots S and H \cdots Cl separations being longer than 2.86 Å (Fig. 2).

Molecular structure of (2)

In $[(\text{cis-RuCl}_2(\text{dmsO}))_2[\text{15}]\text{aneS}_5]$ dinuclear complex, three thiaether sulfur donor atoms, two chloride ions, and a sulfur donor atom of dimethyl sulfoxide molecule are bound to each of two ruthenium(II) ions, forming distorted octahedral environment. In both components of the complex, dimethyl sulfoxide ligands are located in *trans*-positions to the bridging sulfur atom S1 (Fig. 3). Bond lengths around both ruthenium ions are very similar, with Ru–S distances being the shortest for dimethylsulfoxide group. These distances are even slightly shorter than in *cis*- $\text{RuCl}_2(\text{dmsO})_4$ (2.25–2.28 Å) [13] and *trans*- $\text{RuCl}_2(\text{dmsO})_4$ (2.35 Å) [14] and in $[\text{RuCl}_2([\text{9}]\text{aneS}_3)(\text{dmsO})]$ (2.25 Å) [20].

Fig. 2 Packing diagram of $[\text{trans-Ru}([\text{18}]\text{aneS}_6)\text{Cl}_2]$ (**1**), view along [1 0 0] axis



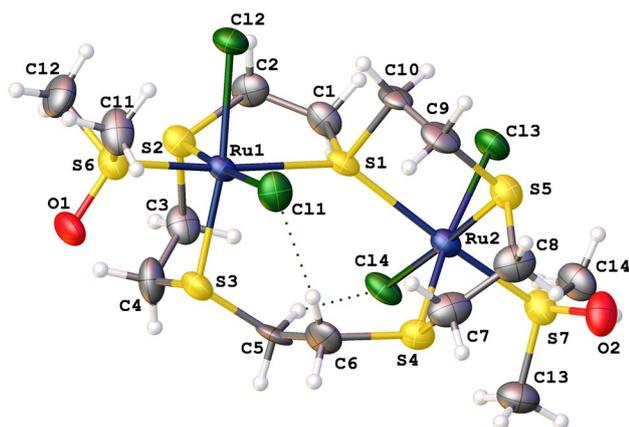


Fig. 3 Molecular structure of $[(cis-RuCl_2(dmsO))_2[15]aneS_5]$ (**2**) with thermal ellipsoids drawn at 50% probability level

Table 1 Selected bond lengths (Å) in for (**2**) with e.s.d.s in parentheses

Ru1–C11	2.425 (3)	Ru2–Cl4	2.419 (3)
Ru1–Cl2	2.444 (3)	Ru2–Cl3	2.457 (3)
Ru1–S1	2.509 (3)	Ru2–S1	2.499 (3)
Ru1–S2	2.290 (3)	Ru2–S5	2.290 (3)
Ru1–S3	2.318 (3)	Ru2–S4	2.293 (3)
Ru1–S6	2.241 (3)	Ru2–S7	2.241 (4)

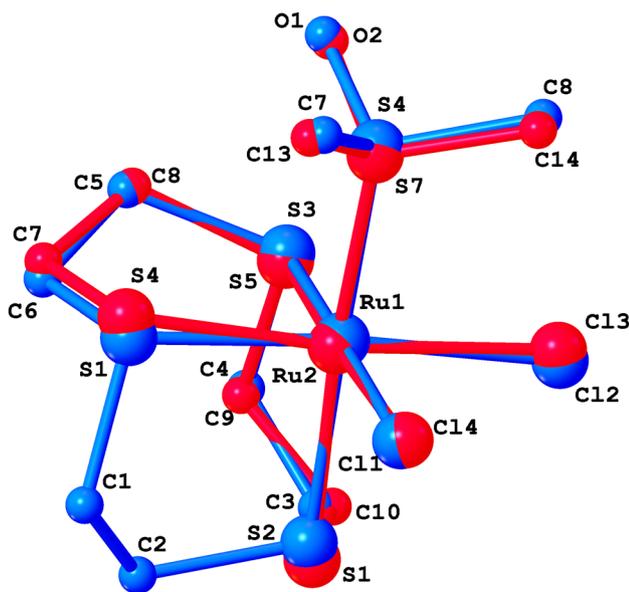


Fig. 4 Overlay of complex **4** (blue) and Ru2 fragment of compound **2** (red). (Color figure online)

For macrocyclic donor atoms, Ru–S bond lengths are in close agreement with those observed in related macrocyclic ruthenium(II) complexes (Table 1).

Table 2 Potential intramolecular hydrogen bonds in **2**

D–H...A	D–H	H...A	D...A	$\angle D-H...A$
C5–H5B...Cl4	0.99	2.47	3.414 (13)	160
C6–H6B...Cl1	0.99	2.51	3.493 (15)	174
C10–H10B...Cl2	0.99	2.52	3.309 (15)	137
C8–H8A...O2	0.99	2.51	3.203 (18)	127
C9–H9A...Cl1	0.99	2.64	3.494 (14)	145

Distances are in Å, angles in (°). Shown are contacts with H...A shorter than 2.7 Å

The only exception is Ru–S1 bonds which connect Ru ions with the bridging sulphur atom: it is longer by almost 0.2 Å. Planes of Ru1–S1–Ru2 triangle and C1–S1–C10 triangle are almost perpendicular to each other.

An attempt to overlay two parts of the dinuclear complex show that while S and Cl donor atoms are relatively close (Fig. S5 in Supplementary), all remaining atoms have different geometry: torsion angles in ethylene groups of macrocycle are different, as well as the orientation of coordinated dimethyl sulfoxide molecules. However, Ru2-containing fragment has essentially the same geometry as $[RuCl_2(9aneS_3)(dmsO)]$ complex (Fig. 4).

In macrocycle molecule four of C–C bonds have *gauche*-conformation. The C5–C6 bond serves as a second bridging unit between two ruthenium complex moieties and has an *anticlinal* conformation [$-145.3 (7)^\circ$]. All four five-membered rings have envelope conformation. Overall conformation of 15-membered macrocycle can be described as $(A^-G^-G^-)(TG^-G^-)(TA^-T)(A^-GG)(T^-GT^-)$. There are a number of intramolecular short contacts that may stabilize this conformation (Table 2).

A number of intermolecular hydrogen bonds connect molecules of (**2**) in a three-dimensional network. Acceptor atoms include coordinated chloride ions as well as oxygen atoms of both coordinated dimethyl sulfoxide molecules (Table 3; Fig. 5).

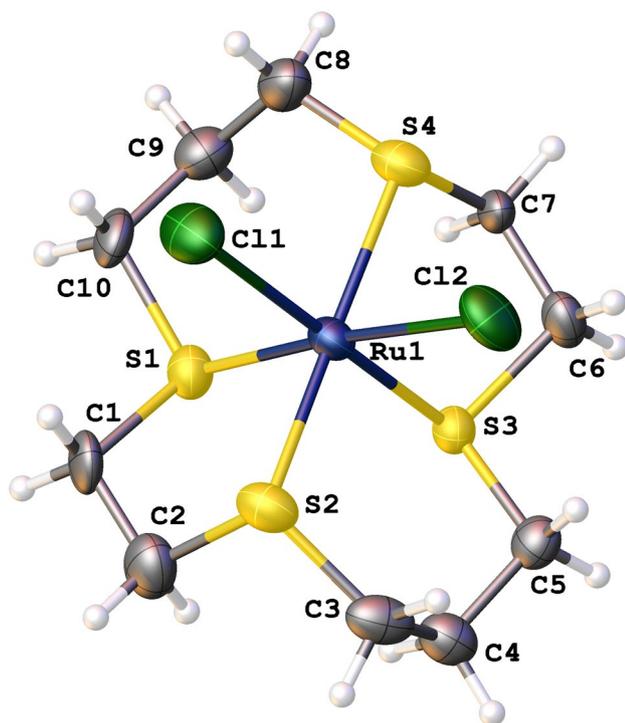
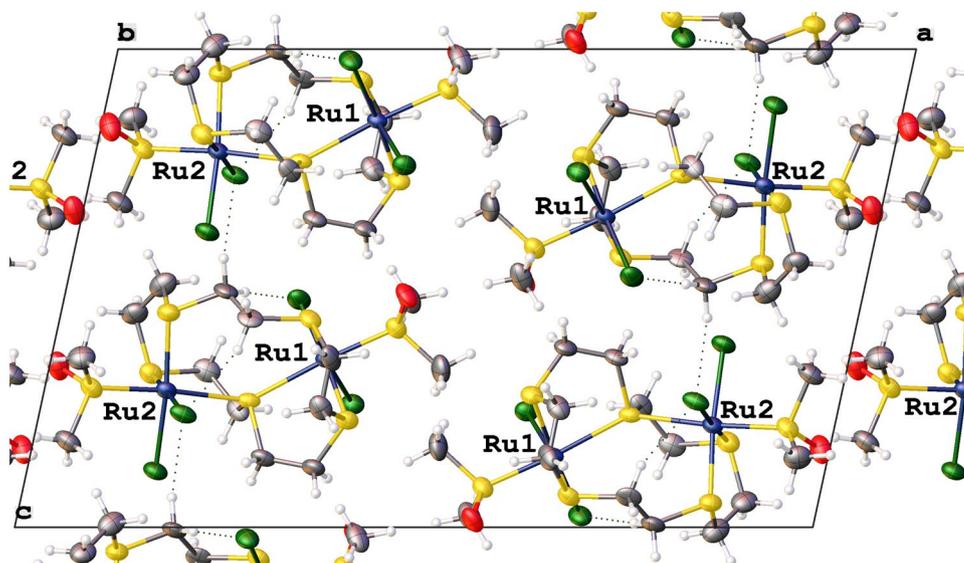
Molecular structure of (**3**)

Crystal structure of (**3**) is very similar to that of $[RuCl_2([14]aneS_4)] \cdot 2H_2O$, which was reported in [16]. The clear difference is smaller unit cell volume because of absence of two water molecules. Two-fold axis going through Ru ion in space group $C2/c$ is obviously absent in our case (space group $P2_1/c$). Nevertheless, the shape of complex compound is very similar (Fig. 5), with two shorter Ru–S separations, [2.259 (4) and 2.276 (3) Å] for atoms S1 and S3 and two longer [2.325 (4) and 2.339 (4) Å] for atoms S2 and S4; Ru–Cl bond lengths are 2.471

Table 3 Potential intermolecular hydrogen bonds in **2**

D-H...A	Symmetry operation for A	D-H	H...A	D...A	\angle D-H...A
C1-H1A...C11	$x, 3/2-y, -1/2+z$	0.99	2.72	3.673 (13)	161
C6-H6A...C14	$x, 1/2-y, 1/2+z$	0.99	2.47	3.428 (13)	164
C9-H9B...C14	$x, 1+y, z$	0.99	2.57	3.486 (12)	154
C11-H11B...O1	$1-x, 1-y, 1-z$	0.98	2.48	3.424 (19)	160
C14-H14B...O2	$2-x, -1/2+y, 1/2-z$	0.98	2.48	3.072 (17)	119

Distances are in Å, angles in ($^{\circ}$). Shown are contacts with H...A shorter than 2.75 Å

Fig. 5 Packing diagram of compound **2**. View along [0 1 0] axis**Fig. 6** Molecular structure of $[cis\text{-RuCl}_2([14]\text{aneS}_4)]$ (**3**) with thermal ellipsoids drawn at 50% probability level

(4) and 2.453 (4) Å. Those sulfur donor atoms that are located opposite to chloride ions, have shorter bond distances (Fig. 6).

Torsion angles of all C-C bonds are *gauche*; C-S bonds are all *trans*. This allows to describe the conformation of [14]aneS₄ ligand as (TGT)(TGG⁻T) (TGT)(TGG⁻T); alternatively, it is [124,124] in Boyens [21] notation. Conformation of five-membered cycles is envelope on C1 and C6 respectively; both six-membered rings have slightly distorted chair conformation.

The crystal structure shows no potential hydrogen bonds with H...A < 2.7 Å. Therefore, in this case the absence of strong hydrogen bonds comparing to dihydrate crystal does not affect macrocyclic complex geometry.

Conclusions

We have reported the synthesis of new ruthenium(II) thiaether complexes containing chloride ligands from the starting material RuCl₂(dms_o)₄. The synthesis of these complexes is a straightforward process, which is carried out under mild conditions. Contrary to reactions in polar solvents which yield mainly cationic ruthenium(II)

complexes with suitable bulky counter-ion added, all our complexes are molecular compounds. All four complexes characterized by X-ray diffraction show an octahedral geometric arrangement, with chloride ions being *trans*- in compound **1** and *cis*- in all other complexes. Reaction with [15]aneS₅ yields a dinuclear compound, with one sulfur atom of [15]aneS₅ forming a bridge between two *cis*-RuCl₂ moieties, which are also connected by –CH₂CH₂– link of fifteen-membered macrocycle. Conformations of 18- and 15- membered macrocyclic rings are different from those in cationic complexes. The absence of additional ions or ligands other than dimethyl sulfoxide solvent molecule may simplify further synthetic use of these compounds. Complex [Ru([18]aneS₆)Cl₂] (**1**) has two sulfur donor atoms available for interaction with metal ions. Such interaction may result in forming polymer compounds similar which were already studied in [22, 23]. Replacement of solvent molecule in [(RuCl₂(dms))₂[15]aneS₅] (**2**) dinuclear complex also give a possibility of chain or network construction.

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