

Crystal Structure of *cis*-Ru(DMSO)₄Cl₂ in different synthetic methods

Tarighi S., Abbasi A.*

School of Chemistry, University College of Science, University of Tehran, Tehran, Iran

*Corresponding author, e-mail: aabbasi@khayam.ut.ac.ir

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Abstract

The structure of the *cis*-dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) have been studied by means of single-crystal X-ray diffraction. The data are described in orthorhombic unit cell with space group Pccn (No. 56) at 295 K, $a = 28.478(4)$ Å, $b = 10.900(6)$ Å, $c = 11.697(13)$ Å, and $V = 3631(4)$ Å³, $Z = 8$. The crystal structure of the title compound comprises a nearly octahedral configuration with a Ru-O bond distance of, 2.151 Å, and the average values of, 2.269 Å and 2.421 Å for Ru-S and Ru-Cl, respectively.

Keywords: Divalent metal ions, Ruthenium, Dimethyl sulfoxide, Coordination Chemistry, Crystal structure

Introduction

Recently, metal-based anti-tumor drugs have been playing a significant role in anti-plastic chemotherapy. In the design of these new drugs, ruthenium complexes such as *cis*-RuCl₂(dmsO)₄, have been interested, and noticed as an anti-tumor drug (Alessio *et al.* 2004). However, a great chemical interests are the use of *cis*-RuCl₂(dmsO)₄ as catalysts.

Dimethyl sulfoxide is the strong Lewis base able to form bonds to metal ions both via oxygen and via sulfur atom (Nakamoto 1997). However, coordination via the sulfur atom takes place only for soft metal ions and the relatively hard metal ions are strongly solvated *via* the oxygen atom. Even though the ruthenium (II) ion is classified as borderline (Pearson 1967) it preferably forms bonds to the S atom of sulfoxides (Alessio *et al.* 2004, Calligaris. 2004). It is also the widely used solvent for the ionic compounds because of its high dipole moment and permittivity. The high affinity of some metal ions to dmsO allows to use this solvent in the processes of selection and concentration. Therefore, it is the field of special interest to study the coordination of metal ions with dmsO and its effect on the ligand structural characteristics.

One aim of the current study is to apply and compare different synthetic methods to synthesize Ru(DMSO)_{6-n}Cl_n compounds. This can be used for the synthesis of analogous complexes. It is also important to investigate the nature of Ru-S bonds and to make a comparison with analogous compounds.

Experimental parts

Synthesis. *cis*-dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) was synthesized by dissolving of ruthenium (III) chloride hydrate (Aldrich, 99.98%) in an excess of dimethyl sulfoxide (Merck, 99%) and the solution kept at 353 K for about 8 hours. The resulting solution was evaporated at reduced pressure in a vacuum desiccator. Crystals suitable for crystallography were obtained after recrystallization from dimethyl sulfoxide solvent.

X-ray Crystallography. The data collections at room temperature were made on a Ru(DMSO)₄Cl₂ crystal placed on a fiber glass, by means of a STOE image-plate diffractometer. No intensity variations due to decomposition of the crystals were observed. Selected crystallographic and experimental details are summarized in Table 1. Absorption corrections were performed with the programs X-RED and X-Shape.

Symmetry equivalent reflections were used to optimize crystal shape and size. The structure were solved by direct methods using SHELXS-97, (Sheldrick 1990) and refined using full-matrix least-squares method on F^2 , SHELXL-97(Mercer 1975) All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at ideal positions and refined using a riding model.

Results and discussion

The structure of the *cis*-dichlorotetrakis (dimethyl sulfoxide) ruthenium(II) complexes were satisfactorily described in the space group Pccn (No. 56), in such a way that the ruthenium(II) ion is coordinated

by one O and three S atoms from four dimethyl sulfoxide molecules and two chloride ions in cis-configuration in a distorted octahedral coordination (see Figures 1 and 2). The mean Ru-S bond distance in the title compound for S *trans* to Cl, 2.274 Å is longer than the Ru-S bond *trans* to the O atoms, 2.260 Å. This is consistent with the stronger *trans* influence of Cl compare to O. The structure was first solved by Mercer, (Attia 1987) in monoclinic crystal system with $P2_1/c$ space group. Calligaris then reported the same structure at ambient and

Srivastava at low temperature in orthorhombic system with Pccn space group (Srivastava 2003). All the crystallographic data from previous studies together with our data are summarized in Table 1. No clear preparation method have been reported for the cis-RuCl₂(DMSO)₄ compound, and that motivate us to investigate a new synthetic method, even though several papers have been published so far. In this paper, we have reported our new approach and a comparison between our structural results and previously reported ones (Table 1).

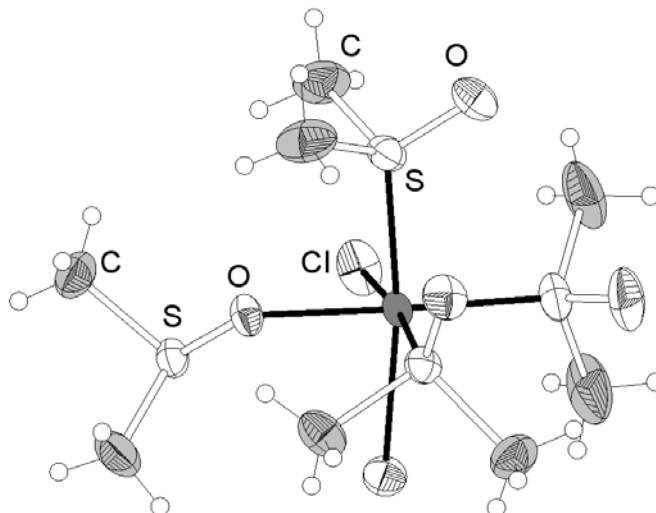


Fig. 1- cis-dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) complex at 295K (50% probability ellipsoids).

We apply different methods to prepare Ru(DMSO)₄Cl₂ complex. After dissolving of ruthenium(III) chloride in an excess of dimethyl sulfoxide, the solution kept at 353 K in different periods of 8, 12, 24, and 72 hours and no changes obtained in the results. We have tried to kick out

chloride from inner sphere of the complex and replace with more DMSO molecules by adding Ag(CF₃SO₃) salts to the DMSO solution of the title compound and no changes were obtained. The above results indicate the difficulty of getting ride of coordinated chloride to metal ion.

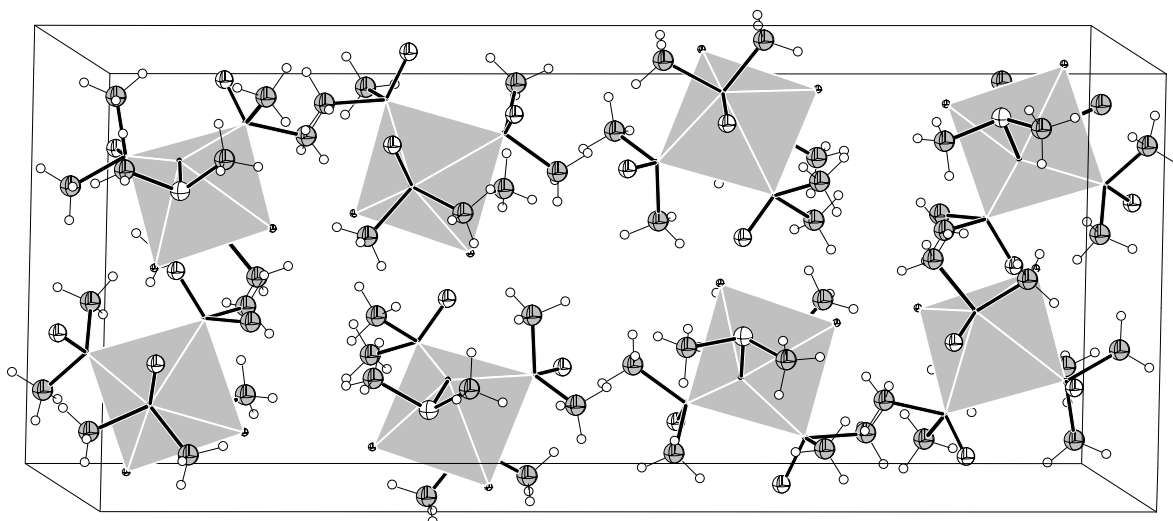


Fig. 2. A packing view of the title compound.

Table 1. Crystallographic data for the *cis*-dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) compounds in different synthesis

Formula	$RuC_8H_{24}O_4S_4Cl_2^a$	$RuC_8H_{24}O_4S_4Cl_2^b$	$RuC_8H_{24}O_4S_4Cl_2^c$	$RuC_8H_{24}O_4S_4Cl_2^d$
M	484.49	484.45	484.48	484.48
Crystal system	monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P2 ₁ /n	Pccn	Pccn	Pccn
<i>a</i> /Å	8.939(3)	28.328(5)	28.167(7)	28.478(4)
<i>b</i> /Å	18.045(7)	10.3831(3)	10.817(2)	10.900(6)
<i>c</i> /Å	11.363(3)	11.751(3)	11.648(2)	11.697(13)
<i>V</i> /Å ³	1832.255	3606(2)	3548.9(13)	3631(4)
<i>T</i> /K	293(1)	293	120	293(2)
<i>Z</i>	4	8	8	8
<i>D</i> _{calcd} /g.cm ⁻³	1.80	1.78	1.813	1.773
μ (Mo-K α)/mm ⁻¹	1.62	1.59	1.66	1.622
Crystal size/mm	0.3×0.35×0.4	0.4×0.3×0.2	0.2×0.17×0.12	0.4×0.2×0.1
Measured reflections	5642	6128	25051	15450
Significant reflections	4107(<i>I</i> >3 σ)	2904(<i>I</i> >3 σ)	3830 (<i>I</i> >2 σ)	3182 (<i>I</i> >2 σ)
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^e	0.033 0.042	0.042 0.051	0.046 0.088	0.0311 0.0702

^a Mercer 1975, ^b Attia 1987, ^c Srivastava 2003, ^d current study

^e R values are defined as: $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$

Conclusions

The crystal structure of the title compound shows discrete octahedrally coordinated *cis*-dichlorotetrakis (dimethyl sulfoxide)ruthenium(II) complexes. Crystallographic results are consistent with a regular structure of the complex in which the ruthenium(II) is surrounded by three sulfur and one oxygen atoms from four dimethyl sulfoxide

molecules and two chloride ions. Different preparation methods were discussed and yielded to the same results.

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