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Molecular Structure of *fac*-Aquadichlorotris(dimethylsulfoxide)ruthenium(II)

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Chiannelli has studied a series of transition-metal sulfides for their ability to catalytically hydrodesulfurize (HDS) dibenzothiophene, with RuS₂ showing greatest activity (Pecoraro and Chianelli 1981). Numerous thiophene compounds have been prepared to model the HDS active site. Of these compounds, none have a coordination sphere consisting entirely of sulfur ligands (Angelici 1990, Rauchfuss 1991). In an attempt to prepare model compounds that more closely resemble the RuS₂ active site for the HDS process, Ru(dms_o)₄Cl₂ was chosen as the starting material due to its versatility in the synthesis of a variety of ruthenium(II) complexes (Evans et al. 1973).

Replacement of the chloride ligands by the potentially chelating CS₃²⁻ moiety was attempted by reacting equimolar amounts of Ru(dms_o)₄Cl₂ and K₂CS₃ in CH₂Cl₂ under air. After filtration and upon crystallization from CH₂Cl₂/hexanes, yellow crystals were obtained in small yield. The yellow crystals were analyzed using single-crystal x-ray diffraction techniques, and were determined to be *fac*-aquadichlorotris(dimethylsulfoxide)ruthenium(II), **I**.

A yellow crystal of **I** with the dimensions of 0.20 mm x 0.20 mm x 0.40 mm was mounted on a Mitegen Micromount and was automatically centered on a Bruker SMART X2S benchtop crystallographic system. Data were acquired using three sets of Omega scans at different Phi settings. The frame width was 0.5°, with an exposure time of 5.0 s. Crystal data are given in Table 1.

The compound *fac*-[Ru(dms_o)₃(OH₂)Cl₂] forms rapidly when Ru(dms_o)₄Cl₂ is placed in H₂O (Barnes and Goodfellow 1979, Alessio et al. 1988). Though compound **I** has been characterized spectroscopically by ¹H NMR (Barnes and Goodfellow 1979), photochemically (Brindell et al. 2007), and investigated for anticancer activity (Brindell et al. 2005), the single-crystal structure had not been determined.

Compound **I** crystallizes with two molecules in the symmetric unit. A 1/8 water of hydration was also

observed. The structure of **I** is seen in Figure 1. The dms_o ligands are in the facial configuration, with two of the dms_o ligands trans to the chloride ligands and the other trans to the H₂O ligand. All of the dms_o ligands are S-bound. Selected bond distances are given in Table 2.

Table 1. Crystallographic data for *fac*-Ru(dms_o)₃(OH₂)Cl₂·1/8 H₂O.

Formula	C ₁₂ H _{40.25} Cl ₄ O _{8.125} Ru ₂ S ₆
Formula weight (amu)	851.04
Temperature (K)	200(2)
Unit cell dimensions	
a (Å)	15.2893(11)
b (Å)	7.8993(5)
c (Å)	49.552(3)
α (°)	90
β (°)	90.131(2)
γ (°)	90
V (Å ³)	5984.6(8)
D _{calc} (Mg/cm ³)	1.889
Space group	monoclinic C2/c
Z	8
F(000)	3434
λ (Å)	0.71073
μ (mm ⁻¹)	1.819
2θ range (°)	2.47 to 25.03
Absorption correction	Multiscan
Total reflections	28113
Unique reflections	5283
R for merge	0.0554
Data for refinement	5283
Parameters	318
Final R [I > 2σ(I)]	R1 = 0.322
	wR2 = 0.0589
R indices (all data)	R1 = 0.0405
	wR2 = 0.0613
GOF	1.077
Largest diff. peak and hole	0.507, -0.413

Molecular Structure of *fac*-Aquadichlorotris(dimethylsulfoxide)ruthenium(II)Table 2. Selected bond distances (Å) for **I**.

Ru1-O1	2.158(3)	Ru2-O5	2.153(3)
Ru1-S1	2.2650(10)	Ru2-S4	2.2801(9)
Ru1-S2	2.2790(10)	Ru2-S5	2.2595(10)
Ru1-S3	2.2412(9)	Ru2-S6	2.2467(10)
Ru1-Cl1	2.4433(10)	Ru2-Cl3	2.4036(10)
Ru1-Cl2	2.24095(10)	Ru2-Cl4	2.4262(9)

The Ru-S bond distances for the dmsoligands trans to the chlorides are longer than the Ru-S distance for the dmsoligands trans to the water molecule. This is consistent with the observed bond distances for the sulfur-bound dmsoligands in $\text{Ru}(\text{dmsol})_4\text{Cl}_2$. The Ru-S distance for the dmsoligands trans to the O-bound dmsoligands is 2.245(1) Å as compared to 2.274(1) and 2.284(1) Å for the Ru-S distances for the dmsoligands trans to chloride (Alessio et al. 1988).

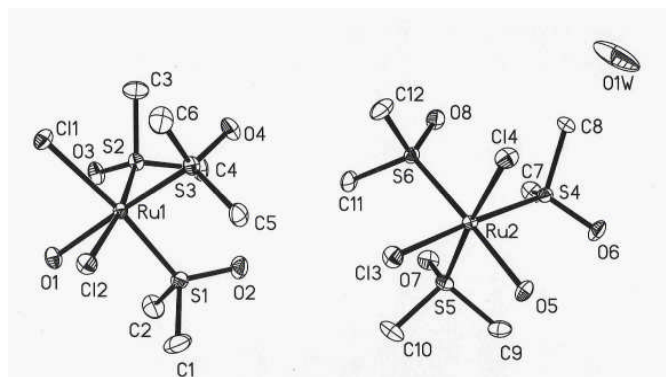


Fig. 1. Ortep of **I** showing atom labeling scheme. Hydrogens have been omitted for clarity.

Though the isolation of crystals of compound **I** was serendipitous, a new structure was obtained. Further reactions of $\text{Ru}(\text{dmsol})_4\text{Cl}_2$ with K_2CS_3 under nitrogen will be investigated.

Supplemental Materials

Supplemental materials are available from the authors upon request.

Acknowledgments

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