

2001

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Thornton, L. A.; Draganjac, Mark; Meza, Andres; and Cordes, A. W. (2001) "Synthesis of a Ruthenium-tetra(tht)dichloride Compound and the Molecular Structure of the Partially Oxidized Compound $\text{RuCl}_2(\text{tht})_{2.2}(\text{tht-O})_{1.8}$," *Journal of the Arkansas Academy of Science*: Vol. 55 , Article 33.

Available at: <https://scholarworks.uark.edu/jaas/vol55/iss1/33>

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Synthesis of a Ruthenium-tetra(tht)dichloride Compound and the Molecular Structure of the Partially Oxidized Compound $\text{RuCl}_2(\text{tht})_{2.2}(\text{tht-O})_{1.8}$

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Attempts to prepare $\text{CpRu}(\text{thietane})_3^+$ from $\text{CpRu}(\text{PPh}_3)_2^+$, in order to model potential ligand interactions in the metal carbonyl-catalyzed cyclooligomerization of thietane (Adams and Falloon, 1995), were unsuccessful. The di-thietane complex, $[\text{CpRu}(\text{PPh}_3)(\text{thietane})_2]\text{OTf}$, can be prepared by direct ligand substitution from the di-tht complex, $[\text{CpRu}(\text{PPh}_3)(\text{tht})_2]\text{OTf}$, tht = tetrahydrothiophene. The shortening of the Ru-P bond distance in the di-thietane complex as compared to the mono-thietane complex, $[\text{CpRu}(\text{PPh}_3)_2(\text{thietane})]\text{OTf}$, may explain why a third thietane ligand can not be attached (Nave et al., 2001).

One method for the synthesis of tri- and tetra-thietane complexes may employ $\text{RuCl}_2(\text{dmsO})_4$ (Evans et al., 1973) as a starting material. Due to less ring strain, initial reactions were carried out with THT as a ligand. Herein, we report the synthesis of $\text{RuCl}_2(\text{tht})_4$ and the crystal structure of the partially oxidized reaction product, $\text{RuCl}_2(\text{tht})_{2.2}(\text{tht-O})_{1.8}$.

Under N_2 , 0.700 g (1.44 mmol) $\text{RuCl}_2(\text{dmsO})_4$ was dissolved in 5 mL THT. The reaction was refluxed overnight. Upon cooling, the precipitate was filtered, washed with acetone, and dried. Yield = 0.279 g, 36.8 %. $^1\text{H NMR}$ (δ , ppm, CDCl_3): 3.0, 2.1.

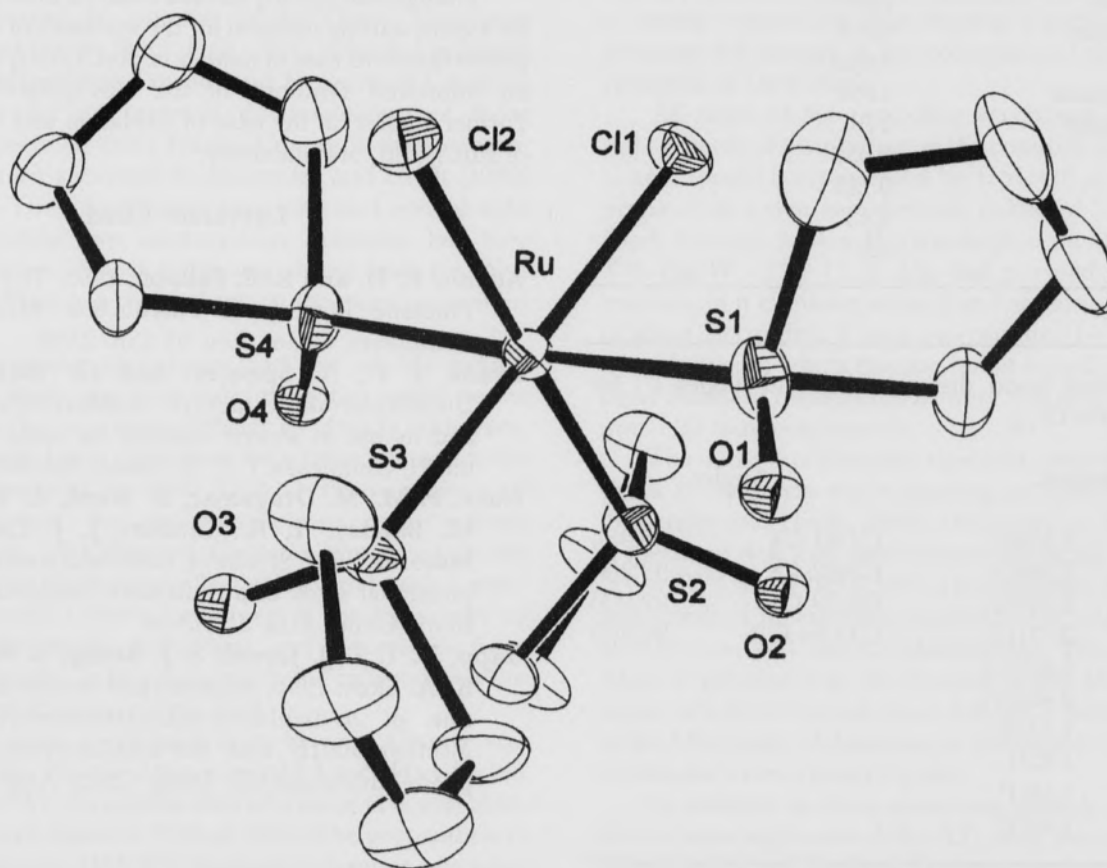


Fig. 1. Ortep (30% probabilities) of $\text{RuCl}_2(\text{tht})_{2.2}(\text{tht-O})_{1.8}$ showing S and O labeling scheme.

Table 1. Crystallographic data for $\text{RuCl}_2(\text{tht})_{2.2}(\text{tht-O})_{1.8}$.

| | |
|---|---|
| Formula | $\text{C}_{16}\text{H}_{32}\text{Cl}_2\text{O}_{1.8}\text{RuS}_4$ |
| Formula weight | 553.49 |
| Unit cell dimensions | |
| a (Å) | 9.1486(8) |
| b (Å) | 11.2865(10) |
| c (Å) | 21.3525(18) |
| α (°) | 90 |
| β (°) | 90.927(4) |
| γ (°) | 90 |
| V (Å ³) | 2204.5(3) |
| D_{calc} (g cm ⁻³) | 1.774 |
| Space group | $P2_1/c$ |
| Z | 4 |
| F(000) | 1208.0 |
| λ (Å) | 0.7107 |
| μ (cm ⁻¹) | 1.35 |
| Scan technique | θ - 2θ |
| Diffractometer | Mercury CCD |
| 2θ range (°) | 4-52 |
| Absorption range | 0.74-1.00 |
| Total reflections | 7307 |
| Unique reflections | 4268 |
| R for merge | 0.043 |
| Data for refinement | 4268 |
| Parameters refined | 249 |
| R(F) | 0.053 |
| $R_w(F)$ | 0.135 |
| GOF | 1.43 |
| Max. Δ/σ | 0.0 |

Table 2. Selected bond distances (Å) and angles (°) for $\text{RuCl}_2(\text{tht})_{2.2}(\text{tht-O})_{1.8}$.

| Bond distances | | Angles | |
|----------------|----------|------------|---------|
| Ru-S1 | 2.350(2) | C1-S1-C4 | 90.9(5) |
| Ru-S2 | 2.286(2) | C5-S2-C8 | 93.2(4) |
| Ru-S3 | 2.296(2) | C9-S3-C12 | 92.9(5) |
| Ru-S4 | 2.371(2) | C13-S4-C16 | 92.5(5) |
| Ru-Cl1 | 2.430(2) | | |
| Ru-Cl2 | 2.422(2) | | |
| S1-O1 | 1.33(2) | | |
| S2-O2 | 1.42(1) | | |
| S3-O3 | 1.36(1) | | |
| S4-O4 | 1.40(2) | | |

The NMR spectrum of $\text{RuCl}_2(\text{tht})_4$ shows two peaks of equal intensity at positions different than the peaks observed for the $\text{RuCl}_2(\text{dmsO})_4$ protons (3.5, 2.8 ppm) (Evans et al., 1973). Also, the IR spectrum of the $\text{RuCl}_2(\text{tht})_4$ compound shows the disappearance of the S=O stretches (1055 cm⁻¹) seen in the $\text{RuCl}_2(\text{dmsO})_4$ compound. This evidence suggests the formulation of $\text{RuCl}_2(\text{tht})_4$.

Attempts to obtain single crystals of $\text{RuCl}_2(\text{tht})_4$ failed. However, single crystals were obtained from the filtrate upon evaporation in air. Crystal data are given in Table 1. Examination of the structure (Fig. 1) shows each of the tht ligands has been partially oxidized to the tht-oxide. The occupancy factors for the O atoms are 0.41, 0.65, 0.47, and 0.27 for O1-O4, respectively, giving an average of 0.45 for the oxidized tht ligands. At present, the source of the oxidation is not known. The IR data for the crystals isolated from the filtrate does show the expected S=O stretches (1064 cm⁻¹).

The Ru-S distances are 2.296(2), 2.286(2), 2.350(2), and 2.371(2) Å for S1-S4, respectively. The shorter Ru-S distances are trans to the Cl⁻ ligands. This effect is also observed in the two different crystallographic forms for *cis*- $\text{RuCl}_2(\text{tht-O})_4$ (Yapp et al., 1990). Selected bond distances and angles are given in Table 2 for $\text{RuCl}_2(\text{tht})_{2.2}(\text{tht-O})_{1.8}$.

Though $\text{RuCl}_2(\text{tht})_4$ formed easily, it does not appear to be a good starting material for the synthesis of thietane complexes due to its ease of oxidation. $\text{RuCl}_2(\text{tht})_4$ may allow for an improved synthesis of the $\text{RuCl}_2(\text{tht-O})_4$ complex. Further studies on the ease of oxidation and crystallization of $\text{RuCl}_2(\text{tht})_4$ are underway.

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