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Activation of Thiourea Bound through Sulfur to Pentaammineruthenium(III): Structure and Reactivity

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Thiourea is an important biological reducing agent that can bond to metals via sulfur or nitrogen. The isostructural urea coordinates Ru(III),[1a] Co(III),[1b] or Pt(II)[1c] as the unstable O-bonded form which isomerizes to the N-bound form in base.

$$M{-}O{=}C(NH_2)_2 \rightleftarrows M{-}NH_2CONH_2 \rightleftarrows M{-}NHCONH_2^- + H^+$$

In contrast $(NH_3)_5Ru^{III}$ forms a highly acid-stable complex with thiourea bound via an sp^3 sulfur atom. Instead of isomerization in aqueous base, there is S−C cleavage and decomposition to $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$. The substitution inertia of Ru(III) can aid studies of reactive sulfur ligands of biological importance.[2,3]

(Thiourea)pentammineruthenium(III) was synthesized from thiourea and $[(NH_3)_5Ru(O_3SCF_3)](CF_3SO_3)_2$ in weakly coordinating solvents.[4] Crystallization from aqueous $Na_2S_2O_6$ gave orange **1**, $[(NH_3)_5RuSC(NH_2)_2](S_2O_6)_{3/2}{\cdot}H_2O$,[4] the stoichiometry[4] confirming the oxidation state. The X-ray crystal structure[4] shows slightly distorted octahedral coordination about a Ru(III) bound to 5 nitrogens and 1 sulfur (Figure 1). The Ru−N bonds (2.108(5)−2.116(5) Å) *cis* to Ru−S are comparable to those (2.090(1)−2.135(3) Å) in other $(NH_3)_5Ru^{III}$ complexes with a sulfur ligand,[5] but the *trans* Ru−N bond is not significantly longer (2.135(5) Å).

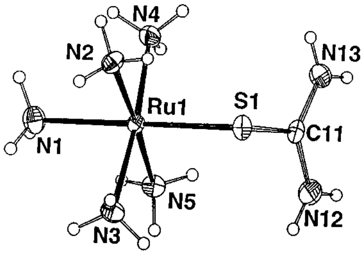

Figure 1. ORTEP drawing for the cation of **1**. Selected bond distances (Å) and angles (deg): Ru(1)−S(1) 2.304(2), S(1)−C(11) 1.762(6), C(11)−N(13) 1.303(8), C(11)−N(12) 1.313(8); N(1)−Ru(1)−S(1) 174.2(2), C(11)−S(1)−Ru(1) 107.0(2), N(13)−C(11)−N(12) 121.5(6), N(13)−C(11)−S(1) 119.6(5), N(12)−C(11)−S(1) 118.9(5).

A key point is that the Ru−S−C bond angle is 107° compared to the ideal 109.5° for an sp^3-hybridized sulfur, while the ligand S−C−N angles (118.9(5), 119.6°) do not differ statistically from free thiourea (120.5(5)°[6]). The M−S−C bond angle deviates less in other metal (M) complexes[5,7] of thiourea (tu) from the ideal 120° for an sp^2-hybridized S atom. The dihedral angle between the tu plane and the Ru(1)/N(2)/N(3)/N(4)/N(5) plane is 23.3°, while the two Ru−S−C−N dihedral angles are 93.8° (N13) and −87.5° (N12). The Ru−S bond (2.304(2) Å) is *significantly shorter* than known Ru(III)−S distances (2.366−2.433 Å)[5] and shorter than in $(tu)_6Ru^{II}$ (2.415−2.427 Å)[5] but comparable to the Fe^{III}−S bond length (2.311(2) Å) in $FeI_3(S{=}C(NMe_2)_2)$[8] and shorter than the Fe^{II}−S bonds (2.61, 2.65 Å) in $[Fe^{II}(S{=}C(NH_2)_2)](NCS)_2$.[9] The S−C bond (1.762(6) Å) is *significantly longer* than in free tu[6] (1.72(1) Å) and S−C distances observed for other tu complexes,[7] including $(tu)_6Ru^{II}$ (1.716−1.720 Å). Also C−N bonds in **1** (1.303(8), 1.313(8) Å) are shorter than in free tu (1.34(1) Å) and $(tu)_6Ru^{II}$ (1.307−1.321 Å).

The data are consistent with LMCT from a filled pπ sulfur orbital to the vacant d_{xy} π-orbital on Ru(III), as expected[10] for the π- and σ-accepting Ru^{III}. A shorter Ru−S bond than in analogous thioether[5] complexes suggests more L→M charge transfer and more resonance than in free thiourea from the following:

$$[(NH_3)_5Ru\{S{=}C(NH_2)_2\}]^{3+} \leftrightarrow [(NH_3)_5Ru\{^-S{-}C(NH_2^+)NH_2\}]^{3+}$$

Paramagnetic **1** has an intense absorption (λ_{max} 461 nM, $\epsilon \sim 6.449 \times 10^3$ M^{-1} cm^{-1}, 0.1 M HCl) assigned to LMCT[10] and a minimum at 330 nm ($\epsilon \sim 327$ M^{-1} cm^{-1}). Thiourea is displaced from Ru(III) ($t_{1/2} \sim 2$ days, 60 °C; 0.1 M HCl) more slowly than urea in $[(NH_3)_5RuO{=}C(NH_2)_2]^{3+}$ ($t_{1/2} \sim 1$h, 25 °C).[1a] In base a reversible color change to pink (λ_{max} 494 nm, $\epsilon \sim 5.260 \times 10^3$ M^{-1} cm^{-1}, 0.1 M Tris) indicates thiourea

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(4) Higher yields in propylene carbonate (60%) than acetone or DMA. Anal. Calcd (found) for $[(NH_3)_5RuSC(NH_2)_2]_2(S_2O_6)_3{\cdot}2H_2O$. C, 2.31 (2.26); H, 4.04 (4.08); $\underline{N}$, 18.84 (19.37), S, 24.61 (25.36). X-ray data: triclinic, space group $P\bar{1}$, $a = 7.237(4)$ Å, $b = 9.857(9)$ Å, $c = 14.126(11)$ Å, $\alpha = 108.33(4)°$, $\beta = 97.18(5)°$, $\gamma = 106.72(4)°$, $V = 890.0(12)$ Å^3, $Z = 2$, $R1$ (w$R2$) = 0.040 (0.104) for 3131 reflections ($I > 2\sigma(I)$).

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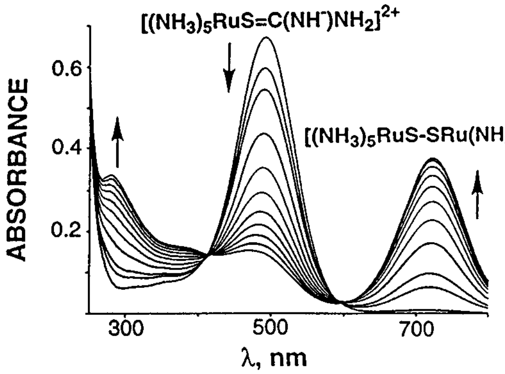

Figure 2. Reaction of **1** in 0.1 M Tris (0.3 mg in 3.0 mL) at 22 °C after 0.5, 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 min.

deprotonation (pK_a 10.8 ± 0.1, 25 °C, $\mu = 1.0$ M $NaClO_4$).

$$[(NH_3)_5Ru\{^-S{-}C(NH_2{}^+)NH_2\}]^{3+} + OH^- \rightleftarrows [(NH_3)_5Ru\{^-S{-}C(:NH)NH_2\}]^{2+} + H_2O$$

In 0.1 M Tris the absorption spectra (Figure 2) initially contain isosbestic wavelengths (409, 592 nm) during formation of the green disulfide dimer[2] **2**, $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$ (λ_{max} 725 nm; $t_{1/2} \sim 17$ min, 0.1 M Tris, 25.0 °C; seconds in 0.1 M NaOH), but they blur after 30 min due to dimer decomposition on a similar time scale to its formation. The kinetics are complex for both formation and decay of **2** and require more detailed studies.

Dimer formation implicates ligand hydrolysis and oxidation of **1** which may be similar to decomposition of isothiuronium salts formed from thiourea and alkyl halides. Deprotonation/hydrolysis in base to mercaptans and aerial autooxidation gives disulfide:[11]

$$2[RS{-}C({=}NH_2{}^+)NH_2] + 2OH^- \rightarrow 2RS^- + 2\text{urea} + 2H^+$$

$$RS^- + O_2 \rightarrow RS^\bullet + O_2{}^{\bullet -}$$

$$RS^- + O_2{}^{\bullet -} \rightarrow RS^\bullet + O_2{}^{2-}$$

$$2RS^\bullet \rightarrow RS{-}SR$$

Hydrolysis and autooxidation to **2** are supported by a zero-order term in $[OH^-]$ and by quantitative conversion of $[(NH_3)_5Ru(OSO_2CF_3)]^{2+}$ in aqueous Na_2S in air to **2** (δ (acetone-d_6): 2.915 (s, 24H, cis-NH_3), 3.234 (br, 6H, trans-NH_3); no EPR signal):

$$2[(NH_3)_5RuS]^+ \rightleftarrows [(NH_3)_5RuSSRu(NH_3)_5]^{4+} + 2e^-$$

In summary, Ru^{III} polarizes thiourea by complexing sulfur, activating it to hydrolysis and thiolate oxidation to **2**. Such decomposition may be common to other metal−sulfur complexes.

Supporting Information Available: Text describing synthetic procedures and analytical data, tables of data, X-ray and figures showing ORTEP diagrams and spectra (13 pages). Ordering information is given on any current masthead page.

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