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A balance of redox and ligand-exchange processes in the reaction of  $\text{H}_2[\text{OsCl}_6]$  with thiourea: isolation and characterization of a novel osmium complex  $[(\text{NH}_2)_2\text{CSSC}(\text{NH}_2)_2]_2[\text{Os}^{\text{IV}}\text{Cl}_6]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$

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**A balance of redox and ligand-exchange processes in the reaction of  $\text{H}_2[\text{OsCl}_6]$  with thiourea: isolation and characterization of a novel osmium complex**  
 **$[(\text{NH}_2)_2\text{CSSC}(\text{NH}_2)_2]_2[\text{Os}^{\text{IV}}\text{Cl}_6]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$**

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## Abstract

A novel complex with the stoichiometry  $[(\text{NH}_2)_2\text{CSSC}(\text{NH}_2)_2]_2[\text{Os}^{\text{IV}}\text{Cl}_6]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  (**1**) is isolated as a product of the reaction of  $\text{H}_2[\text{OsCl}_6]$  with thiourea in concentrated HCl under deliberately optimized conditions favoring a partial thiourea oxidation to  $\alpha,\alpha'$ -dithiobisformamidinium dication but preserving hexachloroosmate  $[\text{OsCl}_6]^{2-}$  anions. A bromide analogue  $[(\text{NH}_2)_2\text{CSSC}(\text{NH}_2)_2]_2[\text{Os}^{\text{IV}}\text{Br}_6]\text{Br}_2 \cdot 3\text{H}_2\text{O}$  **2** is afforded by a similar reaction. A counter synthesis of **1** is accomplished via the direct ion-exchange reaction between  $\text{H}_2[\text{OsCl}_6]$  and  $[\text{S}_2\text{C}_2(\text{NH}_2)_4]\text{Cl}_2$ . Crystal structures of **1** and **2** are unambiguously established by synchrotron radiation-based single-crystal X-ray diffraction at 100 K. The two compounds are isostructural and are crystallized in the orthorhombic space group *Cmcm*, *Z* = 4. Unit cell parameters are for **1**: *a* = 11.279(2) Å, *b* = 13.611(3) Å, *c* = 16.731(3) Å; for **2**: *a* = 11.695(2) Å, *b* = 14.005(3) Å, *c* = 17.015(3) Å. The osmium atoms in  $[\text{OsX}_6]^{2-}$  (X=Cl or Br) anions adopt slightly distorted octahedral coordination. The  $\alpha,\alpha'$ -dithiobisformamidinium cations are paired into rings via the  $\text{NH}\cdots\text{Cl}^-$  hydrogen bonds. The rings are further linked into a spatial network by H-bonds with water molecules and  $\text{S}\cdots\text{Cl}$  nonvalence interactions.

**Keywords:** osmium halide complexes, thiourea,  $\alpha,\alpha'$ -dithiobisformamidinium dication, oxidation, IR and UV-vis spectroscopy, synchrotron X-ray diffraction

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