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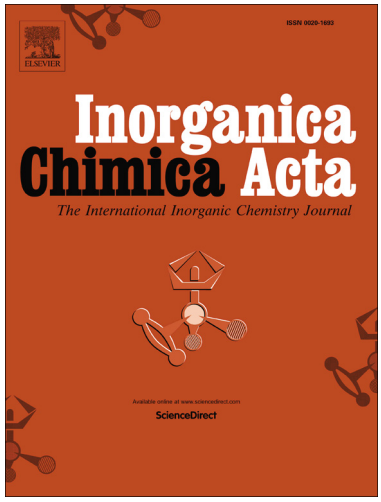

A balance of redox and ligand-exchange processes in the reaction of $H_2[OsCl_6]$ with thiourea: isolation and characterization of a novel osmium complex $[(NH_2)_2CSSC(NH_2)_2]_2[Os^{IV}Cl_6]Cl_2 \bullet 3H_2O$

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A balance of redox and ligand-exchange processes in the reaction of $H_2[OsCl_6]$ with thiourea: isolation and characterization of a novel osmium complex $[(NH_2)_2CSSC(NH_2)_2]_2[Os^{IV}Cl_6]Cl_2 \cdot 3H_2O$

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Abstract

A novel complex with the stoichiometry $[(NH_2)_2CSSC(NH_2)_2]_2[Os^{IV}Cl_6]Cl_2 \cdot 3H_2O$ (**1**) is isolated as a product of the reaction of $H_2[OsCl_6]$ with thiourea in concentrated HCl under deliberately optimized conditions favoring a partial thiourea oxidation to α,α'-dithiobisformamidinium dication but preserving hexachloroosmate $[OsCl_6]^{2-}$ anions. A bromide analogue $[(NH_2)_2CSSC(NH_2)_2]_2[Os^{IV}Br_6]Br_2 \cdot 3H_2O$ **2** is afforded by a similar reaction. A counter synthesis of **1** is accomplished via the direct ion-exchange reaction between $H_2[OsCl_6]$ and $[S_2C_2(NH_2)_4]Cl_2$. 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 $[OsX_6]^{2-}$ (X=Cl or Br) anions adopt slightly distorted octahedral coordination. The α,α'-dithiobisformamidinium cations are paired into rings via the NH…Cl^- hydrogen bonds. The rings are further linked into a spatial network by H-bonds with water molecules and S…Cl nonvalence interactions.

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