

A Stable Monomeric Compound with a Superoxo-ligand: Formation of [Rh(ethylenediamine)₂(NO₂)(O₂)]⁺

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Summary Monomeric superoxo-rhodium(III) species, relatively stable in water, have been synthesised by the action of light and dioxygen upon compounds containing the nitro-rhodium(III) function.

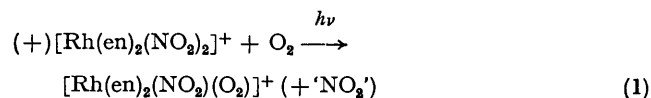
COMPLEX compounds formed by attachment of a dioxygen species to a metal ion are not common, although their properties are of general interest in connection with the activation of molecular dioxygen. Some years ago, we found¹ that, in reducing conditions, complexes of rhodium with pyridine (py) and halide (X⁻) will combine with dioxygen to give first transient red-orange species, then isolable blue dimers involving [XRh(py)₄O₂Rh(py)₄X]³⁺.

Since reduced precursors may be formed² by photolysis of rhodium(III) complexes, and since the intermediate red-orange species seemed likely to contain the species [Rh^{III}-O₂]²⁺ we were intrigued to note that aqueous solutions of salts of the colourless *cis*-dinitrobisethylenediaminerhodium(III) ion, *cis*-[Rh(en)₂(NO₂)₂]⁺, became red in daylight (en = ethylenediamine).

We now find that this photochemical reaction is due to the formation of a monomeric superoxo-rhodium(III) species, [Rh(en)₂(NO₂)(O₂)]⁺. The *cis*-isomer³ of [Rh(en)₂(NO₂)₂]⁺ reacts in this way much more readily than the *trans*. We have confirmed the *cis*-dinitro-configuration of the original compound by comparison with the well known cobaltic analogue (i.r. spectra and X-ray powder photographs of analogous salts are identical). Further, we have resolved *cis*-[Rh(en)₂(NO₂)₂]Cl using (+)K[Co(edta)] (H₄ edta = ethylenediaminetetra-acetic acid) (as was done for the dinitro-cobalt analogue⁴).

Dioxygen is essential for the formation of the red product; irradiation under argon brings about only the formation of aquorhodium(III) species. In the presence of

oxygen, the superoxo-product from the resolved *cis*-dinitro-compound is not optically active (presumably, an intermediate is stereolabile) [equation (1)].



The cation has been isolated as its nitrate and chloride. It has absorption (due essentially to a charge-transfer transition of the O₂⁻ ligand) at 485 nm, and shows a strong Raman absorption at 1052 cm⁻¹ due to ν₀₋₀. It is paramagnetic. A number of derived species [Rh(en)₂(O₂)X]ⁿ⁺ are easily formed, where X = Cl⁻ or H₂O.

In the presence of aquo-rhodium(III) species, the red monomeric superoxides give way to blue or purple dimeric compounds [X(en)₂Rh(O₂)Rh(en)₂X]^{m+} (where X = Cl⁻, NO₂⁻, or OH₂). These absorb around 575 nm (the value for X = Cl is 545 nm), are paramagnetic, show strong Raman bands at 1060 cm⁻¹ [*cf.*⁵ superoxo-dicobalt(III)] and, like the monomers, behave as 1-electron oxidants, instantly oxidising iodide (giving equivalent weights agreeing with our formulations) and hydroxide. The peroxo-products of these reductions are less reactive but still possess oxidising power.

Two classes of water-stable superoxo-rhodium(III) ammine complexes are now known. These are the blue dimers¹ and the more unusual red-orange monomers, with 470 < λ < 500 nm. These include the present [Rh(en)₂X(O₂)]ⁿ⁺, which are surprisingly long-lived in acid solutions, and also the transient red species noted earlier^{1,6} in the tetrakis-pyridine-rhodium(III) system.

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