A Stable Monomeric Compound with a Superoxo-ligand: Formation of $[Rh(ethylenediamine)_2(NO_2)(O_2)]^+$

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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 found[1] 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 $[XRh(py)_4O_2\ Rh(py)_4X]^{3+}$.

Since reduced precursors may be formed[2] by photolysis of rhodium(III) complexes, and since the intermediate red-orange species seemed likely to contain the species $[Rh^{III}-O_2^-]^{2+}$ we were intrigued to note that aqueous solutions of salts of the colourless *cis*-dinitrobisethylenediaminerhodium (III) ion, *cis*-$[Rh(en)_2(NO_2)_2]^+$, 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, $[Rh(en)_2(NO_2)(O_2)]^+$. The *cis*-isomer[3] of $[Rh(en)_2(NO_2)_2]^+$ 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*-$[Rh(en)_2(NO_2)_2]Cl$ using $(+)K[Co(edta)]$ (H_4 edta = ethylenediaminetetra-acetic acid) (as was done for the dinitro-cobalt analogue[4]).

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)].

$$(+)[Rh(en)_2(NO_2)_2]^+ + O_2 \xrightarrow{h\nu} [Rh(en)_2(NO_2)(O_2)]^+ \ (+\text{`}NO_2\text{'}) \qquad (1)$$

The cation has been isolated as its nitrate and chloride. It has absorption (due essentially to a charge-transfer transition of the O_2^- ligand) at 485 nm, and shows a strong Raman absorption at 1052 cm^{-1} due to ν_{O-O}. It is paramagnetic. A number of derived species $[Rh(en)_2(O_2)X]^{n+}$ are easily formed, where $X = Cl^-$ or H_2O.

In the presence of aquo-rhodium(III) species, the red monomeric superoxides give way to blue or purple dimeric compounds $[X(en)_2Rh(O_2)Rh(en)_2X]^{m+}$ (where $X = Cl^-$, NO_2^-, or OH_2). 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 dimers[1] and the more unusual red-orange monomers, with $470 < \lambda < 500$ nm. These include the present $[Rh(en)_2X(O_2)]^{n+}$, 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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