Photochemically Generated Superoxides of Rhodium(III)[†]

Robert D. Gillard * and Julio D. Pedrosa de Jesus
Department of Chemistry, University College, P.O. Box 78, Cardiff CF1 1XL

Bis(ethylenediamine)rhodium(III) compounds containing N-co-ordinated nitrite ion photoreact with molecular oxygen to give the monomeric superoxorhodium(III) ion, $[Rh(en)_2(OH_2)(O_2)]^{2+}$, and dimeric superoxo-bridged dirhodium(III,III) species. Irradiation of *cis*- and *trans*-bis(ethylenediamine)-dinitrorhodium(III) salts, both in the presence and the absence of oxygen, results in nitro–nitrito-isomerization. The visible spectra of the monomers (λ = 490 nm) and dimers (λ = 550 nm) and their Raman frequencies [ν(O–O) at 1 080 and 1 050 cm^{-1}, and 1 050 cm^{-1} respectively] indicate the presence of the $Rh^{III}-O_2^-$ moiety in the complexes. The e.s.r. spectra (*g* tensor *ca.* 2.03) also agree with this formulation. Both monomeric and dimeric species act as one-electron oxidizing agents towards I^- and Fe^{2+}.

The photochemistry of co-ordination compounds of rhodium(III) has been reviewed.[1,2] Much reported work[3-15] relates to the ligand-field (l.f.) and charge transfer-to-metal (c.t.t.m.) irradiation of the penta-ammines $[Rh(NH_3)_5X]^{2+}$ ($X = Cl^-$, Br^-, I^-, or N_3^-) and of $[Rh(NH_3)_5(py)]^{3+}$ (py = pyridine). Ligand-field photochemistry has been studied[16-20] for several *cis* and *trans* ions, $[RhL_4X_2]^+$, where $X = Cl^-$, Br^-, or I^- and L = NH_3, $\frac{1}{2}$ en, or $\frac{1}{4}$ cyclam (en = ethylenediamine, cyclam = 1,4,8,11-tetra-azacyclotetradecane).

Several nitro-compounds of cobalt(III) are reported[11-28] to react in artificial or natural light, and some such reactions have been studied in detail.[27,28] A few nitro-compounds of platinum(IV) are also known[29-32] to react when irradiated. However, there is no such information concerning nitro-rhodium(III).

We report here our detailed findings[‡] in this connection. The ions *cis*- and *trans*-$[Rh(en)_2(NO_2)X]^+$ ($X = NO_2^-$, Cl^-, or ONO^-) photoreact in aqueous solution with dioxygen to yield *superoxide* compounds of rhodium(III). These are of two kinds: monomeric $[Rh(en)_2(H_2O)(O_2)]^{2+}$ ions and dimeric ions of the type $[Y(en)_2Rh(O_2)Rh(en)_2X]^{n+}$. In this paper, we indicate co-ordinated nitrite, in general, as NO_2, the *N*-bonded nitro-form as *N*O_2, and the *O*-bonded nitrito-form as *O*NO.

Results

Dilute aqueous solutions of salts of the geometric isomers of $[Rh(en)_2(NO_2)_2]^+$ are colourless, their electronic spectra showing shoulders at 290 (ε = 7 720) and 242 (38 100) for the *cis* and 300 (1 750) and 255 nm (7 320 dm^2 mol^{-1}) for the *trans* isomers, respectively. Whereas both compounds are kinetically extremely inert in aqueous solution in the dark at room temperature, they do react more readily in light. The nature of the photoproducts depends upon the level of dioxygen present in the solution.

Photolysis of cis-$[Rh(en)_2(NO_2)_2]^+$ *in the Presence of Oxygen.*—When a solution of colourless *cis*-$[Rh(en)_2(NO_2)_2]X$ ($X = Cl^-$, NO_3^-, or ClO_4^-) is left in sunlight it quickly becomes red: the change is quicker on irradiating the solution with a medium-pressure mercury lamp. A typical example of the corresponding spectroscopic changes is shown in the Figure. Whether the reaction vessel is of quartz or Pyrex glass a new band is observed at about 500 nm. In all cases the pH of the solution decreases during the irradiation. For example, the pH of a solution 5.3 × 10^{-3} mol dm^{-3} in *cis*-$[Rh(en)_2(NO_2)_2]^+$ changes from 5.1 to 3.4, after irradiation for 20 min in the presence of oxygen.

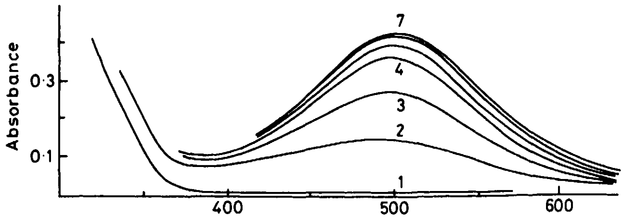


Figure. Successive visible spectra for *cis*-$[Rh(en)_2(NO_2)_2]^+$ (2.4 × 10^{-3} mol dm^{-3}, in water in the presence of oxygen: 1-cm quartz cell) irradiated with a medium-pressure mercury lamp: 1, original solution; 2, after 2 min; 3, after 4 min; 4, after 6 min; 5, after 8 min; 6, after 10 min; 7, after 12 min

When a 1.5 × 10^{-3} mol dm^{-3} solution of *cis*-$[Rh(en)_2(NO_2)_2]^+$ is irradiated in the presence of a high concentration (*ca.* 0.2 mol dm^{-3}) of sodium chloride a red-purple colour develops in solution. However, the intensities of the absorbances at 400 and 600 nm, relative to that at 500 nm, are higher now than in the absence of Cl^-.

Cationic products were separated by column chromatography on cation-exchange resin in the H^+ form, eluting with HCl, HNO_3, or $NaNO_3$ solutions. On elution with 0.2 mol dm^{-3} HCl the first fractions contain the unreacted *cis*-$[Rh(en)_2(NO_2)_2]^+$ ion. Other colourless fractions of the starting material, whose electronic and i.r. spectra suggest the presence of the linkage isomer *cis*-$[Rh(en)_2(NO_2)(ONO)]^+$, were next removed. After these had been collected the column was eluted with 0.5 mol dm^{-3} HCl, yielding two strongly coloured bands. The first, the red compound (A), is normally eluted with 0.5 mol dm^{-3} HCl. After its collection the column usually shows a sharp purple band (B) followed by a much weaker one, (C); (B) and (C) are typically eluted with 1 mol dm^{-3} HCl. Only compounds from bands (A) and (B) were isolated and characterized. It was not possible to crystallize either of these compounds using such anions as NO_3^-, ClO_4^-, PF_6^-, $B(C_6H_5)_4^-$, or BF_4^-. Both rapidly decomposed in the presence of the last two anions. Therefore they were usually freeze-dried and isolated as chlorides or nitrates. Salts of both ions (A) and (B) are very hygroscopic.

The coloured products are not formed in the absence of dioxygen and/or light, and are, therefore, generated by photoreactions of *cis*-$[Rh(en)_2(NO_2)_2]^+$ with O_2. Both (A) and (B)

[†] *Non-S.I. unit employed*: G = 10^{-4} T.

[‡] Preliminary findings were reported in ref. 33 and much of the e.s.r. spectroscopy in ref. 34.

Table 1. Vibrational spectra (cm^{-1}) of some dioxygen compounds

Compound	ν(O–O) [a]	Ref.
$[Rh(en)_2Cl(O_2)]^+$ (A)	1 050, 1 080 (Raman)	*b*
$[\{Rh(en)_2\}_2Cl(NO_2)(\mu\text{-}O_2)]^{3+}$ (B)	1 050 (Raman)	*b*
$[Co(bzacacen)(py)(O_2)]$ [c]	1 128	61
$[Co(acacen)(py)(O_2)]$ [d]	1 140	61
$[\{Co(NH_3)_5\}_2(\mu\text{-}O_2)]Cl_5\cdot 4H_2O$ (solid)	1 122 (Raman)	*e*
$[\{Co(NH_3)_4\}_2(\mu\text{-}O_2)(\mu\text{-}NH_2)]Cl_4\cdot 3H_2O$ (solid)	1 075 (Raman)	*e*
$Co(hb)O_2$ [f]	1 105	61
$Fe(hb)O_2$	1 107	61
$Fe(mb)O_2$ [g]	1 103	61
$[\{Co(NH_3)_5\}_2(\mu\text{-}O_2)][NO_3]_4$ (solution)	800 (Raman)	*h*
$[\{Co(NH_3)_5\}_2(\mu\text{-}O_2)][SO_4]_2$ (solid)	808 (Raman)	*h*
$H_3[\{Co(NH_3)_5\}_2(\mu\text{-}HO_2)][SO_4]_4$ (solid)	815 (Raman)	*h*
O_2	1 556	61
$O_2(^1\Delta)$	1 483	61
KO_2	1 145	61
Na_2O_2	738	61
NH_4HO_2	830	61

[a] Infrared bands except where indicated. [b] This work. [c] py = Pyridine; bzacacen = *NN'*-ethylenebis(benzoylacetone iminate). [d] acacen = *NN'*-Ethylenebis(acetylacetone iminate). [e] T. Shibahara, *J. Chem. Soc., Chem. Commun.*, 1973, 864. [f] hb = Haemoglobin. [g] mb = Myoglobin. [h] T. B. Freedman, G. N. Yoshida, and T. M. Loehr, *J. Chem. Soc., Chem. Commun.*, 1974, 1016.

are paramagnetic, with e.s.r. spectra characteristic[34] of Rh^{III}–(O_2^-) compounds and both react as one-electron oxidants toward Fe^{2+} and I^-. The ratios of the number of O_2^- units to Rh atoms were obtained by analysing for rhodium and for iodine produced in the reaction of solutions with iodide. The ratios are $O_2^- : Rh = 1 : 1$ in compound (A), and 1 : 2 in compound (B).

The Raman spectra of some of the new superoxides were recorded in aqueous solution. Table 1 compares them with spectra of some other transition-metal dioxygen compounds. The dimer (B) resulting from the irradiation of *cis*-$[Rh(en)_2(NO_2)_2]^+$ and isolated from aqueous HCl shows a strong absorption at 1 050 cm^{-1}. The corresponding monomer, however, absorbs at 1 050 and 1 080 cm^{-1}, the intensity of the latter band being about double that of the former. These absorptions are attributed to the superoxide stretching vibration. The Raman spectra of *cis*- and *trans*-$[Rh(en)_2X(Y)]^+$, where $X = Y = Cl^-$ or NO_2^- or $X = Cl^-$ and $Y = NO_2^-$, have no bands in this region.

One feature common to the electronic spectra of the previously known[35] superoxides of Rh^{III} is a strong absorption in the 600-nm region, The dimeric species reported here also show an absorption around 540 nm, while the monomeric compound absorbs strongly near 500 nm. In Table 2 results from the electronic spectra of these are compared with data from other superoxides of Rh^{III}. As the known ammines of Rh^{III} usually do not absorb in these regions, the low-energy absorption bands are good fingerprints for the rhodium(III) superoxides.

The formation of the monomeric and dimeric compounds (A) and (B) was followed by observing the change in absorbance in regions where these were the only absorbing species. It was found that while the monomer forms immediately after the irradiation starts, the dimer needs an induction period.

When optically active *cis*-$[Rh(en)_2(NO_2)_2]^+$ is irradiated in the presence of oxygen the optical activity of the solution diminishes as the irradiation period increases and completely vanishes after a certain time. For example, a solution initially 2.5×10^{-3} mol dm^{-3} in resolved *cis*-$[Rh(en)_2(NO_2)_2]^+$ showed no detectable optical activity after irradiation for 10 min.

Photolysis of trans-$[Rh(en)_2(NO_2)_2]^+$ *in the Presence of Oxygen*.—The species *trans*-$[Rh(en)_2(NO_2)_2]^+$ (usually used as its nitrate) was also studied. In this ion, both co-ordinated nitrite ions are *N*-bonded, as shown by its i.r. and electronic spectra. Irradiation of aqueous solutions containing this ion under conditions similar to those used for its *cis* isomer causes spectroscopic changes similar to those for the *cis* species. Assuming that the products from the photoreactions of the two isomeric ions have identical absorption coefficients for the new visible band (arising, essentially, from co-ordinated superoxide), the irradiation of *cis*-$[Rh(en)_2(NO_2)_2]^+$ gives superoxo-products in higher yield than does the *trans* isomer.

Although they were not characterized so fully as the products from the *cis* isomer, we believe that the main oxygenated products from the *trans* isomer are again monomeric (λ 484 nm) and dimeric (λ 540 nm) species. Products which contained no dioxygen and which showed i.r. evidence for the *O*-bonded nitrito-ligand were also formed.

Further, *freshly prepared trans* salts did not behave photochemically in the same way as did aged samples. Typically, from fresh material, at the start of the irradiation, an absorption band developed at 500 nm, and a much stronger absorption then grew at about 600 nm. Two months later, when the same solid was used to repeat the irradiation, the results agreed with those observed for authentic *trans*-$[Rh(en)_2(NO_2)_2]NO_3$. This 'aged' solid gave i.r. and electronic spectra expected for the dinitro-compound. The corresponding spectra of the *freshly prepared* solid support its formulation * as the linkage isomer *trans*-$[Rh(en)_2(NO_2)(ONO)]NO_3$.

Irradiations of Other Nitrorhodium(III) *Compounds*.—A solution of *trans*-$[Rh(en)_2Cl(NO_2)]NO_3$, irradiated in the presence of dioxygen, rapidly became blue. Rhodium(III) superoxo-complexes are presumably generated. The *cis* isomer behaves in a similar way. Irradiation of a solution containing hexanitrorhodate(III), $[Rh(NO_2)_6]^{3-}$, produced no change in colour of a kind suggesting the intervention of superoxo-species, although minor spectral changes suggest that some photoreaction may occur.

Photolysis of Nitrorhodium(III) *Compounds in the Absence of Oxygen*.—On irradiating aqueous solutions containing *cis*-$[Rh(en)_2(NO_2)_2]^+$ in the absence of oxygen, an isosbestic point is initially observed (*ca.* 323 nm) so a stoicheiometric relation exists between the reactants and products. A plot of the absorbance at 350 nm against time is a straight line. Further, no secondary photolysis occurs during this period. No visible absorption is observed at any time in this experiment. The likely product is the *cis*-$[Rh(en)_2(NO_2)(ONO)]^+$ ion. The irradiation of a solution of *trans*-$[Rh(en)_2(NO_2)_2]^+$ under similar conditions causes a decrease in the absorption for $\lambda < 360$ nm and an increase for $\lambda > 360$ nm. Here also, the decrease in intensity at 300 nm varies linearly with the irradiation time. An isosbestic point is seen around 360 nm.

Discussion

Photoreactions of Rhodium(III) *Nitro-compounds with Dioxygen*.—The light-induced reactions of dioxygen with the *cis*- and *trans*-$[Rh(en)_2X(NO_2)]^+$ ions, where $X = NO_2^-$ or Cl^-, in aqueous solutions, involve the formation of monomeric and dimeric compounds containing the $(en)_2Rh^{III}$–O_2^- moiety. The products depend strongly on the nature of the compound irradiated. Evidence is also found for the formation of linkage isomers in which at least one NO_2^-

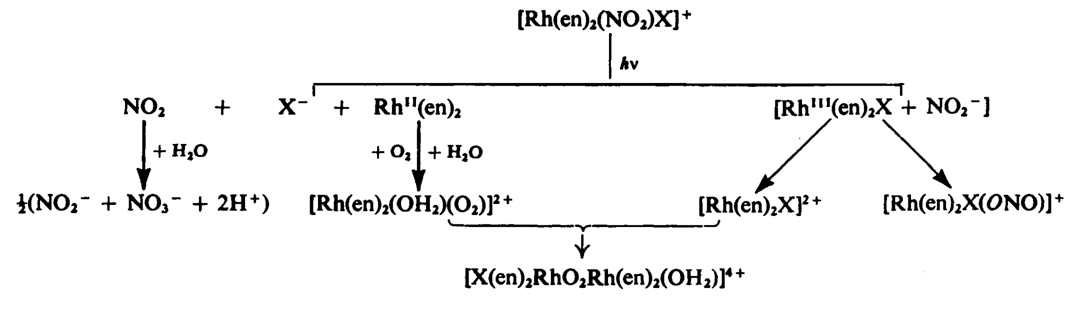
---

* In a similar way, freshly made 'cobaltinitrite' solutions have properties differing from those of the aged substance.

Table 2. Electronic spectra of some dioxygen compounds

Compound [a]	Medium	λ/nm	ν/10^3 cm^{-1}	ε/dm^2 mol^{-1}	Ref.
$[Rh(en)_2Cl(O_2)]^+$	Water	493	20.28	8 700	*b*
		320(sh)	31.25	58 000	
		253	39.53	67 000	
$[\{Rh(en)_2\}_2Cl(NO_2)(O_2)]^{3+}$	Water	540	18.52	9 200	*b*
		320(sh)	31.25	11 000	
		250	40.00	102 500	
$[Rh_2(4Me\text{-}py)_8Cl_2(O_2)][ClO_4]_3 \cdot 2H_2O$	1 mol dm^{-3} H_2SO_4	611	16.4	27 800	35
$[Rh_2(4Me\text{-}py)_8Cl_2(O_2)][BF_4]_3$	1 mol dm^{-3} H_2SO_4	611	16.4	27 800	35
		370(sh)	27.0	21 000	
		295	33.9	228 000	
		266	37.6	287 000	
		259	38.6	214 000	
		225(sh)	44.4	313 000	
$[Rh_2(py)_8(O_2)(OH_2)_2]^{5+}$	1 mol dm^{-3} H_2SO_4	572	17.5	33 000	35
$[Rh_2(py)_8Cl_2(O_2)][ClO_4]_3 \cdot 8H_2O$	1 mol dm^{-3} H_2SO_4	602	16.6	28 500	35
		288	34.8	190 000	
		268(sh)	37.2	331 000	
		262	38.2	358 000	
		255(sh)	39.2	314 000	
		225(sh)	44.4	424 000	
$[Rh_2(py)_8Cl_2(O_2)][BF_4]_3$	1 mol dm^{-3} H_2SO_4	602	16.6	28 500	35
O_2^-	NaCl + KCN	248	40.3	—	61
O_2^-	$NaO_2 + Na_2O_2$	370	27.0	—	61
O_2^-	Pyridine	442	22.6	—	61
$[Co_2(CN)_{10}(O_2)]^{5-}$	Water	486	20.6	11 300	61
		360	27.8	24 000	
		311	36.2	58 900	
		225	44.5	100 000	
$[Co_2(en)_4(NH_2)(O_2)]^{4+}$	Water	685	14.6	4 000	61
		463	21.6	4 650	
		305	32.8	60 000	
$[Co_2(pn)_4(NH_2)(O_2)]^{4+}$	Water	695	14.4	5 000	61
$[Co_2(tetren)_2(O_2)]^{5+}$	$HClO_4$	704	14.2	13 300	61
		486	21.4	5 600	
$[Co_2(en)_2(dien)_2(O_2)]^{5+}$	$HClO_4$	706	14.2	12 100	61
		472	21.2	3 850	
$[Co_2(en)_4(NH_3)_2(O_2)]^{5+}$	$HClO_4$	693	14.4	12 400	61
		471	21.2	350	
$[Co_2(NH_3)_{10}(O_2)]^{5+}$	12 mol dm^{-3} H_2SO_4	663	15.1	7 900	61
		479	20.9	2 800	
		330(sh)	30	30 000	
		297	33.7	230 000	

[a] dien = Diethylenetriamine; tetren = tetraethylenepenta-amine; pn = 1,2-diaminopropane. [b] This work.



Scheme.

ligand is *O*-bonded. These photoreactions are summarized in the Scheme.

The observed decrease in pH found during the reactions is consistent with this Scheme. Also, among the products of irradiated solutions, NO_2^- can be detected. For example, after irradiation for 20 min of a solution 5.3 × 10^{-3} mol dm^{-3} in *cis*-$[Rh(en)_2(NO_2)_2]^+$ the concentration of NO_2^- is of the order 10^{-5} mol dm^{-3}.

There are no reports on the photochemistry of compounds of NO_2^- with Rh^{III}. Gidney [36] mentions the development of a pink colour in solutions of the ions *cis*-$[Rh(bipy)_2(NO_2)_2]^+$ (bipy = 2,2′-bipyridyl) and *cis*-$[Rh(phen)_2(NO_2)_2]^+$ (phen = 1,10-phenanthroline) with time. This colour may well be due to photoreactions of the kind described here, but in view of the unsaturated nature ('non-innocent') of the di-imine ligands other explanations are also feasible.

Adell[25] has observed the nitro–nitrito linkage isomerization of *trans*-$[\mathrm{Co(en)_2(}N\mathrm{CS)(}N\mathrm{O_2)]X}$, where X = $\mathrm{ClO_4^-}$ or $\mathrm{NO_3^-}$, induced either by artificial light ($\lambda > 430$ nm) or by sunlight. The ion *trans*-$[\mathrm{Co(NH_3)_4(}N\mathrm{O_2)_2]^+}$ is reported[26] to be photoreduced in sunlight, yielding cobalt(II) products. The photochemical behaviour of nitroamineplatinum(IV) compounds has been studied by Chernyaev *et al.*[30,31] and Sabbatini *et al.*[32] Both studies suggest that photoreduction of $\mathrm{Pt^{IV}}$ to $\mathrm{Pt^{II}}$ and nitro–nitrito-photoisomerization occurs.

Although the nitro–nitrito-photoisomerization of the nitrorhodium(III) compounds was not investigated in full, the colourless products obtained in the irradiation of both the *trans*- and the *cis*-$[\mathrm{Rh(en)_2(}N\mathrm{O_2)_2]^+}$ ions in the absence or presence of oxygen give i.r. and electronic spectra characteristic of $[\mathrm{Rh(en)_2(}N\mathrm{O_2)(}O\mathrm{NO)]^+}$.

Demonstration of the photogeneration of rhodium(II) species when rhodium(III) compounds are irradiated is not easy because the back reactions of rhodium(II) radicals forming $\mathrm{Rh^{III}}$ occur at nearly diffusion-limited rates.[3] These rhodium(II) species are supposed to be formed when solutions of $[\mathrm{Rh(NH_3)_5X]^{2+}}$, X = $\mathrm{Cl^-}$, $\mathrm{I^-}$, $S\mathrm{CN^-}$, or $N\mathrm{CS^-}$, are irradiated at energies corresponding to charge-transfer (c.t.) bands. Flash photolysis of these compounds at wavelengths corresponding to their ligand-to-metal c.t. bands produces transient halide species and rhodium(II) fragments, the net photoproducts being always the *trans*-$[\mathrm{Rh(NH_3)_4(OH_2)X]^{2+}}$ compounds.[37] For example, flash photolysis of $[\mathrm{Rh(NH_3)_5I]^{2+}}$, in the presence of traces of $\mathrm{I^-}$, yields a transient species identified as $\mathrm{I_2^-}$. As this has only been observed when irradiation takes place at wavelengths corresponding to the c.t.t.m. bands, a redox pathway has been suggested. Since only *trans*-tetra-amminerhodium(III) compounds were obtained, the rhodium(II) species were said to be essentially the tetra-ammine.

It has recently been reported[38] that rhodium(II) ammine complexes, generated by the pulse-radiolytic one-electron reduction of rhodium(III) ammines, react with $\mathrm{O_2}$ according to equation (1). The second-order rate constant was 3.1×10^8

$$\mathrm{Rh(NH_3)_4^{2+} + O_2 \xrightarrow{H_2O} O_2Rh(NH_3)_4(OH_2)^{2+}} \quad (1)$$

$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ (at an unspecified temperature).* The spectrum of the solution recorded 200 µs after the pulse, with $\lambda = 265$ nm ($\varepsilon = 96\,000\ \mathrm{dm^2\ mol^{-1}}$), closely agrees with those of the monomeric superoxides reported here ($\lambda = 253$ nm, $\varepsilon = 67\,000\ \mathrm{dm^2\ mol^{-1}}$). A superoxo cage complex of $\mathrm{Ru^{III}}$, $[\mathrm{Ru(bipy)_3(O_2)]^{2+}}$, has also been postulated[39] to explain the photochemical oxidation of $[\mathrm{Ru(bipy)_3]^{2+}}$ in the presence of $\mathrm{O_2}$.

Presumably a c.t.t.m. excited state is involved in the present system, in which a strong delocalization of charge from the ligand to the metal can be formally represented by a rhodium(II) species and an $\mathrm{NO_2}$ radical, as in the Scheme.

The formation of stereolabile rhodium(II) species as shown in the Scheme would explain the lack of optical activity of the products in the irradiation of optically active *cis*-$[\mathrm{Rh(en)_2(}N\mathrm{O_2)_2]^+}$. Furthermore, *two* e.s.r. signals are observed for frozen solutions at 77 K of the monomers that result from the irradiation of *cis*-$[\mathrm{Rh(en)_2(}N\mathrm{O_2)_2]^+}$. Since the monomeric superoxide from *trans*-$[\mathrm{Rh(en)_2(}N\mathrm{O_2)_2]^+}$ gives only one e.s.r. signal under similar conditions, it is likely that a mixture of *cis*- and *trans*-superoxides is formed from the *cis* complex. Further, the Raman spectrum of the monomer (from the *cis*-dinitro-salts) shows *two* bands (at 1 050 and 1 080 $\mathrm{cm^{-1}}$) while the corresponding dioxygen vibration for the dimer absorbs at 1 050 $\mathrm{cm^{-1}}$ only.

The formation of dimeric species was initially thought[33] to result from the thermal reaction of the monomer with photo-aquated products. However, there is no sign of such a reaction when the monomer is added to a solution of *cis*-$[\mathrm{Rh(en)_2(OH_2)_2]^{3+}}$ either under acidic (pH = 1) or neutral (pH = 7) conditions. Also, there was no reaction with *cis*- and *trans*-$[\mathrm{Rh(en)_2Cl_2]^+}$ or *cis*-$[\mathrm{Rh(en)_2Cl(OH_2)]^{2+}}$ at room temperature or on a steam-bath.

Dioxygen Complexes of Rhodium(III).—The co-ordination of dioxygen to $\mathrm{Rh^I}$ is well known,[40–50] the oxygen ligand bonding side-on. The crystal structures of several of these compounds have been determined,[44–50] the O–O bond distances ranging from 0.142 to 0.146 nm. Complexes of dioxygen with $\mathrm{Rh^{III}}$ are not so well known, although their formation has been suggested by several authors.[35,51–54]

Reducing conditions seem required for rhodium(III) complexes to add molecular oxygen. When conditions are such that $\mathrm{Rh^I}$, or its formal equivalent such as $[\mathrm{RhH(NH_3)_5]^{2+}}$, is present, peroxo-complexes of $\mathrm{Rh^{III}}$ may be formed. This is observed in several cases.[35,51–56] However, if the only reduced state of rhodium formed is $\mathrm{Rh^{II}}$, as in the photochemical pathway, only superoxides are generated. This we examined by trying to oxidize our irradiated solution with $\mathrm{Cl_2}$. No increase occurred in the concentration of superoxide: such an increase would be expected if oxidizable peroxo-compounds were present.

Known superoxides of $\mathrm{Rh^{III}}$ are[35] strong oxidizing agents in aqueous solution, acting as one-electron oxidants towards iron(II) and iodide. The peroxo-complexes formed can be quantitatively reoxidized to the superoxide by $\mathrm{Ce^{IV}}$, $\mathrm{Cl_2}$, or $\mathrm{MnO_4^-}$. In the same way, addition of iodide, iron(II), or hydroxide to the solutions of our photochemically generated superoxides causes fading of colour. The reactions with $\mathrm{Fe^{II}}$ and $\mathrm{I^-}$ yield rhodium(III) peroxo-compounds, which again may act as one-electron reducing agents. Typical reactions are (2) and (3). The reactions of the dimer (B) with both $\mathrm{I^-}$ and

$$\mathrm{[Rh(en)_2(OH_2)(O_2)]^{2+} + I^- \xrightleftharpoons{H_2O(H^+)} [Rh(en)_2(OH_2)(O_2)]^+ + \tfrac{1}{2}\,I_2} \quad (2)$$

$$\mathrm{[Rh(en)_2(OH_2)(O_2)]^+ + 2I^- + 4H_3O^+ \rightleftharpoons [Rh(en)_2(OH_2)_2]^{3+} + 5H_2O + I_2} \quad (3)$$

$\mathrm{Fe^{2+}}$ are faster than those of the monomer (A).

The superoxides of $\mathrm{Rh^{III}}$ are surprisingly stable in concentrated acid solution at room temperature. However, on heating such solutions the characteristic colour of the superoxide does disappear. The change in the electronic spectrum of a solution of compound (A) in concentrated HCl was followed at 329 K. Gas is evolved and the final solution is yellow. The spectrum of the final solution suggests the presence of a mixture of *trans*- and *cis*-$[\mathrm{Rh(en)_2Cl_2]^+}$ ions. The spectroscopic changes also indicate that there is substitution of both $\mathrm{O_2^-}$ and $\mathrm{H_2O}$ ligands by $\mathrm{Cl^-}$.

Superoxide is supposed[57] to have a ligand-field strength between those of water and $\mathrm{NH_3}$ and closely compares with *N*-bonded thiocyanate. The absorption (Table 2) around 320 nm, observed as a shoulder for superoxides containing the $\mathrm{Rh(en)_2}$ moiety, may be assigned to a *d–d* transition of the rhodium(III) centre. The assignment of the low-energy band of superoxocobalt(III) compounds has generated some controversy.[58–60] More recently, for $[\{\mathrm{Co(NH_3)_5}\}_2(\mu\text{-}\mathrm{O_2})]^{5+}$ ('deca-ammine') and $[\{\mathrm{Co(CN)_5}\}_2(\mu\text{-}\mathrm{O_2})]^{5-}$ ('decacyanide') ions, the low-energy bands were assigned[57] to metal-to-ligand

---

* This is probably why we were not able to observe the formation of superoxides by microsecond-flash photolysis of aqueous solutions of *cis*-$[\mathrm{Rh(en)_2(}N\mathrm{O_2)_2]^+}$.

Table 3. E.s.r. parameters for various superoxide complexes of Rh^{III} and Co^{III}

Complex	g_1	g_2	g_3	$g_{av.}$	g_{iso}	Ref.
trans-$[Rh(en)_2Cl(O_2)]^+$	2.076 8	2.022 9	1.999 6	2.033 1	2.033 0	This work [a]
cis-$[Rh(en)_2Cl(O_2)]^+$	2.086 1	2.022 9	1.991 9	2.033 6	2.033 0	This work [a]
$[\{Rh(en)_2\}_2Cl(NO_2)(\mu\text{-}O_2)]^{3+}$	2.097 2	2.030 1	1.988 9	2.039 7	2.037 8	This work [a]
$[\{Rh(4Me\text{-}py)_4Cl\}_2(\mu\text{-}O_2)]^{3+}$	2.091 7	2.026 8	1.989 8	2.036 1	—	This work [a]
$[Co(salen)(O_2)]$ [b]	2.08	—	1.99	—	2.02	61
$[Co(Hdmg)_2(py)(O_2)]$ [c]	2.06	—	2.00	—	2.01	61
$[Co(NH_3)_5(O_2)]^{2+}$	2.07	—	2.00	—	—	61
$[\{Co(dien)(en)\}_2(\mu\text{-}O_2)]^{5+}$	—	—	—	—	2.03	61
$[\{Co(NH_3)_5\}_2(\mu\text{-}O_2)]^{5+}$	—	—	—	—	2.03	61

[a] For details, see ref. 34. [b] salen = *NN'*-Ethylenebis(salicylideneiminate). [c] Hdmg = Dimethylglyoximate(1 –).

(m.l.c.t.) transitions of the type d $\Pi \rightarrow \Pi_v(O_2^-)$. The photochemistry of these compounds may help to confirm the assignment as m.l.c.t., since if this is correct, irradiation at wavelengths corresponding to this band might well yield M^{IV} and O_2^{2-} species. Results [54] for some superoxides of Rh^{III} and Co^{III} seem to suggest that these are stable towards visible light.

E.s.r. spectra of solutions of all complexes were very similar. At room temperature a single line of half-width *ca.* 10 G centred at *ca.* $g = 2.04$ was observed. Frozen solutions at 77 K yielded spectra showing three *g* values, two >2 and one <2 with linewidths *ca.* 14 G. In no case was there evidence of hyperfine coupling to rhodium or any other nuclei. The e.s.r. spectra of the monomeric compounds resulting from the irradiation of *cis*-$[Rh(en)_2(NO_2)_2]^+$ give two sets of signals, at 77 K, in dimethylformamide (dmf). However, the corresponding product from the irradiation of *trans*-$[Rh(en)_2(NO_2)_2]^+$ gives only one set of lines. The *g* values of the latter coincide with those of one of the sets of the *cis* products. The most likely explanation for these results is that *trans*-$[Rh(en)_2(OH_2)_2(O_2)]^{2+}$ alone results from the irradiation of the *trans*-dinitro-ion, while the *cis* isomer gives both *trans*- and *cis*-superoxides.

The absence of detectable hyperfine coupling to ^{103}Rh suggests values < *ca.* 5 G. Such small values would be expected since the nuclear magnetic moment of ^{103}Rh is about 2% that of ^{57}Co. From the already small hyperfine couplings to ^{57}Co (typically 20 G) in the related cobalt complexes, hyperfine couplings to ^{103}Rh would be expected to be < 1 G. The e.s.r. results tell us that the unpaired electron is in a π^* orbital largely on the O_2, as in O_2^-, but the actual amount of charge is difficult to assess. Indeed, the very close similarity of the *g* tensors to those of HOO [61] and ROO [62,63] suggests that the unpaired electron is in a π^* orbital on O_2 having only a small amount of d_{yz} contribution. Nevertheless, for electron-accounting purposes, it is convenient *formally* to represent the oxidation states as $Rh^{III}\text{-}O_2^-$. The observation of three *g* values (Table 3) strongly supports a bent Rh–O–O configuration.

The work described here reveals new pathways to the preparation of superoxide complexes of transition-metal ions. An adequate choice of the metal and of the appropriate co-ordination sphere may be very important in determining the success of photochemical reactions with oxygen. A strong-field environment around the metal and an easily oxidizable ligand seem to be requirements for the photochemical generation of superoxide species. These will probably favour the population of reactive c.t.t.m. states, as against l.f. states. Also, the selection of M^{n+} metal ions with $(n - 1)^+$ highly reducing oxidation states may favour the photoaddition of oxygen. These include a number of transition-metal ions whose dioxygen compounds would be very interesting, and preparative studies continue.

Co-ordination compounds of superoxide with Rh^{III}, remarkably stable in aqueous solution, provide useful systems to study the properties of such compounds, although full characterization of some of the photochemical products is extremely difficult.

Experimental

Electronic spectra were recorded on a Unicam SP800 or on a Beckman DK-II spectrophotometer. Circular dichroism measurements were made using a Roussel-Jouan Dichrographe model IB, a Jasco J-20A, and a Dichrographe III (Jobin-Yvon). Infrared spectra were recorded on Perkin-Elmer 257 and 457 spectrometers for the 4 000—625 and 4 000—250 cm^{-1} regions, respectively. E.s.r. spectra were obtained using a Varian E3 spectrometer. Degassed solutions of the compounds in dmf were usually used. Raman spectra were measured on a Coderg T800 triple monochromator, using radiation at 647.1 nm from a krypton laser (Spectra Physics model 164). Aqueous solutions were used for obtaining the spectra of the dioxygen compounds. Atomic absorption analysis of Rh was done with a Varian Techtron AA6, using either air–acetylene or dinitrogen oxide–acetylene flames. Calibration was made with $RhCl_3 \cdot 3H_2O$ solutions. Conductivity measurements were made on a Pye Unicam conductivity bridge. Commercially available chemicals of high purity were usually employed. In particular, $RhCl_3 \cdot 3H_2O$ was supplied by Johnson Matthey Ltd.

Irradiation.—A GEC 250-W type ME/D medium-pressure lamp was used in the photolytic experiments. These were usually carried out with *ca.* 10^{-2}—10^{-3} mol dm^{-3} solutions of complex. Irradiations of *trans*-$[Rh(en)_2(NO_2)_2]^+$ were usually done using solutions 10 times more concentrated. The solution was normally put in a 1-cm silica cell, and this was kept in a cell holder in front of the lamp (*ca.* 5 cm apart). Dioxygen (or N_2) was bubbled through the solutions. Irradiations were usually done at room temperature (± 2 °C), the cell being flushed with a stream of N_2 as the photolysis proceeded. Alternatively, the solution was put in a 50-cm^3 crystallizing dish (solution depth *ca.* 1 cm) and the lamp clamped on the top of the dish, at about 7 cm from the liquid surface. In most of these experiments the temperature of the solution was not controlled and increased significantly during the irradiation period. In one experiment the temperature of the solution was kept at around 273 K by immersing the vessel in ice. The relative amount of dimer obtained in this particular experiment was much smaller than previously.

Kinetics.—Irradiations were done in a 1-cm silica cell held in front of the lamp as described above and taken off every 30 s to record the visible spectrum of the solution. Using the dinitrogen stream to cool the cell, temperatures were usually near ambient (293 ± 2 K).

Flash Photolysis.—An Applied Photophysics GD-20 μs apparatus with photoelectric detection was used. A solution 1.1×10^{-3} mol dm^{-3} in *cis*-$[Rh(en)_2(NO_2)_2]^+$ in a 10-cm silica cell was used in the experiments. No transients were observed.

Separation of the Products.—A column, *ca*. 15 cm long and 1.5 cm in diameter, filled with Sephadex C-25 cation-exchange resin (H^+ form) was used. The irradiated solution was placed on the column and eluted first with water (50 cm^3). The solution collected was used for titration of the NO_2^- produced using the method described by Vogel.[64] The column was then eluted with 0.2 mol dm^{-3} HCl, checking the products by recording the u.v. spectra of successive aliquots. The first colourless product collected is the unreacted complex. Then linkage isomers of this compound are eluted. The coloured products were eluted with HCl as described in the text.

Reactions of the Superoxides with I^-.—Solutions (typically 3×10^{-4} mol dm^{-3}) of monomer $[Rh(en)_2(OH_2)(O_2)]^{2+}$ were allowed to react at room temperature with an excess of I^-. The I_2 formed was then extracted with several portions of CCl_4 and titrated with $S_2O_3^{2-}$. The end-point was determined by the fading of the purple colour of I_2 in CCl_4 and by using starch as an indicator. From these results the concentration of 'O_2^-' in the solution of superoxo-complex was then calculated. Atomic absorption analysis for Rh was done on the resultant solutions, to determine the ratio Rh : O_2^- in the compound. The absorption coefficients given for the superoxides are mean values obtained from titrations of 'O_2^-' in the respective solutions. These agreed with values obtained from the spectra of weighed samples. The peroxo-solution resulting from the reaction of superoxo-complexes with samples isolated by freeze-drying solutions of the superoxides in hydrochloric acid were used for C, H, and N analysis. The aqua ligands are substituted by Cl^-.

Acknowledgements

We thank the Instituto Nacional de Investigacao Cientifica for a fellowship (to J. D. P. de Jesus), the University of Aveiro (Portugal) for leave of absence (to J. D. P. de Jesus), and the British Council for support of our work (R. D. G.).

References

1 A. W. Adamson and P. D. Fleischauer (eds.), 'Concepts of Inorganic Photochemistry,' Wiley-Interscience, New York, 1975.
2 P. C. Ford, J. D. Petersen, and R. E. Hintze, *Coord. Chem. Rev.*, 1974, **14**, 67.
3 T. L. Kelly and J. F. Endicott, *J. Am. Chem. Soc.*, 1972, **94**, 1797.
4 T. L. Kelly and J. F. Endicott, *J. Phys. Chem.*, 1972, **76**, 1937.
5 L. Moggi, *Gazz. Chim. Ital.*, 1967, **97**, 1089.
6 J. Kelly and J. F. Endicott, *J. Am. Chem. Soc.*, 1970, **92**, 5733.
7 R. Wang and F. Basolo, *J. Am. Chem. Soc.*, 1972, **94**, 7173.
8 G. Ferraudi and J. F. Endicott, *Inorg. Chem.*, 1973, **12**, 2389.
9 G. Ferraudi and J. F. Endicott, *J. Am. Chem. Soc.*, 1973, **95**, 2371.
10 J. L. Reed, H. G. Gafney, and F. Basolo, *J. Am. Chem. Soc.*, 1974, **97**, 1363.
11 P. C. Ford and J. D. Petersen, *J. Am. Chem. Soc.*, 1975, **14**, 1404.
12 T. Inoue, J. F. Endicott, and G. J. Ferraudi, *Inorg. Chem.*, 1976, **15**, 3098.
13 P. C. Ford, *Inorg. Chem.*, 1975, **14**, 1440.
14 P. C. Ford, G. Malouf, J. D. Petersen, and V. A. Durante, *Adv. Chem. Ser.*, 1976, **150**, 187.
15 J. D. Petersen, R. J. Watts, and P. C. Ford, *J. Am. Chem. Soc.*, 1976, **98**, 3188.
16 C. Kutal and A. W. Adamson, *Inorg. Chem.*, 1973, **12**, 1454.
17 M. M. Muir and W. M. Huang, *Inorg. Chem.*, 1973, **12**, 1831.
18 D. Strauss and P. C. Ford, *J. Chem. Soc., Chem. Commun.*, 1977, 194.
19 J. Selan and R. Rumfeldt, *Can. J. Chem.*, 1976, **54**, 519.
20 J. Selan and R. Rumfeldt, *Can. J. Chem.*, 1976, **54**, 1061.

40 V. J. Choy and C. J. O'Connor, *Coord. Chem. Rev.*, 1972—1973, **9**, 145.

41 L. M. Haines and E. Singleton, *J. Organomet. Chem.*, 1971, **30**, C81.

42 L. Haines, *Inorg. Chem.*, 1971, **10**, 1685.

43 L. Vaska, L. S. Chen, and W. V. Miller, *J. Am. Chem. Soc.*, 1971, **93**, 6671.

44 J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Am. Chem. Soc.*, 1969, **91**, 603.

45 M. Laing, M. J. Nolte, and E. Singleton, *J. Chem. Soc., Chem. Commun.*, 1975, 660.

46 M. J. Nolte and E. Singleton, *Acta Crystallogr., Sect. B*, 1975, **31**, 2223.

47 M. J. Nolte and E. Singleton, *Acta Crystallogr., Sect. B*, 1976, **32**, 1410.

48 C. Busetto, A. D'Alfonso, F. Maspero, and G. Perego, *J. Chem. Soc., Dalton Trans.*, 1977, 1828.

49 M. J. Bennett and P. D. Donaldson, *Inorg. Chem.*, 1977, **16**, 1581.

50 M. J. Bennett and P. D. Donaldson, *Inorg. Chem.*, 1977, **16**, 1585.

51 J. A. Osborn, A. R. Powell, and G. Wilkinson, *Chem. Commun.*, 1966, 461.

52 D. N. Lawson, M. J. Mays, and G. Wilkinson, *J. Chem. Soc. A*, 1966, 52.

53 L. E. Johnston and J. A. Page, *Can. J. Chem.*, 1969, **47**, 4241.

54 A. W. Addison, Ph.D. Thesis, University of Kent at Canterbury, 1970.

55 H. L. Roberts and W. R. Symes, *J. Chem. Soc. A*, 1968, 1450.

56 R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc. A*, 1970, 3126.

57 V. M. Miskowski, J. L. Robbins, I. M. Treitel, and H. B. Gray, *Inorg. Chem.*, 1975, **14**, 2378.

58 M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, 1961, **308**, 254.

59 J. Barrett, *Chem. Commun.*, 1968, 874.

60 K. Garbett and R. D. Gillard, *J. Chem. Soc. A*, 1968, 1725.

61 G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, 1976, **19**, 1.

62 R. C. Catton and M. C. R. Symons, *J. Chem. Soc. A*, 1969, 1393.

63 G. S. P. Verma, Ph.D. Thesis, University of Leicester, 1967.

64 A. I. Vogel, 'A Textbook of Quantitative Analysis,' Longmans, London, 1962.

65 J. D. Pedrosa de Jesus, Ph.D. Thesis, University of Wales (University College, Cardiff), 1977.

Received 7th November 1983; *Paper* 3/2085