

Oxidants Containing Rhodium

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Nearly all the substances generated in water and said to involve rhodium-(iv), -(v) and -(vi) species, such as 'Claus' blue,' are in fact superoxides of rhodium(III); the superoxide ligand in Claus' blue results from oxidation of hydroxide by dichlorine.

Variable oxidation states are common among transition metals. For rhodium in aqueous media, the trivalent state is the most familiar. Reduced compounds may involve a genuine rhodium(I) or rhodium(II) species, or alternatively a hydride or rhodium(III), where the reducing power is in the simple ligand rather than the metal ion.

In a similar way, the many known oxidants containing rhodium [generated by oxidizing simple rhodium(III) species] have been thought to divide into (A) true higher oxidation states of rhodium [rhodium-(iv), -(v) and -(vi)] or (B) superoxides of rhodium(III). We now show that nearly all the

higher oxidation states are actually superoxorhodium(III) species; *i.e.* that **A** and **B** are very much the same.

The known (and well-established¹) superoxorhodium(III) species **B** in aqueous media are of two general types: (i) the monomeric orange-yellow class with $\text{Rh}^{\text{III}} : (\text{O}_2^-) = 1 : 1$, and (ii) the blue-violet dimeric superoxo-bridged dirhodium-(III,III) with $\text{Rh}^{\text{III}} : (\text{O}_2^-) = 2 : 1$. Reported syntheses involve (a) the action of dioxygen, ozone or hydrogen peroxide upon various nitrogen-ligand complexes,²⁻⁴ as in $[\{\text{Rh}(\text{py})_4\text{Cl}\}_2(\mu\text{-O}_2^-)]^{3+}$, where py is pyridine: this has $g_{\text{iso}} = 2.019$;³ sometimes these are photochemically activated as in the

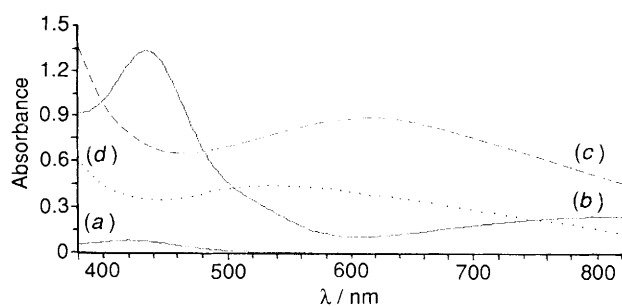


Fig. 1 Absorption spectra showing the effect of dichlorine on $8.02 \times 10^{-4} \text{ mol dm}^{-3} \text{ RhCl}_3 \cdot 3\text{H}_2\text{O}$ in $0.21 \text{ mol dm}^{-3} \text{ KOH}$ solution with time: (a) yellow (no Cl_2); (b) orange; (c) deep blue; and (d) deep violet

Table 1 Properties of 'oxidized' species of rhodium

| Complex | Colour | $\lambda_{\text{max}}/\text{nm}$ (log ϵ) | ESR | Ref. |
|---|------------------|---|---|-----------|
| [Claus' blue] $^{n-}$ | Deep blue a | 628 (3.05) | $g_{\text{iso}} 2.044$ | This work |
| [Claus' blue] $^{n+}$ | Deep violet a | 526 (2.72) | $g_{\text{iso}} 2.044$ | This work |
| $[\{\text{Rh}(\text{OH})(\text{H}_2\text{O})_4\}_2(\mu\text{-O}_2^-)]^{3+}$ | Violet a | 560 (2.34) 420 (2.15) | $g_{\text{iso}} 2.041$ | 5 |
| $[\{\text{Rh}(\text{py})_4\text{Cl}\}_2(\mu\text{-O}_2^-)]^{3+c}$ | Blue a | 602 (3.45) | $g_{\text{iso}} 2.019$ | 2 |
| $\text{cis-}[\text{Rh}(\text{en})_2\text{Cl}(\mu\text{-O}_2^-)]^{3+c}$ | Orange a | 493 (3.94) | $g_{\text{iso}} 2.033$ | 2 |
| $[\{\text{Rh}(\text{en})_2\}_2\text{Cl}(\text{NO}_2)(\mu\text{-O}_2^-)]^{3+}$ | Purple a | 540 (3.96) | $g_{\text{iso}} 2.038$ | 2 |
| 'Rhodium(IV) sulfate' | Violet a | (n.a.) d | $g_{\text{iso}} 2.036$ | 11 |
| 'Rhodium(IV) sulfate'-mer- | Blue a | 570 (n.a.) | $g_{\text{iso}} 2.040$ | 11 |
| $[\text{Rh}(\text{H}_2\text{O})_3(\text{OH})_3]^+$ | | 410-420 (n.a.) | | |
| $\text{Ba}_n[\text{Claus' blue}]$ | Green b | | $g_1 2.030$ $g_2 2.012$ $g_3 1.999$ $g 2.05$ | This work |
| $\text{Ba}[\text{Rh}(\text{OH})_6]$ | Dark green b | | | 11 |

a In solution. b As solid. c py = pyridine; en = ethylenediamine. d n.a. = not available.

orange 2 $[\text{Rh}(\text{en})_2(\text{NO}_2)(\text{O}_2)]^+$ (en = ethylenediamine: this has $g = 2.033$), and (b) the addition of dioxygen to dirhodium(II,II) species, 5,6 giving a blue-violet superoxodimer such as $[(\text{H}_2\text{O})_4(\text{OH})\text{Rh}(\mu\text{-O}_2^-)\text{Rh}(\text{OH})(\text{H}_2\text{O})_4]^{3+}$ (X). 5 This has $g_{\text{iso}} = 2.041$. Several crystal structures are available through the work of Springborg and Zehnder 4 and of Baranovskii and associates 6 on the prototype with nitrogenous ligands.

All the known aqueous generated higher oxidation states of rhodium (A) have been made using a small range of oxidants. These are principally: (a) electrochemical 7 or bismuthate 8 oxidation of acidic solutions containing Rh^{III} ; (b) the reaction of dichlorine or dibromine (directly or *via* hypochlorite or hypobromite) on alkaline trivalent rhodium solutions; 9,10 and (c) the treatment of various aqueous chloride, hydroxide and oxide systems of rhodium(III) with ozone. 11

All the ill-defined products A are blue or violet and have been generally formulated as tetra-oxoanions of rhodium-(IV), -(V) or -(VI), $[\text{RhO}_4]^{(8-n)-}$ (where n is the oxidation state), similar to the well-established ruthenates and osmates. In a typical preparation, a strongly alkaline solution of rhodium(III) is treated with dichlorine, and the resultant blue solution (Claus' blue) 9 yields a precipitate with barium hydroxide.

Fig. 1 shows (in part) the course of this preparation: the intermediate absorbing at about 430 nm is particularly significant, since it resembles other monomeric dioxigen-

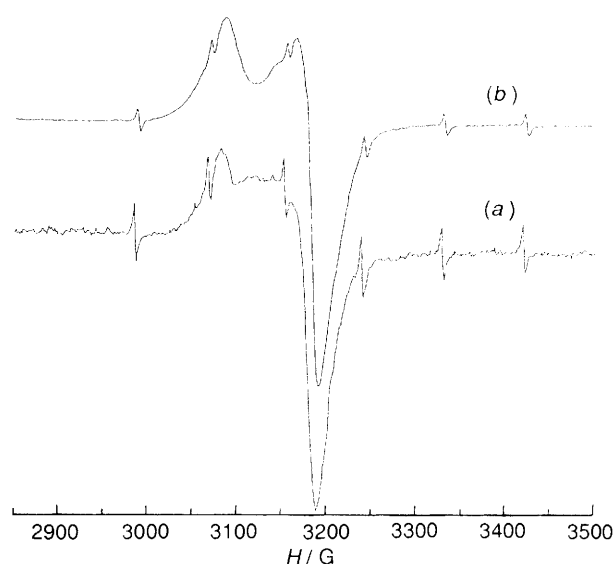


Fig. 2 (a) ESR spectrum of the barium salt of Claus' blue dissolved in $3 \text{ mol dm}^{-3} \text{ HClO}_4$ (77 K) with manganese(II) markers and (b) ESR spectrum of $[\{\text{Rh}(\text{OH})(\text{H}_2\text{O})_4\}_2(\mu\text{-O}_2^-)]^{3+}$ in $3 \text{ mol dm}^{-3} \text{ HClO}_4$ (77 K). $1 \text{ G} = 10^{-4} \text{ T}$.

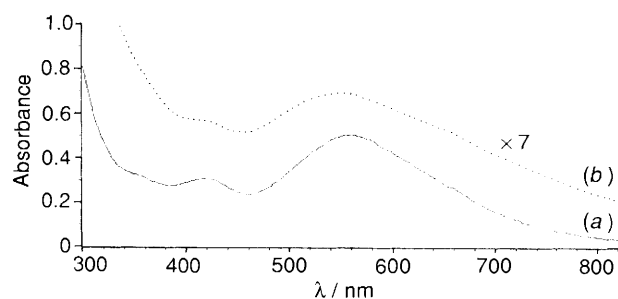


Fig. 3 Absorption spectrum of: (a) $0.01 \text{ mol dm}^{-3} [\{\text{Rh}(\text{OH})(\text{H}_2\text{O})_4\}_2(\mu\text{-O}_2^-)]^{3+}$ and (b) a fraction of Claus' blue eluted from a Dowex 50W-X2 column using $2\text{-}3 \text{ mol dm}^{-3} \text{ HClO}_4$ (this absorbance is multiplied by seven)

rhodium(III) intermediate species. The ESR and chemical behaviour of the blue product are very similar to those of the known superoxide X ($g = 2.041$) above (Fig. 2); the measured g -tensor (acid or base $g_{\text{iso}} = 2.044$) for Claus' blue, quite unlike that for Ir^{IV} , indicates that the free electron is not delocalised in the empty orbitals of an electron deficient metal centre. Table 1 compares spectra.

Like the known superoxides, Claus' blue is long-lasting in acid but slowly decomposes in base. The visible absorption spectra in acid and base differ; the complex species is cationic and violet in acid, but anionic and deep blue in base. Since the species is dependent on pH, it is not surprising that the preparation can yield the blue or violet solution with increasing pH as dichlorine transforms the alkaline conditions to acid.

Hence, the nature of 'oxidized' rhodium species has been misinterpreted; Grube and Autenrieth electrolysed rhodium solutions 7 and suggested the presence of higher oxidation states over fifty years ago, but noted that the properties of the species may be due to other moieties. However, subsequent workers 7,8,10,11 have continued to assign the anionic and cationic species to changes of oxidation state *via* such a dismutation as that in reaction (1). Various 'oxidations' have



been the basis of many spectroscopic determinations of rhodium. 12 The analytical methods are usually calibrated

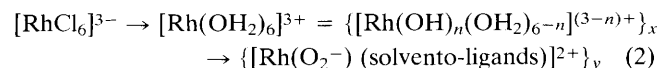
against known rhodium contents, so do not require a correct formulation of the species responsible for the colour.

In fact, the observed switch with pH points to the simple acid-base equilibrium of water ligands, while the identical ESR spectra of the blue and violet species proves that a single oxidation state is present.

The preparation of a solid sample of Claus' blue by adding barium hydroxide to a purple solution obtained from a chlorinated alkaline-rhodium(III) species is not simply precipitation: barium chloride gives no precipitate. The hydroxide neutralizes the acid produced by dichlorine in water, with the consequent transformation of the purple rhodium species into its blue anion, which gives its insoluble barium salt. This barium salt, of course, redissolves in acids giving purple solutions extremely similar to those of the known superoxide **X** made from Rh_2^{4+} with dioxygen.⁵

Claus' blue forms equally well in the absence of dioxygen. The superoxide presumably arises in the oxidation of hydroxide by dichlorine. (Indeed, the production of the coloured species very much depends on the initial hydroxide concentration.) Such non-enzymic production of O–O links at room temperature in water is novel.

The equilibria and reactions involved in the production of Claus' blue and similar blue-violet species are complex, so it is not possible to give a short statement of the known chemistry of 'oxidized' rhodium. The many available analyses of such blue and violet substances are consistent with a range of formulations involving rhodium(III) of the type $\text{Ba}_z\text{-}[\text{Rh}_y(\text{O}_2^-)_x(\text{OH})_n(\text{OH}_2)_v(\text{O}_2^{2-})_u(\text{O}_2^-)_i]\cdot s\text{H}_2\text{O}$, often with halide present (particularly where this derives from the oxidant) Claus' blue contains a variety of closely related species (Fig. 3). Despite this, the essential elements can be shown [reaction (2)].



The present finding that ostensibly straightforward oxidations in water actually yield superoxo-species rather than metal ions in their higher oxidation states will require reexamination of some other cases. The one simple genuine quadrivalent species of rhodium is the water-unstable green salt $\text{Cs}_2[\text{RhCl}_6]$, originally made¹³ via the oxidation of an ice-cold suspension of $\text{Cs}_3[\text{RhCl}_6]$. However, the nature of

other simple species made by the oxidation of ions like rhodium(III) in aqueous media [such as the oxidized species thought¹⁴ to contain aquo-iridium-(IV) and -(V)] may require reevaluation.

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