Synthesis, Characterization and Reactivity of Claus' Blue, a Superoxodirhodium(III,III) Species long said to contain Rh^{VI}†

Ian J. Ellison, [a] **Robert D. Gillard,**[a] **Monika Moszner,**[b] **Michal Wilgocki**[b] **and Jozef J. Ziolkowski**[b]

[a] *Department of Chemistry, University of Wales, PO Box 912, Cardiff CF1 3TB, UK*
[b] *Institute of Chemistry, University of Wroclaw, 14 F. Joliot-Curie Str., 50-383 Wroclaw, Poland*

Spectroscopic study of the ill defined Claus' blue, '$[Rh^{VI}O_4]^{2-}$', and the better characterized $[Rh^{III}_2(OH)_2(H_2O)_n(\mu\text{-}O_2)]^{3+}$ ion has revealed that the two ostensibly very different syntheses involved both give aquasuperoxorhodium(III) species; the properties of the two products are compared and contrasted. The O–O link in Claus' blue derives from the oxidation of co-ordinated hydroxide to give a peroxo-, then a superoxo-form. The properties of Claus' blue are rationalized in terms of its synthesis. The $[Rh^{III}(O_2)Rh^{III}]^{5+}$ core can be utilized to form other rhodium(III) superoxide complexes.

Dioxygen is essential for aerobic processes in living organisms. Its utilization is not without problems. For example, mammalian respiration transforms O_2 into superoxide [hyperoxide, dioxide(1−)], O_2^-; this very reactive anion must be deactivated. This is achieved[1] by co-ordination to a metal centre as in haemoglobin. Hence, the synthesis and characterization of model carriers for dioxygen has been an area of much activity.

Superoxides are well known for cobalt,[2] but less so for its eutrope rhodium.[3] Superoxorhodium(III) complexes containing oxygen, nitrogen and halide ligands are now recognized.[4] Their synthesis has presented problems: often small quantities only are generated using intricate and/or lengthy procedures; $[Rh^{III}_2(OH)_2(H_2O)_n(\mu\text{-}O_2)]^{3+}$ **X** is formed[5] by insertion of O_2 into the highly reducing $[Rh_2]^{4+}$ dimer, itself generated by reduction of the hexaaquarhodium(III) ion with Cr^{II} under N_2.

Ellison and Gillard[6] recently showed that many 'oxidations' (using conventional oxidants such as Cl_2, OCl^-, anodes, *etc.*) of Rh^{III} in water, giving products previously formulated as containing any or all of Rh^{IV}, Rh^{V} and Rh^{VI}, actually generate species containing the $[Rh^{III}(\mu\text{-}O_2)Rh^{III}]^{5+}$ fragment; this allows large quantities of superoxodirhodium(III,III) to be made quickly and effectively. For example, 'Claus' blue' **Y**, a violet-blue *solution* originally formulated[7] as containing $[Rh^{VI}O_4]^{2-}$, is formed simply by passing Cl_2 into an alkaline solution made from $RhCl_3$; a deep blue *solid* **Z** readily separates on the addition of $Ba(OH)_2$ solution. Isolation of the barium salt(s) **Z** allows soluble impurities to be removed from the rhodium species: **Z** readily redissolves in acid enabling further analysis. The name 'Claus' blue' has been used to denote any solution made by chlorinating initially alkaline rhodium(III) and also the solid obtained therefrom by precipitation with barium. We denote the solid as **Z**. The solutions we represent by **Y**, but emphasize that their colours vary from violet to blue, depending on several factors, notably pH.

Initial spectroscopic observations suggested[6] that a variety of closely related aquasuperoxodirhodium(III,III) species is present in **Y**: one major fraction is identical to the well defined complex **X**. We present here spectroscopic results on the synthesis and properties of **Y**. These permit us not only to compare and contrast the well defined **X** and ill characterized **Y**, but also to propose a mechanism for the formation of the O–O link and for the generation of a range of species in **Y**. We rationalize apparently anomalous observations. Further, we show that the $[Rh^{III}(O_2)\ Rh^{III}]^{5+}$ core in **Y** can be utilized to form defined[8] carboxylatorhodium(III) superoxide complexes and that **X** may be converted into a species resembling **Y**.

Results

(*a*) *Spectroscopic Studies of the Preparation of Claus' Blue,* **Y**, *and its Barium Salt,* **Z**.—The addition of very small quantities of dichlorine to alkaline solutions of rhodium(III) chloride causes large changes in the electronic absorption and ESR spectra; selected spectra from the preparation are featured in Fig. 1. The successive colours observed during the addition of Cl_2 to a solution 8.02×10^{-4} mol dm^{-3} in rhodium, made from commercial $RhCl_3$ in 0.21 mol dm^{-3} KOH solution [yellow '$Rh(OH)_3$'; λ = 418 nm], are: orange (436), brown (436, > 800), green (436, > 800, 525, 650), violet (532, 642), blue (616) and violet (530 nm on complete Cl_2 saturation). The colour of the final solution, **Y** varies depending upon factors including the pH of the medium: it is deep blue in base (typically λ = 616; ε = 1122) and violet in acid (typically λ = 530 nm, ε = 690 dm^3 mol^{-1} cm^{-1} per Rh). The colour of the solution thus depends upon the $H_2O:{}^-OH$ ligand ratio of the superoxo species, *i.e.* the degree of acidification caused by Cl_2 in water (see below). Indeed, superoxodirhodium(III,III) complexes have a strong electronic absorption in the region 500–630 nm depending upon the nature of the ligands. In the present case, addition of 3 mol dm^{-3} HCl, to make the conditions entirely acidic, produces a species that absorbs at a slightly higher energy (λ = 500 nm, ε = 483 dm^3 mol^{-1} cm^{-1} per Rh).

The ESR study of the preparation of **Y** (Fig. 1 and Table 1) reveals a complex series of dichlorine-dependent compositional changes. At least two independent paramagnetic species are probably generated, one not associated with a metal centre (causing signals in the free-spin region) and the other with resonances at low magnetic field reflecting involvement of one or more rhodium nuclei. The solution is ESR silent when all rhodium nuclei are transformed into the orange species (sample 4 in Fig. 1); λ = 430 nm was previously thought[9] to be indicative of monomeric rhodium(III) superoxide complexes (see later). Violet **Y**, produced by an excess of chlorine, also shows very few features in the ESR spectrum (reasons unknown), but isolation of its Ba^{2+} salt **Z** clearly distinguishes it from the barium salt of the orange species: the former has a very strong ESR signal (Fig. 2), whereas the latter exhibits only a broad, weak paramagnetic resonance.

The ESR spectrum of the solid **Z** formed on the addition of

---

† *Non-SI units employed:* G = 10^{-4} T, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

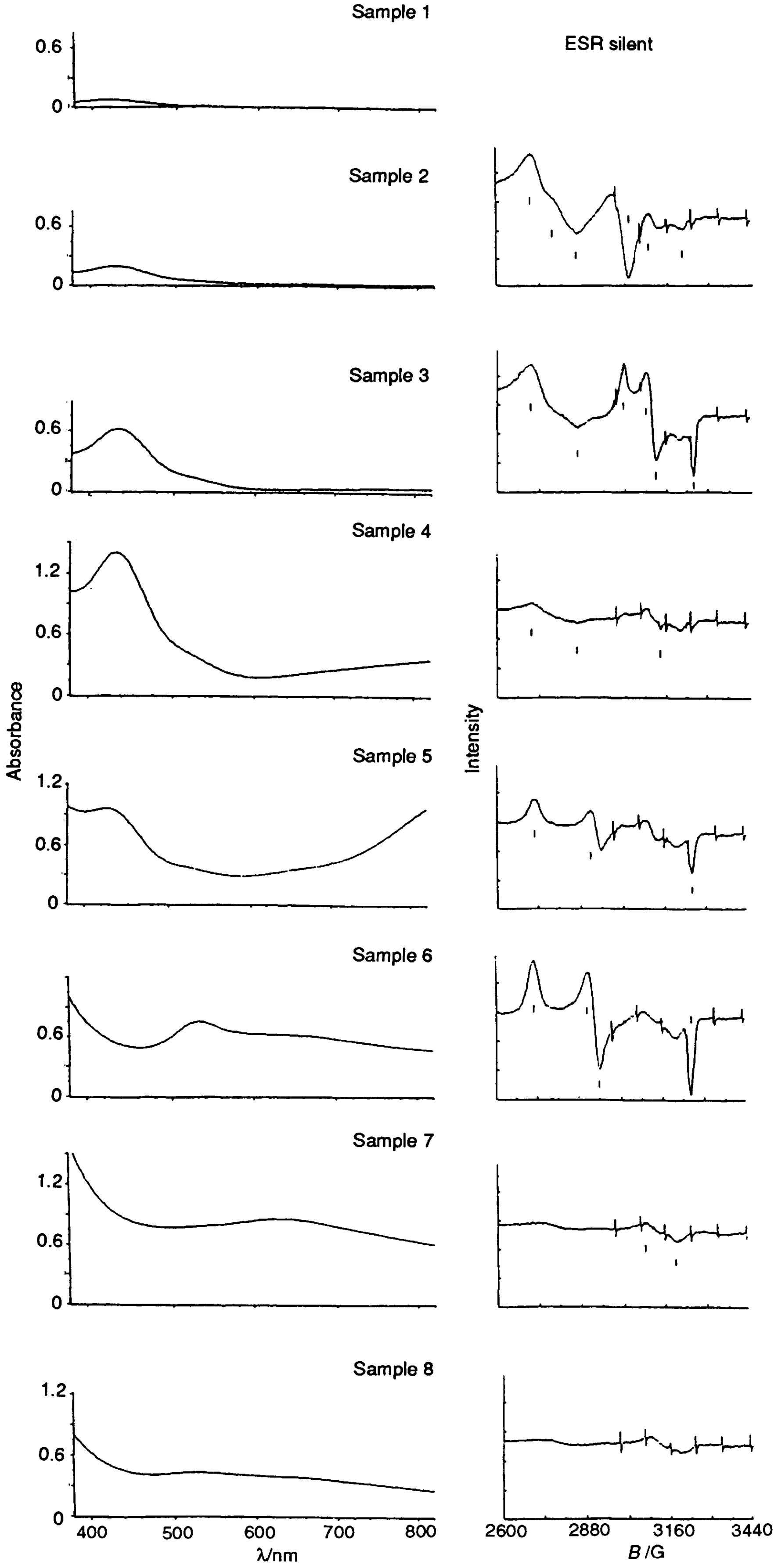


Fig. 1 Absorption (left) and ESR spectra (right) for selected samples from the action of dichlorine on 8 × 10^{-2} mol dm^{-3} $RhCl_3$ in 5 mol dm^{-3} KOH solution with time (cell length 0.1 cm, ESR measured at 77 K)

Table 1 Variation in g values as dichlorine is added to 8×10^{-2} mol dm^{-3} $RhCl_3$ in 5 mol dm^{-3} KOH solution, *i.e.* as **Y** forms

Sample	g^a	Comments^b
1	ESR silent	Yellow solution, no Cl_2 added
2	2.370, 2.306, 2.244, 2.119, 2.074, 2.000	ESR signal maximum
3	2.361, 2.237, 2.127, 2.073, 2.049, 1.972	
4	2.366, 2.208, 2.014 (almost ESR silent)	Orange colour maximum
5	2.350, 2.206, 1.971	Green
6	2.348, 2.202, 2.174, 1.971	Violet solution intermediate
7	2.076, 2.009 (almost ESR silent)	Blue solution **Y**
8	ESR very weak	Violet solution **Y**

^{a} Parameters relate to markers in samples featured in Fig. 1, from left of the figure (high g values) to right (low g values). ^{b} The colour descriptions are approximate; the electronic spectrum of the sample is in Fig. 1.

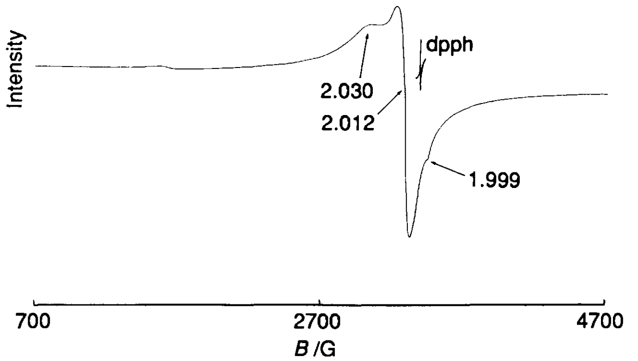


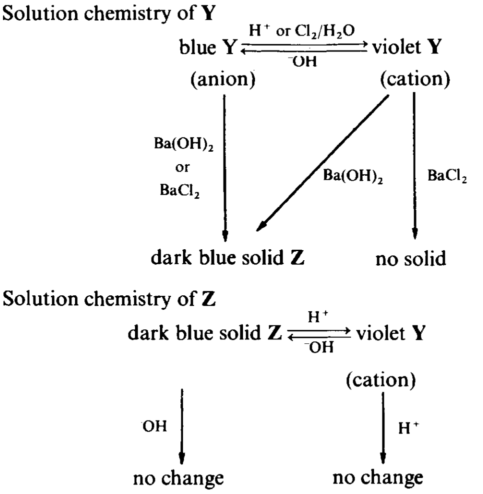
Fig. 2 The ESR spectrum of the barium salt of Claus' blue **Z** (g_z = 2.030, g_y = 2.012, g_x = 1.999 at 77 K); dpph = diphenylpicrylhydrazyl

barium hydroxide to (weakly paramagnetic) violet **Y** is featured in Fig. 2; it displays all the characteristics[10] of O_2^- in a non-axially symmetric environment, *i.e.* the Rh–O–O–Rh system is neither collinear nor coplanar.

(*b*) *Stability and* pH *Dependence of Claus' Blue Solution* **Y** *and its Barium Salt* **Z**.—The compound $Cs_2[RhCl_6]$ contains quadrivalent rhodium;[11,12] it decomposes readily in water. That in itself casts some doubt on the proposed much higher formal oxidation state (VI) of the metal in Claus' blue **Y** and its barium salt **Z**. The original formulation[7] of Claus' blue solution as containing the $[RhO_4]^{2-}$ ion seems to have rested on no more than the implicit analogy with the insolubility of other $BaXO_4$ (X = S or Cr). This hexavalent rhodium was believed[7,13] to be stable in all aqueous media with respect to reduction; $[Rh^{VI}O_4]^{2-}$ requires a reducing agent to bring out its oxidizing ability.

The isolation of dark blue solid **Z** from violet **Y** (λ = 530 nm) with $Ba(OH)_2$ solution is not mere precipitation, since the addition of $BaCl_2$ to a fully chlorinated (*i.e.* acidic) solution of Claus' blue has no effect on state or colour. However, subsequent treatment of *this* solution with ^-OH does precipitate **Z**. That is, neutralization of the acid gives an anion which *is* precipitated by Ba^{2+}. This equilibrium between an acidic cation and basic anion had been mistaken for redox dismutation by others, possibly by implicit analogy with genuine $[XO_4]^{n-}$ ions, with X being, for example, Mn or Ru [see section (*e*)].

The simple pH dependence of the coloured species is summarized in Scheme 1 and is consistent with the alkaline blue **Y** species being anionic and the acidic violet **Y** form cationic; this is confirmed using ion-exchange resins and electrophoresis. The reversible pH behaviour of **Y** can be followed spectrophotometrically. A distinct and rapid 'switch' of colour from violet **Y** to deep blue **Y** can be observed, even by eye, as the pH increases. The pH at which this change of colour occurs may be related to a pK_a value of 4.1, typical for simple acid–base equilibria involving water ligands. The complex $[Rh_2(OH)_2(H_2O)_n(\mu\text{-}O_2)]^{3+}$ is violet (λ = 420, 560 nm) in acid, but turns deep blue (λ = 455, 588 nm) at higher pH,[8] while chloride substitution in **X** causes a change from violet to blue (λ = 465, 602 nm) in $HClO_4$.[14] Moreover, the finding here and elsewhere[15] that violet solutions are not formed directly by the action of hypochlorite on acidic rhodium(III) solutions, only by the acidification of blue alkaline mixtures of rhodium and hypochlorite, suggests that ^-OH is important in the initial production of the coloured species.



Scheme 1 The pH behaviour of Claus' blue **Y** and its barium salt **Z**

Violet **Y** is stable in acid for periods > 6 months, but blue **Y** occasionally develops a flocculent precipitate on standing; this redissolves to produce violet **Y** in acid. No base, aprotic solvent, methanol or ethanol react with or solubilize **Z**. Dissolution of the barium salt of the orange species in $HClO_4$ gives a violet solution [λ = 380 (sh), 558 nm].

(*c*) *Spectroscopic Characteristics of the Superoxorhodium Species present in Claus' Blue* **Y**.—Both (violet) acidic and (blue) basic solutions of Claus' blue **Y** have broad absorption spectra indicating the presence of many species.[6] This is not surprising given: (*a*) the possible formation of a variety of unstable and strong oxidants (*e.g.* Cl$^{\bullet}$, HOCl and possibly transient Rh^{IV}) during the preparation of **Y**; (*b*) the gradual acidification of the initially basic medium by Cl_2 (aqua ligands in both reagents and products will show acid–base behaviour; hydroxide ligands may be terminal or bridging); (*c*) the synthesis of 'intermediates' that may themselves be relatively stable *e.g.* mono-, di- and polymeric peroxides and superoxides; and (*d*) the affinity of chloride (deriving from either the rhodium precursor or the oxidant) for rhodium.

The possible creation of fluxes of related species in the preparation of Claus' blue is supported by separation of violet **Y** into fractions using a cation-exchange resin. The visible absorption spectrum of one fraction closely resembles that of the pure **X** ion.[6] This is predictable: the rhodium precursor is 'rhodium(III) hydroxide' (formed by the action of $^-$OH on $RhCl_3$) and those species that do not undergo substitution by chloride during chlorination approach the form of **X** (see below).

Raman spectroscopy has been used in some instances (Table 2) to check for the presence of superoxide. The barium salt of the orange species is IR inactive and sample preparation, for Raman analysis, gives a violet superoxo complex in HCl with sharper (O–O) absorptions than those of an acidic solution of **Z**.

(*d*) *Voltammetric Properties*.—The voltammetric behaviour of the perchloric acid solution of solid **Z** is quite different from that known[19] for complex **X**. A reversible redox couple at $E° = 1.21$ V can be removed by repetitive cycling; 20 scans at 0.02 V s^{-1} suffice. This relates to chloride and the chlorine radical and is confirmed by: (*a*) the signal intensity increasing on the addition of Cl^- and (*b*) the cyclic voltammogram of HCl in 3 mol dm^{-3} $HClO_4$. Similarly, the O_2^-–O_2^{2-} couple is not observed for purified and characterized samples of $[Rh_2Cl_2(OH)_2(H_2O)_n(\mu\text{-}O_2)]^+$, which may be synthesized[14] from **X**.

(*e*) *Characterization of the Product of Chemical and Electrochemical Reduction*.—The $[Rh_2(\mu\text{-}O_2)]^{5+}$ moiety, stabilized within a framework of nitrogen-containing ligands, is known[3,20] to produce the peroxo analogue on reduction. Iodide is one useful agent. In view of this, and the importance of iodometry in previous choices of oxidation state for 'oxidized rhodium', those results and the analysis of the reduction product of Claus' blue were re-examined. Interpretations of iodometric results have conflicted: Ayres[15] assigned blue and purple rhodium solutions, resulting from oxidation of Rh^{III} by ClO^-, to pentavalent rhodium. However, Sarangiapani and Earley[13] proposed that the similar oxidation by hypobromite formed rhodium(V) in the blue solutions, but Rh^{VI} in the purple.

Reduction of solid **Z** (dissolved in acid) with I^- ions produces a yellow solution (λ = 282 nm). Similarly, the same species can be electrochemically generated by reduction at +0.4 V; the reduction in ESR signal intensity with time of electrochemical reduction is featured in Fig. 3. This electronic absorption at 282 nm could originate from either $[Rh(O_2)Rh]^{4+}$ or a rhodium oxide. Neither dichlorine nor cerium(IV) restores the violet colour. Further, a chemiluminescence test, which may be used[21] to detect O_2^{2-} in the presence of O_2^-, gives no indication of peroxide in the reduction product.

For several samples taken from one preparation of **Z** the measured oxidation equivalents varied. For a particular mass of **Z** more iodine was liberated as the time of contact with I^- increased. Ayres[15] noted similar anomalies in his careful work. The electron change per mole of rhodium was found to vary from 1 to 2.3 for purple solutions; the value was thought[15] to be solely dependent on the amount of alkali used in the initial hypochlorite oxidation (to produce the blue solution) prior to acidification. We attribute these observations to catalysis by trivalent rhodium(III) ions of the oxidation of I^-; similar behaviour has been noted[22] for Ir^{3+} ions.

Moreover, unlike most of the known μ-superoxo-dirhodium(III,III) complexes[3,20] (which are stabilized by nitrogen-containing ligands) reduction of the superoxide moiety in Claus' blue is accompanied by destruction of the dioxygen bridge. Complex **X** shows similar behaviour.[19] However, even some nitrogen-stabilized dirhodium peroxides are thought to generate their superoxide analogues *via* disproportionation.[3,20] Co-ordinated water may play a role in the decomposition; the ready availability of 'internal' protons may favour the formation of H_2O_2 from any peroxorhodium species realized, *via* a mechanism that is not possible for nitrogen-ligand analogues, such as the increased σ-donor nucleophilic characteristics in the peroxide group. Alternatively, the decay in the case of Claus' blue may be due to co-ordinated chloride; our voltammetric studies suggest that Cl^- may affect[14] the stability of the $[Rh_2(O_2)]^{5+}$–$[Rh_2(O_2)]^{4+}$ couple.

(*f*) *Chemical Relationship between Claus' Blue* **Y** *and* $[Rh_2(OH)_2(H_2O)_n(\mu\text{-}O_2)]^{3+}$ **X**.—(*i*) *Neutral species*. Preparations of **Y** probably pass through uncharged species: the HCl produced by Cl_2 in water neutralizes the alkaline media in which the rhodium-containing compounds are generated. The neutral complex is intermediate between the two extremes [equation (1)]. This description is based on the simplified

$$\underset{\text{(blue)}}{[Rh_2(OH)_n(\mu\text{-}O_2)]^{(n-5)+}} \underset{-\,nH^+}{\overset{+\,nH^+}{\rightleftharpoons}} \underset{\text{(violet)}}{[Rh_2(H_2O)_n(\mu\text{-}O_2)]^{5+}} \quad (1)$$

formula $[Rh_2(OH)_5(H_2O)_n(\mu\text{-}O_2)]$, but **Y** is in reality a mixture of several aquachlorohydroxo-complexes, each with individual values of pK_a. Solid neutral species $[Rh_2(OH)_{2+m}(H_2O)_{n-m}(O_2)]$ relating to blue solutions (λ = 455, 588 nm) form[5,8] from **X** by addition of base. No cations are present in the solids. The superoxide moiety remains in the neutral

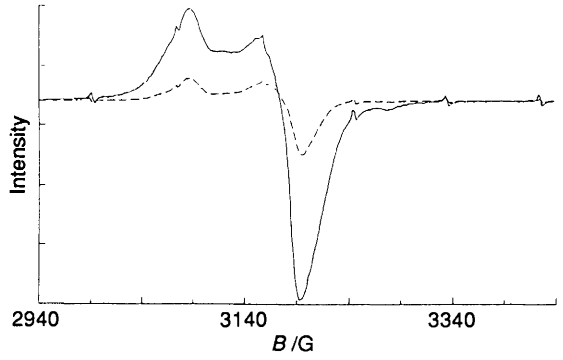


Fig. 3 The ESR spectra of Claus' blue **Z** in 3 mol dm^{-3} $HClO_4$ before (——) and after (- - - -) electrochemical reduction at +0.4 V *vs.* saturated calomel electrode (SCE) (0.4 cm^3 sample; 888 mC after 540 s); manganese(II) markers

Table 2 Selected Raman bands (cm^{-1}) for metal(III)–dioxygen complexes

Complex	Medium	ν(O–O)	Ref.
Claus' blue (violet **Y**)	1 mol dm^{-3} HCl	1088	*a*
$[Rh_2Cl_m(OH)_2(H_2O)_{n-m}(\mu\text{-}O_2)]^{(3-m)+}$ [b]	1 mol dm^{-3} HCl	1058	14
$[Rh_4(OH)_3(O_2CMe)_8(O_2)]\cdot 5H_2O$	Water	1040	8
$[Rh_4(OH)_2(O_2CCF_3)_9(O_2)]\cdot 8H_2O$	CF_3CO_2H	1068	8
$[Rh_2(en)_4Cl(NO_2)(\mu\text{-}O_2)]^{3+}$	Water	1050	9
$[Rh_2(\mu\text{-}OH)(py)_6(H_2O)_2(\mu\text{-}O_2)][ClO_4]_3$ [c]	*d*	833	16
$[Co_2(NH_3)_{10}(\mu\text{-}O_2)]Cl_5\cdot 4H_2O$	Solid	1122	17
$[Co_2(NH_3)_{10}(\mu\text{-}O_2)][NO_3]_4$ [c]	Water	800	18

[a] This work. [b] $m = 1$ or 2. [c] Peroxo compound. [d] Mulls in liquid paraffin and fluorinated oil.

precipitates from **X** and **Y**: $[Rh_2(OH)_{2+m}(H_2O)_{n-m}(\mu\text{-}O_2)]$ has[8] $g_{iso} = 2.04$ and a similar substance sometimes precipitates during preparations of Claus' blue when they are near neutrality. This is found to contain no Ba^{2+} ions and has a magnetic moment of 1.46 μ_B per rhodium.

(*ii*) *Characterization of superoxorhodium*(III) *chlorides synthesized from* $[Rh_2(OH)_2(H_2O)_n(\mu\text{-}O_2)]^{3+}$ **X**. The co-ordination of chloride to rhodium in Claus' blue solution can be simulated[14] for complex **X**. This affinity of rhodium for chloride precludes the replacement of co-ordinated halide by water ligands in Claus' blue; attempts to do this by refluxing in perchloric acid destroy the superoxo-moiety.

The substitution of chloride for water ligands in complex **X** can be monitored[14] by using the electronic absorption spectrum. In this study the complex containing two chloride ligands has absorptions at 386 (sh), 459 and 599 nm. The ESR spectrum of the product ($g_1 = 2.082$, $g_2 = 2.027$, $g_3 = 2.016$) clearly indicates the retention of the superoxo-moiety, *i.e.* the formula is of the type $[Rh_2Cl_2(OH)_2(H_2O)_{n-2}(\mu\text{-}O_2)]^+$.

(*iii*) *Characterization of superoxorhodium*(III) *carboxylates synthesized from Claus' blue*. The $[Rh(O_2)Rh]^{5+}$ core in Claus' blue can be utilized to form carboxylatorhodium(III) superoxides, a defined class of compound.[8] Previously generated by the action of RCO_2H (R = Me, $CHCl_2$ or CF_3) on $[Rh_2(OH)_{2+m}(H_2O)_{n-m}(\mu\text{-}O_2)]$ (itself formed from HO^- on **X**), superoxorhodium(III) carboxylates have[8] a strong absorption band at 568 nm, ESR parameters of $g_1 = 2.089$, $g_2 = 2.041$ and $g_3 = 1.993$, and a Raman-active O–O vibration at 1040 cm^{-1}.

The co-ordination of carboxylate groups to rhodium can be monitored using the electronic isotropic absorption or ESR spectrum.[8] Dissolution of solid **Z** in concentrated ethanoic acid results in a shift of the maximum at 532 to 556 nm over 48 h. The presence of such absorption around 550 nm acts as a fingerprint for rhodium(III) superoxides containing carboxylate: carboxylates of trivalent rhodium do not absorb in this region.[8] Removal of the excess of acid from this solution of **Z** gives a solid the ESR spectrum of which, in 3 mol dm^{-3} $HClO_4$ ($g_1 = 2.090$, $g_2 = 2.041$ and $g_3 = 1.996$; Fig. 4) is identical to that of the compound derived from **X**. Interestingly, this deep blue substance exhibits a small shoulder at $g = 2.018$, from unreacted Claus' blue. Reduction of the superoxo-moiety is achieved at +0.4 V, producing a yellow solution which cannot be reoxidized to superoxide, presumably because the O–O link is broken.

The solid carboxylate complex made from Claus' blue shows strong infrared absorption in the region between 3650 and 3050 cm^{-1}, very similar to that for co-ordinated water molecules. As in the case of $[Rh_2(OH)_{2+m}(H_2O)_{n-m}(\mu\text{-}O_2)]$ with ethanoic acid, a strong doublet is observed in the $\nu_{asym}(CO_2)$ region (1564 and 1558 cm^{-1}) and a strong singlet in the $\nu_{sym}(CO_2)$ region (1418 cm^{-1}). The value of $\Delta\nu[\nu_{asym}(CO_2) - \nu_{sym}(CO_2)]$ is 140 cm^{-1} and indicates[23] bridging (rather than uni- or bidentate) co-ordination of carboxylate in the complex derived from **Z**. This value compares favourably with carboxylates obtained from **X** ($\Delta\nu$ = 100–150 cm^{-1}),[8] and to the value for $[Rh_2(O_2CMe)_2(CO)_3(PPh_2)]$, known to contain acetate groups only as bridges.

Finally, the carboxylato-complex arising from Claus' blue has a formal cyclic voltammetry (CV) potential $E° = 1.21$ V *vs.* SCE, which is similar to that of Claus' blue; this is assigned to co-ordinated chloride ligands. It is likely that the tendency of carboxylate to replace a ligand *trans* to the O_2^- moiety is much reduced when compared to the *cis* position, which permits bridging; whether carboxylate is able to displace chloride at all is open to debate.

(*g*) *Mechanism of Formation of Claus' Blue*.—The synthesis of Claus' blue, in the absence of oxygen, by passing dichlorine through an alkaline solution of rhodium(III), represents an unusual formation of an O–O link in the aqueous medium. The colour of Claus' blue solutions and its rate of production depends upon the concentration of hydroxide. Moreover, as O_2 is not a precursor, it appears that the dioxygen link comes from the oxidation of ^-OH. The combination of two resultant hydroxyl radicals would generate peroxide, which may readily be oxidized to superoxide.

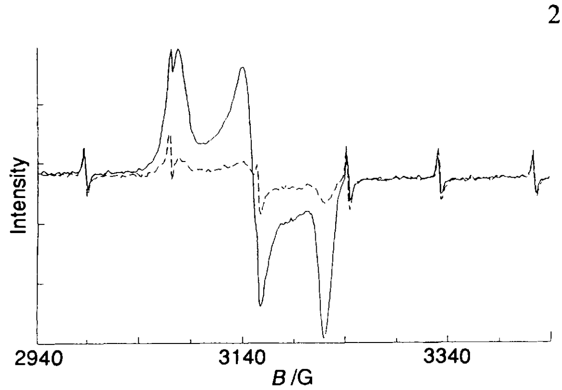


Fig. 4 The ESR spectra (77 K) of the superoxorhodium(III) carboxylate solid formed from Claus' blue **Z** dissolved in 3 mol dm^{-3} $HClO_4$ before (——) and after (– – – –) electrochemical reduction at +0.4 V *vs.* SCE (0.3 cm^3; 22 mC after 60 s); manganese(II) markers

Two possible mechanisms may govern the generation of the peroxide moiety: (*a*) 'free' peroxide might be formed independently of the metal centre, and then interact with rhodium leading to a rhodium peroxide species, which would be oxidized to yield superoxorhodium complexes; (*b*) two hydroxide ligands may be oxidized and couple forming peroxide, again oxidizable to superoxide. We favour the latter mechanism for two reasons. First, there is no evidence in homogeneous aqueous solution that dichlorine or its derivatives (hypochlorite and the like) generate dioxygen species, though the interaction of hypochlorite with pre-existing peroxide is well known to form dioxygen in reactive excited states. However, it must be said that catalysis of such homogeneous reactions by rhodium complex ions is certainly conceivable. Secondly, while peroxorhodium(III) ammine complexes have been deliberately prepared[20] by substitution of external ('free') hydrogen peroxide into the co-ordination sphere, such reactions not only require a gross excess of peroxide but are very slow[24] and show relatively poor yields.[20,24]

Indeed, the experimental evidence supports the coupling of oxidized hydroxide ligands. The electronic absorption and ESR spectra of the preparation are shown in Fig. 1; the spectroscopic signals are complicated, but some features of the synthesis can be established. The mechanism must take the following into account: (*i*) the (extreme) oxidizing conditions; (*ii*) the gradual acidification (Cl_2 in water) of an initially basic medium; (*iii*) the presence of paramagnetic species from the first addition of dichlorine; (*iv*) the ESR spectrum shows signals both close to 'spin-only' values, g_e, and remote from them; (*v*) an (orange) *diamagnetic* intermediate; and (*vi*) no appreciable shift in the electronic spectrum prior to production of the diamagnetic species.

Orange-yellow peroxodirhodium(III,III) species are well documented.[16,20,24] The crystal structure of diamagnetic, orange $[\{Rh(py)_3(H_2O)\}_2(\mu\text{-}OH)(\mu\text{-}O_2)][ClO_4]_3\cdot 2H_2O$ (py = pyridine) is known.[16] This complex can be oxidized with 1 equivalent of cerium(IV) sulfate per dimer to give[16] the superoxide analogue (λ = 600 nm, $g_1 = 2.094$, $g_2 = 2.025$, $g_3 = 2.004$ in pyridine solution); the barium salt of the orange species deriving from Claus' blue preparation is readily transformed by $HClO_4$ to yield the paramagnetic violet solution **Y** and signifies the *relative* instability (in the aqueous medium) of the peroxo- compared to the superoxo-form with predominantly oxygen-containing ligands. The diamagnetic intermediate (λ = 436 nm) in the preparation of Claus' blue may be thought of as typical of such orange species. Some other orange compounds have previously been seen in systems like the present, which have been described as monomeric superoxides, containing the $Rh^{III}(O_2^-)$ unit. Examples include[9] $[Rh(en)_2Cl(O_2)]^+$ (en = ethane-

1,2-diamine) with $\lambda = 485$ nm, $g_{iso} = 2.033$ and strong Raman bands at 1050 and 1080 cm^{-1}. The possibility that these were, in fact, orange samples of salts of bridged peroxodirhodium(III,III) ions contaminated with traces of bridged superoxodirhodium(III,III) ions requires evaluation. In the present work we have obtained superior ESR spectra from such diamagnetic host lattices with a paramagnetic 'doped' superoxide.

Our ignorance of speciation in alkaline solutions containing rhodium(III) complicates exegesis. For simplicity of discussion, we take them to contain '$[Rh(OH)_6]^{3-}$'. It appears that direct oxidation of the ligand occurs *i.e.* to '$[(HO)_5Rh^{III}(^{\bullet}OH)]^{2-}$' {with its canonical form '$[Rh^{IV}(OH)_6]^{2-}$'}. A peroxo-bridged dirhodium(III,III) species, $[Rh^{III}(O{-}O)Rh^{III}]^{4+}$ (proton abstraction by base), can be formulated as in Scheme 2. The vibrational spectrum of the orange solid is inconsistent with a monomeric peroxide, resulting from the oxidation of two hydroxides co-ordinated to the same trivalent metal centre.

The free-spin signals observed before diamagnetic complex formation probably come from a small amount of peroxide being oxidized; the basic conditions generally favour the immediate reduction of O_2^-. Once all dimeric peroxide has formed, subsequent electron loss from the peroxo-bridge can begin in earnest; the increasing acidity (from Cl_2 in water) begins to support peroxide oxidation and possibly even quadrivalent rhodium production, which could complicate the ESR spectrum. Thereafter the limited variation in the visible spectrum after the decay of the band at > 800 nm indicates that protonation and deprotonation of water ligands and any ligand substitution at the metal take place independently of the superoxo-moiety, which is preserved.

Eventually, a $[Rh^{III}(O_2)Rh^{III}]^{5+}$ core results. The combination of various ligands and the possibility of polymers forming makes more detailed clarification difficult at this stage. Indeed, the source of the ESR signal at $g > 2.2$ is, as yet, unknown: it may come from transient amounts of Rh^{II}, Rh^{IV} or the immediate environment (symmetry) of the superoxide moiety.

Conclusion

Claus' blue **Y**, the blue-violet product of the reaction of dichlorine with alkaline rhodium(III) solutions, contains superoxodirhodium(III,III) complexes, $[Rh^{III}(O_2)Rh^{III}]^{5+}$, and not hexavalent rhodium, $[RhO_4]^{2-}$, as previously formulated. It forms equally well in the absence of dioxygen: the O–O link derives from the oxidation of co-ordinated hydroxide. In the first instance an orange peroxodirhodium(III,III) species results, which is then oxidized to the blue-violet species.

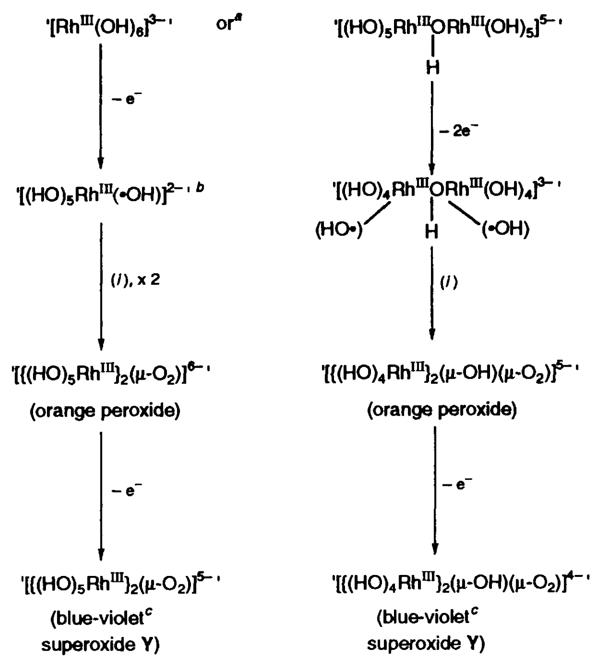
The presence of the superoxo-moiety in **Y** is confirmed by ESR and Raman measurements; X-ray photoelectron spectroscopy and the stability of the complex in solution contrast with those of Rh^{IV} and indicate[11,12] that trivalent rhodium only is present in **Y**.

Solution **Y** consists of a mixture of species. Most resemble the characterized ion $[Rh_2(OH)_2(H_2O)_n(\mu\text{-}O_2)]^{3+}$ **X**; the various ligands attached to the superoxodirhodium(III,III) core derive from the solvent, oxidant and rhodium precursor. Owing to its water ligands, Claus' blue has marked pH dependence: it is blue and anionic in base, but violet and cationic in acid. The addition of barium ions to the anion gives a solid **Z**, which redissolves in acids giving violet solutions extremely similar to those of the known superoxide **X**.

As with complex **X**, the $[Rh(O_2)Rh]^{5+}$ core in **Y** has not been reduced to a stable peroxide form, but can be utilized to form defined carboxylatorhodium(III) superoxide complexes.

Experimental

Ultraviolet and visible spectra were recorded with quartz cells using either a Hewlett-Packard 8452A diode-array spectrophotometer or a Uvikon 930 spectrophotometer. The ESR spectra were measured on ESR-Radiopan (Poland) or Bruker 300E spectrometers at 77 K. Calibration of the magnetic field was achieved using diphenylpicrylhydrazyl (dpph) or manganese(II) markers. Measurements of magnetic susceptibility were performed using a Johnson Matthey MSB1 balance at ambient temperature. Corrections for the diamagnetism of constituent atoms used Pascal's constants. Infrared spectra were recorded on a Nicolet 510 FTIR or a Specord M-80 spectrometer over the range 400–4000 cm^{-1} using pressed KBr discs or Nujol mulls. For the region 400–200 cm^{-1} a Perkin-Elmer 783 spectrometer was employed, using CsI plates and Nujol. Raman spectra were recorded on a JEOL JRS-S1 laser Raman spectrometer equipped with rotary sample cells, using 488 nm excitation.



Scheme 2 Proposed mechanism for superoxorhodium(III) complex formation in Claus' blue **Y**. (*i*) Proton abstraction by base. [a] The structure of rhodium trichloride in strong alkali is unknown. The precursor to oxidation may be mono- or di-meric (possibly with two hydroxo-bridges), and may initially contain co-ordinated chloride or water as well as hydroxide. Here, the most simple case of a mono- and di-meric precursor is illustrated. [b] This is a canonical form of '$[Rh^{IV}(OH)_6]^{2-}$'. See text. [c] The final product in pH < 7 (*i.e.* Cl_2 in water) almost certainly has co-ordinated chloride and water, and may possibly contain hydroxide ligands; colour depends on the degree of chlorination (*i.e.* acidification)

Voltammetric studies were performed on EG & G Princeton Applied Research potentiostat/galvanostat associated with an IBM PS/2 computer. The voltammetric cell was a closed 'jacketed' vessel (with thermostatted water flow), which was provided with a planar platinum working electrode, Luggin capillary, salt bridge, reference (Hg_2Cl_2–Hg, saturated NaCl) electrode, platinum spiral auxiliary electrode, a side-arm for introducing the test solution and a glass tube for gas inlet and outlet. Controlled-potential coulometric measurements were carried out with a Radelkis OH 404A potentiostat associated with an OH 404C digital integrator unit. Bulk electrolyses were performed in a 50 cm^3 cell and in a microcell (0.5 cm^3 sample). The 50 cm^3 cell permitted both coulometric and polarographic studies to be made in the same cell. In both cells (macro and micro) the cathodic and anodic compartments were separated by a fine-porosity frit. The working electrode was a platinum gauze, the auxiliary electrode a platinum spiral and the reference a saturated calomel electrode (SCE) with a fine salt bridge. The anodic and cathodic compartments of both cells were provided with a glass tube for argon inlet and outlet and a side-arm for transferring the sample solution by argon pressure into a deoxygenated ESR capillary or UV/VIS cell. Thus, the progress of the electrolysis could be monitored coulometrically, voltammetrically or by ESR and electronic spectroscopy.

The hydrogen-ion concentration was determined using a Radiometer pHM85 electrode after calibration with standard buffer solutions.

Reagents were of standard grade (BDH); analytical grade reagents were used for quantitative work (BDH, Aldrich). The complex $[Cr(H_2O)_6][ClO_4]_3$ was supplied by Fluka. 'Rhodium trichloride', of approximate composition $RhCl_3\cdot3H_2O$, was obtained from Johnson Matthey. Dowex 50W-X2 (H+) and Amberlite IRA-420 (Cl^-) exchange resins were from BDH. Distilled water was used in all aqueous reactions. Gases were supplied by B.O.C.: nitrogen was of 'white spot' grade and O_2 of 'research grade'.

Claus' Blue Solution **Y** *and its Barium Salt* **Z**.—Concentrations of rhodium(III) trichloride and base were varied for different experiments. A typical bulk preparation of **Y** and **Z** was as follows: $RhCl_3\cdot3H_2O$ (1.054 g, 4.0 mmol) was placed into a quickfit flask (1 l, with a side-arm tap attached to a bubbler) with a magnetic follower. Water (100 cm^3) was added with stirring: when all solid had dissolved, 1 mol dm^{-3} KOH (100 cm^3, 0.1 mol) was added, the flask sealed (septum) and the mixture stirred. A clear yellow solution (λ = *ca.* 418 nm) developed: we refer to this in the text, without prejudice to its true nature, as containing '$[Rh(OH)_6]^{3-}$'. Dichlorine was slowly passed into the solution by means of a Teflon needle (with the side-arm tap open) until a deep violet solution **Y** (λ = *ca.* 530 nm) developed.

The addition of an excess of saturated barium hydroxide solution to the violet solution, under CO_2-free conditions, was achieved using a positive pressure of nitrogen to transfer the barium solution from one sealed flask (septum) to the sealed solution of **Y** *via* a Teflon cannula fitted with a filter [to remove solid $Ba(OH)_2$ and $BaCO_3$]; at this point, the side-arm tap was open. When the volume of fluid within the litre flask had reached about 800 cm^3 the side-arm tap was closed and the Teflon cannula removed. The mixture was then allowed to stand for 1 d to settle. Supernatant was removed using a positive pressure of N_2 and cannula, taking care not to disturb the dark blue solid. The remaining solution and flocculent precipitate was then filtered using a no. 5 sinter (and standard buchner funnel under vacuum) fitted with a septum, *i.e.* the solution and solid could be transferred from the flask to the sinter by cannula under dinitrogen pressure and filtered without exposure to the atmosphere. However, to ensure that the pressure above the sinter was sufficient to permit 'normal' filtration (and to ensure that no CO_2 was present during the filtration), a second supply of N_2 was passed over the sinter before and during filtration *via* two (inlet and outlet) Teflon needles. The barium salt (**Z**) was washed with a little water and dried over P_2O_5 at atmospheric pressure.

Combined electronic and ESR spectra were recorded using $RhCl_3\cdot3H_2O$ (1.057 g, 4.01 mmol) in water (50 cm^3); KOH pellets (14.010 g, 0.25 mol) were added and mixed to give a yellow solution (λ = 418 nm). Dichlorine was slowly passed into the solution and, at desired intervals, a sample removed and its ESR and electronic spectrum recorded (*cf.* Fig. 1), after which the samples were returned to the bulk mixture for further chlorination.

Solutions of fully chlorinated Claus' blue, after degassing under vacuum (to remove the excess of Cl_2), with (λ = 616 nm) or without (λ = 530 nm) the addition of a few drops of 10 mol dm^{-3} NaOH, were placed onto exchange columns containing anion or cation resin prewashed with water. The movement of the coloured species with increasing molarity (0.1–7 mol dm^{-3}) of NaOH or $HClO_4$ solutions was observed.

For paper electrophoresis, (*a*) violet **Y**, (*b*) blue **Y**, (*c*) a 1 mol dm^{-3} HCl solution of **Z** and (*d*) 0.05 mol dm^{-3} $KMnO_4$ solution (as a reference) were placed across the centre in a line, 'spotted' equidistant from one another (*ca.* 2 cm) using a Pasteur pipette and dried using a hot-air blower. The process was repeated until a small, concentrated spot of compound was formed. The paper was soaked with electrolyte (water) for 250 min.

Spectrophotometric pH titrations were performed as follows: a solution (50 cm^3) of (fully chlorinated) violet **Y** was degassed under vacuum to remove dissolved Cl_2, then vigorously saturated with N_2 for 10 min. The electronic spectrum and pH were recorded. The stirred solution was titrated (microburette) with 10 mol dm^{-3} KOH (to avoid dilution effects); after each addition the pH was noted, the spectrum recorded and the spectroscopic sample returned to the bulk mixture. The volume of alkali added was plotted against the pH recorded for different wavelengths.

Orange Peroxo-precursor to Claus' Blue **Y**.—The electronic spectrum was monitored during the slow chlorination of basic solutions made from rhodium(III) chloride (see above). When the peak at *ca.* 430 nm was at its maximum (for the particular concentrations of reactants), saturated barium hydroxide solution was added. The orange-brown solid was collected (no. 5 sinter), washed with water and dried over phosphorus pentaoxide at atmospheric pressure.

$[Rh_2(OH)_2(H_2O)_n(\mu\text{-}O_2)]^{3+}$ **X**.—This was prepared using the method described by Moszner and Ziolkowski.[5]

$[Rh_2Cl_2(OH)_2(H_2O)_{n-2}(\mu\text{-}O_2)]^+$.—This compound was prepared from **X**, as outlined elsewhere.[14] Typically, [**X**] = *ca.* 9.5×10^{-3} mol dm^{-3} and KCl was used as the source of Cl^-. After standing for 5 d, K^+ in the deep blue mixture was removed as $KClO_4$ by filtration and the filtrate loaded onto a column containing Dowex 50W-X2 (200–400 mesh) exchange resin. Chloride ions were removed by washing the column with water (using $AgNO_3$ solution to monitor the eluate) and the adsorbed cation was eluted by 3 mol dm^{-3} $HClO_4$.

Superoxorhodium(III) *Carboxylates*.—Based on the method described by Moszner and Ziolkowski,[8] these were formed by dissolution of complex **Z** (0.03 g, *ca.* 4.5×10^{-5} mol based on $Ba_2[\{Rh(OH)_4\}_2(\mu\text{-}OH)(\mu\text{-}O_2)]$ in concentrated ethanoic acid (*ca.* 5 cm^3); the ESR and absorption spectra of the stirred solution were monitored over 24 h. A solid was obtained by removing unreacted acid by evaporation under reduced pressure (rotary pump), monitored by IR spectroscopy (KBr disc). The black solid was dried over KOH pellets.

Acknowledgements

We acknowledge financial support from the SERC in the form of a research studentship (to I. J. E.) and a grant for visits (I. J. E. and R. D. G.) to Wroclaw. We have had helpful advice from Professor W. P. Griffith (Imperial College) and from Dr. J. P. Maher (University of Bristol) on aspects of spectroscopy.

References

1 R. W. Hay, *Bio-inorganic Chemistry*, Ellis-Horwood, Chichester, 1984, p. 103; H. A. O. Hill, in *New Trends in Bio-inorganic Chemistry*, eds. R. J. P. Williams and J. J. R. F. da Silva, Academic Press, New York, 1978, p. 173.
2 D. A. Buckingham and C. R. Clark, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, p. 636.
3 A. W. Addison and R. D. Gillard, *J. Chem. Soc. A*, 1970, 2523.
4 P. S. Sheridan, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, p. 901.
5 M. Moszner and J. J. Ziolkowski, *Inorg. Chim. Acta*, 1988, **145**, 299.
6 I. J. Ellison and R. D. Gillard, *J. Chem. Soc., Chem. Commun.*, 1992, 851.
7 C. Claus, *Petersb. Akad. Bull.*, 1860, **2**, 177.
8 M. Moszner and J. J. Ziolkowski, *J. Coord. Chem.*, 1992, **25**, 255.
9 R. D. Gillard, J. D. Pedrosa de Jesus and L. R. H. Tipping, *J. Chem.*

Soc., Chem. Commun., 1977, 58; J. B. Raynor, R. D. Gillard and J. D. Pedrosa de Jesus, *J. Chem. Soc., Dalton Trans.*, 1982, 1165; R. D. Gillard and J. D. Pedrosa de Jesus, *J. Chem. Soc., Dalton Trans.*, 1984, 1895.

10 N. S. A. Edwards, I. J. Ellison, R. D. Gillard, B. Mile and J. P. Maher, *Polyhedron,* 1993, **12**, 371.

11 I. J. Ellison, Ph.D. Thesis, University of Wales, Cardiff, 1993.

12 A. N. Buckley, J. A. Busby, I. J. Ellison and R. D. Gillard, *Polyhedron*, 1993, **12**, 247.

13 S. Sarangiapani and J. E. Earley, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2991.

14 M. Moszner and J. J. Ziolkowski, *Transition Met. Chem.*, 1993, **18**, 248.

15 G. H. Ayres, *Anal. Chem.*, 1953, **25**, 1622.

16 I. B. Baranovskii, A. N. Zhilyaev, L. M. Dikareva and A. V. Rotov, *Russ. J. Inorg. Chem.*, 1986, **31**, 1661.

17 T. Shibahara, *J. Chem. Soc., Chem. Commun.*, 1973, 864.

18 T. B. Freedman, G. N. Yoshida and T. M. Loehr, *J. Chem. Soc., Chem. Commun.*, 1974, 1016.

19 M. Moszner, M. Wilgocki and J. J. Ziolkowski, *J. Coord. Chem.*, 1989, **20**, 219.

20 J. Springborg and M. Zehnder, *Helv. Chim. Acta*, 1984, **67**, 2218.

21 R. D. Gillard and A. Spencer, *J. Chem. Soc. A*, 1970, 1761.

22 S. I. Ginzburg and M. I. Yuz'ko, *Russ. J. Inorg. Chem.*, 1965, **10**, 444.

23 K. Nakamoto, *Infra-red and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.

24 J. Springborg and M. Zehnder, *Acta Chem. Scand., Ser. A*, 1987, **41**, 484.

Received 31*st March* 1994; *Paper* 4/01956C