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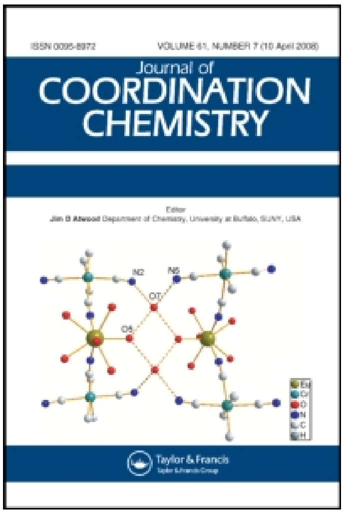

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SYNTHESIS AND CHARACTERIZATION OF SUPEROXO RHODIUM(III) CARBOXYLATES

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Treatment of an aqueous $HClO_4$ solution of $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{+2}$ (I) with OH^- yields at pH *ca* 6 a dark, greenish-blue, gel assumed to be $[Rh_2(O_2^-)(OH)_{2+m}(H_2O)_{n-m}]$ (II). Reactions of (II) and RCO_2H gave three new superoxo rhodium(III) carboxylates, which on the basis of electronic, IR, ESR and Raman evidence, elemental analysis, redox equivalent determination and magnetic susceptibility measurements have been formulated as $[Rh_4(O_2^-)(OH)_m(RCO_2)_n \cdot xH_2O]$ [R = CH_3 (III), $CHCl_2$ (IV), n = 8, m = 3; R = CF_3 (V), n = 9, m = 2].

Keywords: Rhodium(III) complexes, carboxylate, superoxide

INTRODUCTION

There is much interest in the chemistry of transition metal complexes containing activated dioxygen. Peroxo and superoxo compounds are of great interest because of their relevance as potential model systems for the superoxide dismutase enzymes, which in organic tissues, catalyze the disproportionation of O_2^-.[1] No less important is their possible application as catalysts for the mild and selective oxygenation of organic substrates.[2]

Though paramagnetic dioxygen complexes of cobalt(III) are numerous and well established,[3,4] the corresponding paramagnetic complexes of rhodium(III) are comparatively rare.[5,6] Peroxo and superoxo complexes are very often synthezised by oxidative addition of dioxygen to low valent metal compounds.[6-9] An alternative method is the application of a rhodium(III) complex as a precursor in a substitution with H_2O_2 or HO_2^-.[10]

The $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{+3}$ cation, the product of oxidative addition of dioxygen to the $[Rh_2(H_2O)_{10}]^{+4}$ dimer was separated by us and examined in aqueous perchloric acid.[6,11] Attempts at its isolation as a solid have failed thus far, but the water molecules coordinated to the $[Rh_2(O_2^-)]^{+5}$ unit were found to undergo substitution relatively easily. The subject of this paper is the reaction of (I) with hydroxide ions and carboxylic acids. We report for the first time the synthesis and characterization of superoxo rhodium(III) carboxylates.

EXPERIMENTAL

Electronic spectra were recorded in quartz cells with a Specord M-40 spectrophotometer. Infrared spectra were measured in KBr discs or Nujol mulls on a

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Specord M-80 spectrometer over a range of 400–4000 cm^{-1}. ESR spectra were monitored for solutions and solids on a Jeol JS 3X spectrometer. Raman spectra were recorded on a Jeol JRS-S1 laser Raman spectrometer equipped with rotating sample cells, with 488 nm excitation. Molecular weight was measured by the vapour pressure method in $CHCl_3$ on a Perkin Elmer 115 molecular weight apparatus and pH measurements were performed using a Radelkis OP-211 pH meter with a glass/SCE(NaCl) (Radelkis) combined electrode.

Magnetic susceptibility measurements were performed by the Gouy method in the range 77–298K. The magnetic moments were calculated from the equation $\mu_{ef} = 2.828(\kappa_M \cdot T)^{1/2}$, where κ_M was corrected for diamagnetism of constituent atoms by the use of Pascal's constants.

Rhodium was analysed by the AAS method using a Perkin Elmer 1100 spectrometer. All starting materials were commercially available and of reagent grade purity. Organic solvents were purified by known methods prior to use. Water used as solvent was redistilled from alkaline potassium permanganate in an all-glass still. Argon and/or nitrogen were used to maintain an inert atmosphere.

The $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{+3}$ cation was prepared and standardized as previously described.[6] Concentrated NaOH, CO_3^{-2}/HCO_3^--free solution was prepared by a published method.[12] It was diluted to concentrations 3–0.1 M with water free of CO_2 by boiling under an Ar atmosphere and standardized by acid-base titration.

Titration of $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{+3}$ (I) *with* OH^-

Treatment of (I) with aqueous solutions of NaOH and/or NH_4OH was carried out under Ar and/or N_2 atmosphere, at 263–273K. To *ca* 1×10^{-2}–1×10^{-3} mol dm^{-3} aqueous solution of (I) in 3 mol dm^{-3} $HClO_4$, hydroxide was added with vigorous stirring. The reaction was monitored by following pH and changes in electronic spectra in the range 30000–11000 cm^{-1}.

Reactions of (I) *with* RCO_2H $(R = CH_3, CHCl_2, CF_3)$.

Reactions between (I) and RCO_2H were studied at room temperature, as follows. To an aqueous solution of (I) in 3 mol dm^{-3} $HClO_4$ more than a 10-fold excess of neat RCO_2H was added [final concentration of (I) = 4×10^{-3}–5×10^{-3} mol dm^{-3}, RCO_2H = 4–5 mol dm^{-3}]. The reaction was followed by measuring changes in electronic spectra in the range 30000–11000 cm^{-1} with time and ESR spectra.

Synthesis of $[Rh_4(O_2^-)(OH)_3(CH_3CO_2)_8 \cdot 5H_2O]$ (III)

A solution of (I) (0.6 mmol, 1.2 mmol of Rh) in 3 mol dm^{-3} $HClO_4$ was cooled in an ice/NaCl bath to *ca* 263K and aqueous ammonia added with stirring until a greenish-blue precipitate ceased to appear. This solid was collected by filtration and then copiously washed with water until the washings were free from ammonia and perchlorate ion. An aqueous suspension (5 cm^3 of this precipitate was treated with excess acetic acid (10 cm^3), with stirring. The mixture was left to stand at room temperature for *ca* 40 h. Unreacted acetic acid was removed by evaporation under reduced pressure and the dry residue was dissolved in a minimum of methanol. Addition of heptane–diethyl ether (1 : 20 v/v, *ca* 100 cm^3) led to the separation of a dark-blue solid which was filtered off, washed with heptane and dried *in vacuo*. Yield 0.2 g (64% per Rh used). Complex (III) is soluble in water, methanol, ethanol and acetone, sparingly so in chloroform and insoluble in hexane and heptane.

Determination of the Redox Equivalent of (III)

To (III) (5.97 mg) dissolved in deaerated (Ar, N_2) 2 mol dm^{-3} $HClO_4$ (10 cm^3), sodium iodide was added in a 10-fold excess. The solution was kept in the dark for 20 min. Titration of liberated iodine (extracted with 5 cm^3 CCl_4) required 16 cm^3 of 1×10^{-3} mol dm^{-3} $Na_2S_2O_3$, thus giving an equivalent weight of 372 (calc. 352). The redox equivalent value was estimated for several independent titrations.

Synthesis of $[Rh_4(O_2^-)(OH)_3(CHCl_2CO_2)_8 \cdot 11H_2O]$ (IV)

To an aqueous suspension of greenish-blue product obtained from (I) (0.6 mmol) as described above, $CHCl_2CO_2H$ (4 cm^3) was added with stirring. After 48 h, excess of $CHCl_2CO_2H$ was removed on a vacuum line to give a thick, dark, syrupy liquid. Addition of hexane gave the complex as an oil. The solvent, still containing a certain amount of product was decanted off and the oily residue further washed with hexane to remove any remaining $CHCl_2CO_2H$. A minimum amount of Et_2O was then added to the oil to dissolve it. Addition of excess hexane to the ether solution resulted in the precipitation of a dark-blue solid, which after filtration and washing with hexane was dried *in vacuo*. Further crops of this product could be obtained upon concentration of the mother liquor using the above procedure. Yield 0.6 g (60%). Complex (IV) is soluble in methanol, ethanol, diethyl ether, acetone and chloroform but insoluble in water, heptane and hexane. Iodometric determination for (IV) was unsatisfactory because of the insolubility of (IV) in water (obscured end point).

Synthesis of $[Rh_4(O_2^-)(OH)_2(CF_3CO_2)_9 \cdot 8H_2O]$ (V)

The greenish-blue product from (I) (0.6 mmol) was obtained as described for the synthesis of (III). An aqueous suspension of this product (5 cm^3) with CF_3CO_2H (4 cm^3) was allowed to stand for 24 h. After the excess CF_3CO_2H evaporated, the crude solid was dissolved in the minimum amount of Et_2O. Addition of excess hexane resulted in the separation of a dark violet powder, which was filtered off, washed with hexane and dried *in vacuo*. Yield 0.34 g (70%). Complex (V) is soluble in methanol, ethanol, Et_2O and acetone, sparingly so in water and chloroform, but insoluble in hexane and heptane.

Determination of the Redox Equivalent of (V)

To (V) (2.02 mg) dissolved in deaerated (Ar, N_2) 2 mol dm^{-3} $HClO_4$ (20 cm^3), sodium iodide was added in a 10-fold excess. The solution was kept in the dark for 20 min. Titration of liberated iodine (extracted with 5 cm^3 of CCl_4) required 3.8 cm^3 of 1×10^{-3} mol dm^{-3} $Na_2S_2O_3$ thus giving an equivalent weight of 532 (calc. 546).

RESULTS AND DISCUSSION

Reactions of $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{+3}$ (I) *with OH.*

Treatment of (I) dissolved in 3 mol dm^{-3} $HClO_4$ at *ca* 273K with aqueous ammonia results in a change of colour with increasing pH. At pH 5.2–5.6 the blue-violet solution of (I) turns deep blue. Bands at λ_{max} 28000sh, 23880 ($\varepsilon = 280$ M^{-1}cm^{-1}), and 17880 cm^{-1} ($\varepsilon = 534$ for the starting material shift to λ_{max} 22000, 17000sh, and

14500 cm^{-1}. At pH 5.8–6 a dark, greenish-blue solid precipitates. The dried product shows in the IR strong bands at 540 [ρ_w(HOH)], 1620 [δ(HOH)] and a doublet at 3200–3400 cm^{-1} [ν(OH)].[13] The solid, when dry but fresh, dissolves readily in mineral acids, less so in organic acids and sparingly in bases. After dissolution in 3 mol dm^{-3} $HClO_4$, the electronic spectrum of (I) is reproduced. It is ESR active; at liquid nitrogen temperature it displays a single line at g = 2.04 and is considered to be $[Rh_2(O_2^-)(OH)_{2+m}(H_2O)_{n-m}]$ (II) [at room temperature, a single line centred at g = 2.0414 is observed for (I)[6]]. When kept in a desiccator over NaOH, its solubility strongly decreases, and over a period of months it decomposes to a yellow-green and then to a yellow powder, which is ESR silent. An aqueous suspension of freshly prepared (II) dissolves very easily in acids. This suspension was used as the starting material for the synthesis of superoxo rhodium(III) carboxylates (*vide infra*).

Titration of (I) in solution can also be performed by sodium hydroxide. However, this solution must be CO_3^{-2})/HCO_3^- free. If it is not, bands at 1370 and 1470–1500 cm^{-1} deriving from HCO_3^-, and/or CO_3^{-2} [13,14a] are observed in the IR spectrum of the resulting precipitate. The presence of carbonate in the solid has been confirmed by elemental analysis. Low temperature ESR spectra of a powder sample, showing a broad singlet at g = 2.05, are indicative of O_2^- bound in the species. The same results were obtained when $NaHCO_3$ was used as a neutralizing agent and after bubbling CO_2 through a solution of (I) previously neutralized under argon atmosphere with ammonia to pH 4–5. This suggests that carbon dioxide fixation involves reaction of CO_2 with the hydroxy ligands of superoxo aqua hydroxo rhodium(III) species.[14] It is remarkable that the carbonate compound is much more stable than (II). This product is of current interest.

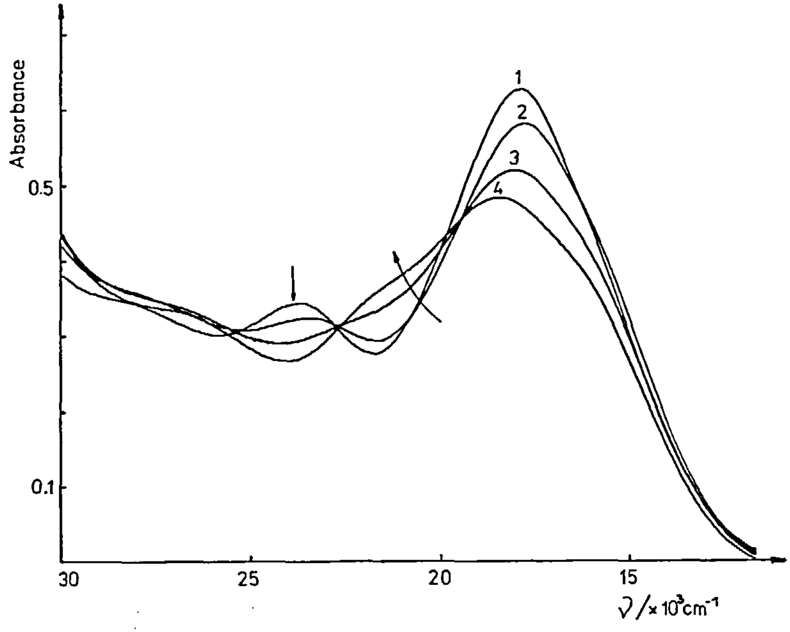

FIGURE 1 Spectrum changes observed in the reaction of 5 × 10^{-3} mol dm^{-3} $[Rh_2O_2^-)(OH)_2(H_2O)_2]^{+3}$ (1) in 3 mol dm^{-3} $HClO_4$ with CH_3CO_2H at 5 mol dm^{-3} (a) after 5 min, (b) 7 h, (c) 24 h, (d) 48 h.

Synthesis of superoxo rhodium(III) carboxylates

Replacement of water ligands in (I) by carboxylate ions has been examined. The reactions were studied in aqueous mixtures of $HClO_4/RCO_2H$, ($R = CH_3$, $CHCl_2$, CF_3). They proceeded quite slowly at ambient temperature (within a few days), under conditions described in the Experimental section. Bands at $\lambda_{max} = 28000$sh and $23880\,cm^{-1}$ ($\varepsilon = 280\,M^{-1}\,cm^{-1}$) for the rhodium starting material shift to lower energies and the band at $17880\,cm^{-1}$ ($\varepsilon = 534$) shifts to higher energy depending on R in RCO_2H (Figure 1, Table I). Reaction products are not adsorbed on cation or anion exchangers.

TABLE I

Electronic spectrum and ESR data for the superoxo Rh(III) carboxylates.

Complex	λ_{max}/cm^{-1} ($\varepsilon/M^{-1}\,cm^{-1}$)			ESR (130 K)	
(III)	17600 (1110)	26000sh[a] (1770)		$g_1 = 2.089$ $g_3 = 1.993$	$g_2 = 2.041$ $g_{av} = 2.041$
	17100 (1180)	25600sh (1760)	38500[b] (20600)		
	17000 (1160)	25600sh (1520)	38100[c] (19320)		
(IV)	18400 (1020)	25000sh[d] (1720)		$g_1 = 2.087$ $g_3 = 1.993$	$g_2 = 2.037$ $g_{av} = 2.039$
	17900 (1028)	25600sh (1948)	38900[b] (23880)		
(V)	19200 (1210)	26000sh[e] (1530)		$g_1 = 2.088$ $g_3 = 1.993$	$g_2 = 2.037$ $g_{av} = 2.039$
	18300 (1296)	25600sh (1639)	39200[b] (21250)		
	18000 (1130)	25400sh (1160)	39800[c] (17860)		

[a] In CH_3CO_2H. [b] In CH_3OH. [c] In H_2O. [d] In $CHCl_2CO_2H$. [e] In CF_3CO_2H.

The ESR spectrum of (I) in $3\,mol\,dm^{-3}$ $HClO_4$ shows at 130K a signal with $g_\parallel = 2.082$ and $g_\perp = 2.018$ ($g_{av} = 2.039$) related to the presence of O_2^- in the complex. Frozen solutions (130K) of the reaction products of (I) with the carboxylic acids yield spectra displaying three g features (two > 2 and one < 2 Figure 2, Table I) which are remarkably similar to e.g., $[Rh_2(ap)_4(O_2)]^-$ ($g_1 = 2.094$, $g_2 = 2.016$. $g_3 = 1.998$, in CH_2Cl_2; $g_{av} = 2.039$),[8] to those of type $[Rh_2L_8Cl_2O_2]^{+3}$ ($g_{av} = 2.019$–2.039),[9,15–17] and to superoxides of $[Rh_2(CO)L(bipy)(\mu \cdot RNNNR)]^+$ ($g_{av} = 2.026$–2.031)[18] thus strongly suggesting that the present values are also due to superoxide coordination in the complexes under study. No splitting was observed and which could be attributed to hyperfine interaction with the rhodium nuclei. The same results were obtained when sodium caboxylates were used.

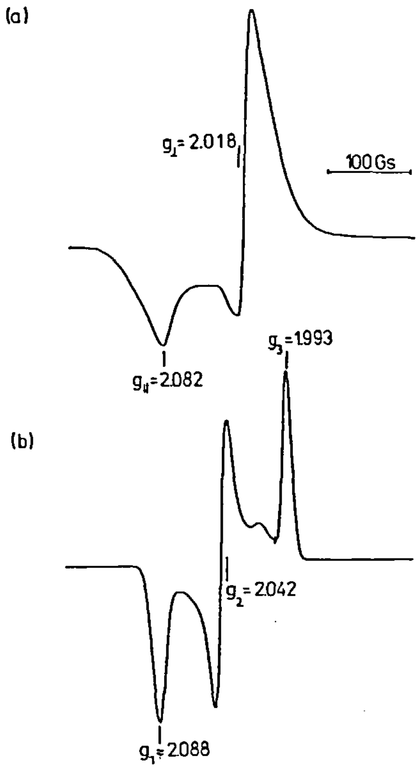

FIGURE 2 (a) The ESR spectrum of 1×10^{-2} mol dm^{-3} $[Rh_2O_2^-)(OH)_2(H_2O)_n]^{+3}$ (1) (a) in 3 mol dm^{-3} $HClO_4$ at 130 K, (b) after 48 h reaction of (1) at 5×10^{-3} mol dm^{-3}, in 3 mol dm^{-3} $HClO_4$ with CH_3CO_2H at 5 mol dm^{-3}, at 130 K.

TABLE II
Analytical and magnetic moment data for the superoxo Rh(III) carboxylates.[a]

Complex	Analysis(%)				Molecular Weight	μ (B.M.)
	Rh	C	H	Cl		
(III)	38.75 (38.95)	18.59 (18.17)	3.79 (3.50)		1116 (1056.6)	2.06
(IV)	24.11 (23.98)	11.24 (11.19)	1.42 (1.52)	31.92 (32.09)	1762.2 (1716.2)	2.10
(V)	25.4 (25.12)	13.66 (13.18)	1.1 (1.09)		1596 (1639)	2.06

[a] Calculated values in parentheses.

Attempts to isolate the carboxylate derivatives from the solutions containing $HClO_4$ were unsuccessful. Evaporation of these solutions led to syrups. In other procedures, the precipitate from the titration of (I) by aqueous ammonia and the appropriate carboxylic acid was used. The superoxo rhodium(III) carboxylates were prepared *via* a sequential procedure [reactions (*1*)–(*2*)].

$$\underset{\text{(I)}}{[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{+3}} \underset{H^+}{\overset{OH^-}{\rightleftarrows}} \underset{\text{(II)}}{[Rh_2(O_2^-)(OH)_{2+m}(H_2O)_{n-m}]_{solid}} \qquad (1)$$

$$\text{(II)} + RCO_2H \longrightarrow \underset{\text{(III) or (IV) or (V)}}{[Rh_4(O_2^-)(OH)_m(RCO_2)_n{\cdot}xH_2O} \qquad (2)$$

Complex	R	m	n	x
(III)	CH_3	3	8	5
(IV)	$CHCl_2$	3	8	11
(V)	CF_3	2	9	8

Evidence for the tetranuclear nature of the complex unit comes from the stoichiometry, molecular weight estimation, redox equivalent determination, electronic, ESR, IR, and Raman spectra and magnetic susceptibility measurements. Analytical data indicate that (III) and (IV) contain four carboxylate ligands per rhodium dimer unit, whereas (V) contains four and one half (Table II).

It has been found that the superoxides synthesized are strong oxidizing agents in acid solution, acting as three electrons oxidants towards iodide. On this basis, the redox equivalents of 372 and 532, and corresponding molecular weights of 1116 and 1596 for (III) and (V), respectively, have been estimated (calc. 352 and 546; 1056.6 and 1638, respectively).

Experiments with one equivalent of iodide gave variable end-points thus suggesting a lack of selectivity towards peroxide formation or further decomposition of peroxo products. Molecular weight measurements gave a value of 1762 for (IV) (calc. 1726.6). All these data indicate that in the reactions between (II) and RCO_2H, tetranuclear units containing one O_2^- anion are formed.

The electronic and ESR spectra of isolated complexes have the similar shapes and parameters as those of reaction products of (I) and RCO_2H. Absorption maxima, corresponding absorption coefficients and related g parameter values are given in Table I. One feature common to the electronic spectra of previously described superoxides of Rh(III) is a strong absorption in the 17000 cm^{-1} region.[6,9,16] The compounds reported here show an absorption around 18000 cm^{-1}. As known carboxylates of Rh(III) usually do not absorb in the regions, these low-energy absorption bands are good fingerprints for rhodium(III) superoxides. The absorption probably arises from a transition involving the odd electron in the π orbitals of the O_2^- anion.[16]

IR spectra of the isolated superoxo rhodium(III) carboxylates are very similar in profile and indicate that the compounds have the same structure. Relevant bands are listed in Table III. The spectra of all the complexes show at 3200–3400 cm^{-1} a broad doublet suggesting bridging O–H for waters of hydration.[13] Complexes (IV) and (V) exhibit a week but distinct band at 3620 and 3670 cm^{-1}, respectively, and

(III) at 3520 cm^{-1}(sh), which can be assigned to the bridging OH group.[13,19] In the ν_{asym} (CO_2) region strong, doublets are observed. Vibrations around 1620 cm^{-1} for (IV) and (V) can be attributed to a combination of ν_{asym} (CO_2) and δ (H–O–H). In contrast to (IV) and (V), the band corresponding to δ (H–O–H) for (III) appears at 1620 cm^{-1} as a shoulder of medium intensity. The Δ $[\nu_{asym}(CO_2) - \nu_{sym}(CO_2)]$ values are indicative of chelating and/or bridging carboxylate groups.[13,20] However, splitting of the $\nu_{asym}(CO_2)$ absorption suggests "pseudo-bridging" carboxylate ligands, where one oxygen of RCO_2^- is coordinated to the metal and the other is hydrogen bonded to another ligand (e.g., OH or H_2O).[20a]

The Raman spectra of the new superoxides were recorded in solution and band positions are given in Table III. Presence of peaks in the range 1040–1070 cm^{-1} due to $\nu(O_2^-)$ strongly suggests the bridging coordination of the O_2^- anion in the molecules.[9,13] Increase of the $\nu(O_2^-)$ frequencies in the order $CH_3 < CHCl_2 < CF_3$ reflects the effect of the donor–acceptor properties of the R substituent in the RCO_2^- ligands on the O–O bond strength.

TABLE III

Selected IR and Raman data (cm^{-1}) for the superoxo Rh(III) carboxylates.

Complex		IR			Raman
	ν(OH)[a]	$\nu_{asym}(CO_2)$[a,b]	$\nu_{sym}(CO_2)$[a]	$\Delta\nu$[f]	ν(O-O)
(III)	3520w(sh) 3200–3400m 1630m(sh)	1520vs 1570s(sh)	1420vs	100–150	1040[c]
(IV)	3620w 3480w 3200w(sh)	1570vs 1620s(sh)	1400vs	170–220	1060[d] 1052[b]
(V)	3670w 3200–3300m	1630vs 1670vs	1432m	202–244	1068[e]

[a] Nujol mull. [b] KBr disk. [c] In H_2O. [d] In $CHCl_3$. [e] In CF_3CO_2H. [f] $\Delta\nu = \nu_{asym}(CO_2) - \nu_{sym}(CO_2)$.

The susceptibilities of powdered samples of the complexes are presented in Table II. All the complexes are weakly paramagnetic. The magnetic moments of (III), (IV) and (V) (2.06, 2.10 and 2.06 B.M., respectively) are temperature-independent and in agreement with one unpaired electron per tetranuclear unit. According to all the experimental data the composition of the tetranuclear unit of the superoxo rhodium(III) carboxylates is considered to be $[Rh_2(OH)(RCO_2)_4(O_2^-)(OX)Rh_2(OH)(RCO_2)_4 \cdot nH_2O]$, (R = CH_3, $CHCl_2$, X = H: R = CF_3, X = CF_3CO). However, with the presence of bridging OH groups and waters of hydration, more polymeric formulations in the solid state cannot be excluded and questions concerning structure remain open at this stage. As yet no crystalline samples have been isolated.

The synthesized compounds are air-stable in the solid at ambient temperature. Nevertheless, in solution they undergo slow decomposition (within weeks), losing O_2^- anion to give unidentified rhodium(III) carboxylates. This was indicated by absorption spectral changes (the yellow decomposition products give one band around 25000 cm^{-1}) and the simultaneous disappearance of the bands in the ESR and

Raman indicative of O_2^-. It has been found that all the superoxo derivatives are reactive toward CO, H_2, cyclohexene, $(CH_3)_2S$, DMSO, and PPh_3. The reactivity and electrochemical behaviour of the complexes will be reported separately.

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