

22. Synthesis and Crystal Structure of *meso-A,A-μ-Peroxo-μ-hydroxobis[bis(ethylenediamine)rhodium(III)]trifluoromethane Sulfonate*

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Dedicated to Prof. Dr. *Silvio Fallab* on the occasion of his 60th birthday

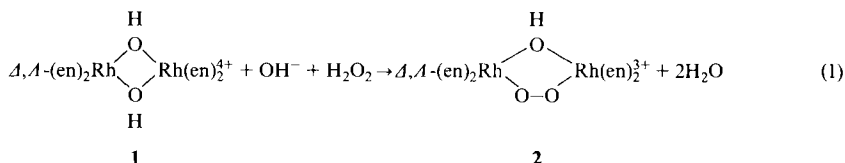
(23.IX.85)

The reaction of the *meso*-diol, $A,A-[(en)_2Rh(OH)_2Rh(en)_2]^{4+}$, with aqueous H_2O_2 and 1 equiv. of NaOH at 90° forms the μ -peroxo- μ -hydroxo-bridged species $A,A-[(en)_2Rh(O_2,OH)Rh(en)_2]^{3+}$ in a yield of ca. 50%. The compound was crystallized as perchlorate and trifluoromethanesulfonate salts. The structure of the latter salt was determined by single-crystal X-ray diffraction. The crystals are triclinic with space group $P\bar{1}$ and lattice constants $a = 11.895(5)$, $b = 12.491(4)$, $c = 13.053(5)$ Å, $\alpha = 103.98(3)$, $\beta = 92.59(3)$, $\gamma = 119.52(6)^\circ$. The distances of the metal centres to the bridging peroxo ligand are 1.999(8) and 1.983(6) Å. The O–O distance in the peroxo group is 1.521(14) Å, and the dihedral angle of the Rh–O–O–Rh unit deviates 65° from planarity. The peroxo complex reacts reversibly with acid, and spectrophotometric studies suggest that the reaction involves protonation of the peroxo bridge, with $pK_a = 2.70(2)$ at 25° in 1M NaClO₄.

Introduction. – The existence of both monomeric and dimeric Rh(III) complexes of the *Werner*-type containing peroxide and superoxide as ligands has been proposed in a number of papers during the last ten years [1–8]. It is, however, only recently that true peroxo and superoxo complexes of Rh(III) have been characterized [9] [10] for the first time by crystal-structure analysis, *viz.* the yellow peroxo-bridged complexes $fac-[(H_2O)(NH_3)_3Rh(O_2)(OH)Rh(NH_3)_4](ClO_4)_3$ and $[(NH_3)_4Rh(O_2)(OH)Rh(NH_3)_4](ClO_4)_3$, and the corresponding red superoxo-bridged complexes $fac-[(H_2O)(NH_3)_3Rh(O_2)(OH)Rh(NH_3)_4](NO_3)_4$ and $[(NH_3)_4Rh(O_2)(OH)Rh(NH_3)_4](NO_3)_4$. The former peroxo-bridged complexes are formed by reaction of the dihydroxo-bridged cation $(NH_3)_4Rh(OH)_2Rh(NH_3)_4^{4+}$ with H_2O_2 at 90°, and they can be oxidized by *e.g.* Ce^{4+} to give the red superoxo-bridged complexes.

In the reaction between $(NH_3)_4Rh(OH)_2Rh(NH_3)_4^{4+}$ and H_2O_2 the yields of the two peroxo-bridged ammine species depend on the reaction time, and only the octaammine complex [10] has been obtained in reasonable yield (16%), while the aquaheptaammine complex [9] was obtained in negligible amounts (~2%). The low yields of these peroxo complexes are primarily the result of facile hydrolysis of the ammine ligands. Hydrolysis of the non-bridging N-ligands should be considerably reduced in complexes containing the more stable polydentate amines, and here we report on our results for the reaction of the *meso*-diol, $A,A-(en)_2Rh(OH)_2Rh(en)_2^{4+}$, with H_2O_2 .

Results and Discussion. - *Syntheses.* Heating a solution of equimolar amounts of the *meso*-diol (**1**), Δ, Δ -[(en)₂Rh(OH)₂Rh(en)₂](ClO₄)₄ and NaOH in aqueous H₂O₂ (20%) at 90° led to formation of the peroxo-bridged complex **2** (Eqn. 1).

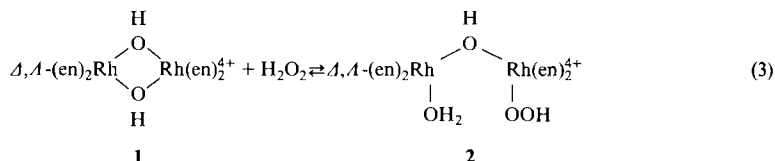
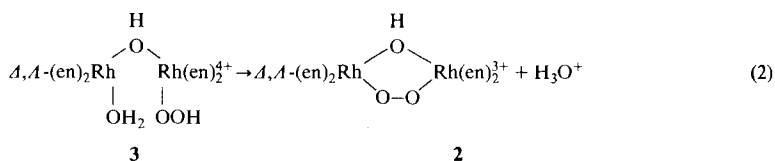


The reaction was complete after 4 min, and the peroxo-bridged cation **2** could be crystallized as an anhydrous perchlorate salt (yield 51%) or as a trifluoromethanesulfonate salt (yield 45%). The latter salt was crystallized both as an anhydrous salt and as a dihydrate, and the crystal structure of the dihydrate is described below.

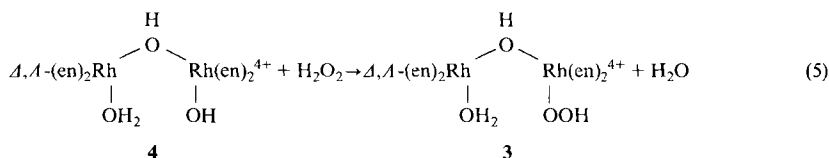
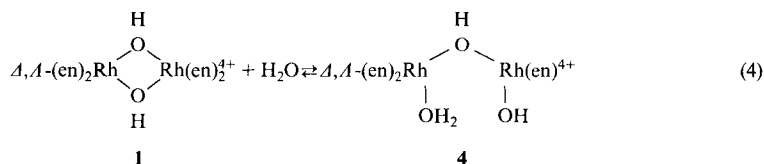
In the reaction between **1** and H₂O₂, the color gradually changed from yellow to yellowish-brown during the first 3 min. Within the same period, a vigorous evolution of O₂ was observed. Subsequent addition of H₂O₂ did not lead to a similar (vigorous) evolution of O₂. Similar observations were made for the reaction between (NH₃)₄Rh(OH)₂Rh(NH₃)₄⁴⁺ and H₂O₂, but in this case a much more intense (and intermediate) brown color was observed [9]. The disproportionation of H₂O₂ into O₂ and H₂O seems to be associated with the formation of the strongly colored intermediates, but the nature of these is still unknown.

The addition of base is important and heating **1** with H₂O₂ alone gave only minor yields of **2**. The reaction between **1** and H₂O₂ to give **2** produces acid, and **2** is unstable in acidic solution (see below). Also from a thermodynamic point of view, it follows from Eqn. 1 that formation of **2** is facilitated by the addition of base. Finally, a high pH may also be of kinetic importance in the reaction, *e.g.* HO₂⁻ would be a better nucleophile than H₂O₂.

The formation of **2** must clearly proceed in (at least) two consecutive steps: formation of a singly bonded peroxide complex **3** with subsequent bridge formation.



The initial step could be the *Reaction(s) 3* between H_2O_2 (or HO_2^-) and **1**, which would be in accord with the observation that the analogous *Reaction(s) 4* between H_2O (or OH^-) and **1** is known [11] to be shifted to the right and to be fast ($t_{1/2}$ for *Eqn. 4* is ca. 2 s at 90°). The fact that establishment of the *Equilibrium 4* is fast implies, however, that the formation of the singly bonded peroxide intermediate **3** might equally well occur *via* the substitution *Reaction 5* between the singly bridged species **4** and H_2O_2 .



It should be noted that the bridged complexes **1** and **2** have the same configurations Δ, Δ with respect to the ethylenediamine rings, and this is in agreement with the general tendency of Rh(III) to undergo thermal substitution without rearrangement.

It seems likely that the *Reaction 1* may serve as a general method for the preparation of peroxo-bridged complexes not only of Rh(III) but also of other trivalent metal ions such as Co(III) and Ir(III). Peroxo-bridged complexes of Co(III) are well-known [12] and can be made easily by oxidation of Co(II)-amine complexes with dioxygen. Oxidation of $\text{Co(en)}_2(\text{H}_2\text{O})_2^{2+}$ gives a mixture of the *meso*- and *rac*-isomers of $(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2^{3+}$ in a ratio of ca. 1:1 [13], and both isomers have been isolated. However, the fact that the *meso*-complex isomerizes to the *rac*-isomer under the basic conditions used in the preparative procedure makes it difficult to prepare this isomer in good yield. It is, therefore, of interest that we found that the reaction between $\Delta, \Delta\text{-(en)}_2\text{Co}(\text{OH})_2\text{Co}(\text{en})_2^{4+}$ and H_2O_2 at $\text{pH} \sim 6$ gives the pure *meso*-isomer of $(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2^{3+}$. Preliminary experiments show that the reaction between $\Delta, \Delta\text{-(en)}_2\text{Ir}(\text{OH})_2\text{Ir}(\text{en})_2^{4+}$ and H_2O_2 also gives a peroxo-bridged complex, and this aspect is now being pursued.

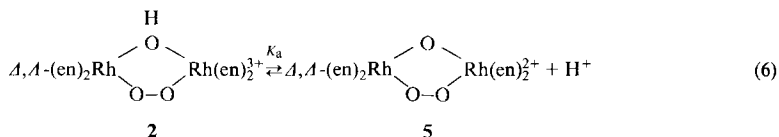
Spectra. Spectral data for **2** in various media are given in *Table 1*. It is seen that the first ligand-field band of **2** is obscured by a very intense charge-transfer band $(\epsilon, \gamma)_{\text{max}} = (5020, 289)$. A similar intense band is also observed in the corresponding ammine-Rh(III) complexes and in the analogous Co(III) species, and may be assigned as a $\pi^* \rightarrow d_\sigma$ transition [12] [14–16]. Spectral data for acidic and basic media are discussed below.

Acid-Base Equilibria. The peroxo-bridged complex is kinetically stable in neutral and basic media, and the fact that the spectra in 1M NaClO_4 and in 0.1M NaOH , 0.9M NaClO_4 are identical implies that the acid-base *Equilibrium 6* must have $\text{p}K_a \gg 13$. That the tripositive cation **2** is a very weak acid is in keeping with the fact that the tetrapositive cation **1** has $\text{p}K_a > 14$ [11].

Table 1. Spectroscopic Data of Peroxo-Bridged Dirhodium(III) Complexes

Compound	Medium	$(\epsilon, \lambda)_{\max}$	$(\epsilon, \lambda)_{\max}$	$(\epsilon, \lambda)_{\min}$
Δ, Δ -[(en) ₂ Rh(O ₂)(OH)Rh(en) ₂](ClO ₄) ₃	1M NaClO ₄	(5010, 289)	(10400, 221)	(3210, 261)
Δ, Δ -[(en) ₂ Rh(O ₂)(OH)Rh(en) ₂](CF ₃ SO ₃) ₃	1M NaClO ₄	(5020, 289)	(10200, 221)	(3220, 261)
–	0.1M NaOH, 0.9M NaClO ₄	(4930, 289)	(10300, 221)	(3130, 261)
–	0.1M HClO ₄ , 0.9M NaClO ₄	(829, 330) _{sh}	(1351, 290) _{sh}	^{a)}
–	1.0M HClO ₄	(822, 330) _{sh}	(1320, 290) _{sh}	^{a)}

^{a)} These values correspond to the spectrum of the μ -hydrogenperoxo- μ -hydroxo complex and were obtained from measurements at 1.0° and extrapolation back to the time of dissolution. The remaining spectral data were obtained at 25°.



An instantaneous and reversible reaction of **2** with acid was demonstrated spectrophotometrically. This reaction is followed by a slower reaction (see below), and the tabulated spectra in acid media were, therefore, obtained by extrapolation of the absorbancies back to the time of dissolution.

The initial and fast reaction with acid is reversible, since addition of an excess of strong base to acidic solutions of the complex reforms **2**, shown spectrophotometrically. Considering the well-known kinetic stability of Rh(III) complexes it seems unlikely that the process involves bridge-cleavage reactions, and it is, therefore, assumed to involve only acid-base equilibria.

The spectral changes as a function of pH could be interpreted on the basis of a single acid-base equilibrium, and from measurements in the [H⁺] region 10⁻⁵ – 1.0M at two temperatures (1.0° and 25°) the acid dissociation constant for the protonated species was determined to be pK_a = 2.70(2) at 25° in 1M (Na,H)ClO₄ ($\Delta H^\circ = 14.8(16)$ kJ mol⁻¹ and $\Delta S^\circ = -2(6)$ Jmol⁻¹K⁻¹). Spectral data for the protonated species (0.1M HClO₄, 0.9M NaClO₄, or 1M HClO₄) are given in *Table 1* and *Fig. 1*.

Two sites of protonation are possible, *viz.* the hydroxo and the peroxo bridge. Protonation of the hydroxo bridge seems unlikely for several reasons: kinetic studies [11] [17] of the acid hydrolysis of corresponding dihydroxo-bridged complexes suggest that aqua-bridged dirhodium(III) complexes are very labile and that they are strong acids with pK_a < 0. The intense charge-transfer band, which is characteristic of peroxo-bridged complexes of Rh(III) and Co(III), is observed for **2**, but not for its protonated form, which also suggests that it is the peroxo bridge which is protonated rather than the hydroxo bridge. Furthermore, it is noted that a similar spectral change has been observed for Δ, Δ -(en)₂Co(O₂)(NH₂)Co(en)₂³⁺ and its protonated form [18]. The initial and fast reaction with acid is, therefore, proposed to involve formation of a μ -hydrogenperoxo- μ -hydroxo species, as shown in *Eqn. 7*.

Owing to the instability of the peroxo-bridged species in acidic solution, attempts to crystallize salts of the protonated cation **6** have so far been unsuccessful. Corresponding protonation of peroxo-bridged dicobalt(III) species has also been reported. The amido-

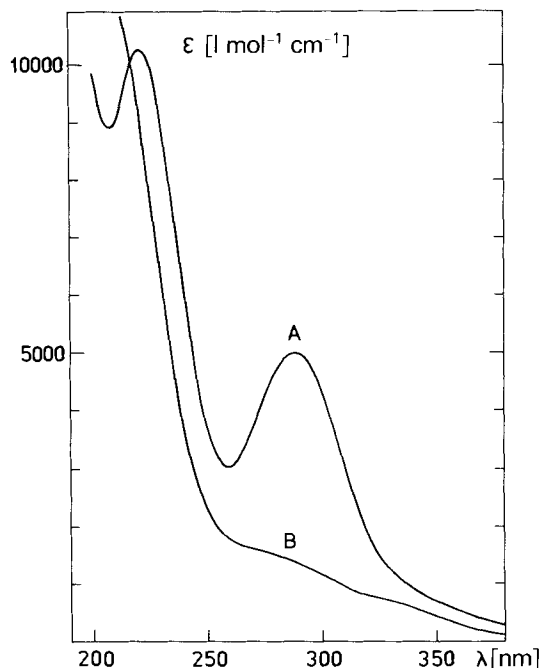
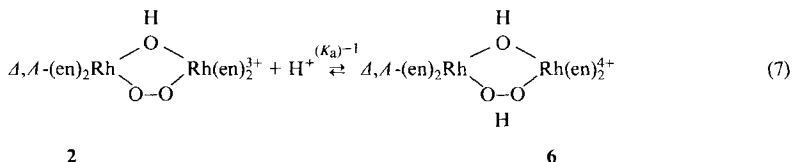


Fig. 1. Absorption spectra of **2** (A) and **6** (B) (at 1.0° in 1.0M (Na,H)ClO₄)



bridged complex $\Delta,\Delta\text{-en}_2\text{Co}(\text{HO}_2)(\text{NH}_2)\text{Co}(\text{en})_2^{4+}$ has $\text{p}K_a = 0.9$ and is, therefore, significantly more acidic than the present dirhodium(III) complex [18]. Kinetic studies of the acid decomposition of μ -peroxo- μ -hydroxo-dicobalt(III) species to give Co(II) and dioxygen have been interpreted in terms of the formation of protonated intermediates, and $\text{p}K_a$ values in the region 0.4–2.5 have been reported [12] [13] [19] [20].

Decomposition in Acid. As mentioned above, the peroxo-bridged complex decomposes in acidic solution, and the rate of decomposition increases with increasing $[\text{H}^+]$: at 25° $t_{1/2} \approx 15$ min in 10^{-3} M HClO₄, 1M NaClO₄, and $t_{1/2} \approx 4$ min in 0.1M HClO₄, 0.9M NaClO₄. Several Rh(III) species are formed and preliminary studies have shown that the product distribution depends on the Rh(III) concentration. Among the products is a red species ($\lambda_{\text{max}} = 503$ nm) which, in keeping with the chemistry of the analogous ammine-rhodium(III) systems [9] [10], is assumed to be a μ -superoxo- μ -hydroxo dimer. This red superoxo-bridged complex can also be made by oxidation of **2** with oxidants such as Ce⁴⁺ and S₂O₈²⁻, and these reactions are currently being investigated.

Description of the Structure. The asymmetric unit contains one discrete binuclear complex cation, three anions and two crystal waters. Fig. 2 shows an ORTEP plot of the

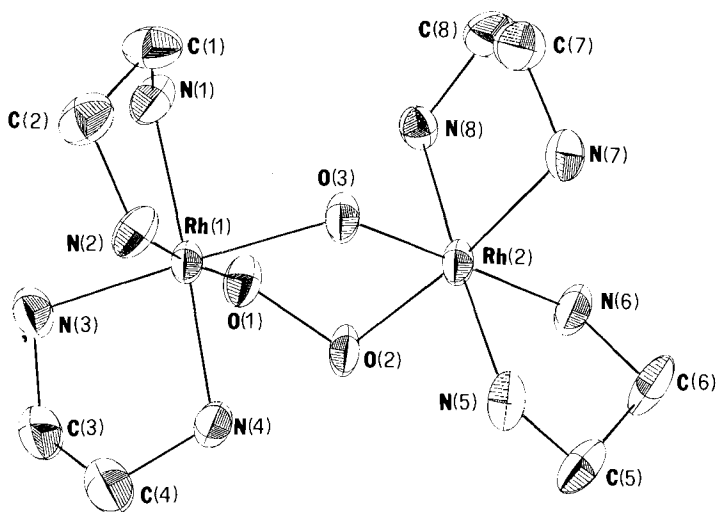


Fig. 2. ORTEP drawing of the structure of **2**

cation. The O–O distance of 1.521(14) Å marks it as a true peroxo compound, although the bond length is significantly longer than that found for the corresponding dicobalt compound [13] (1.460(13) Å). The Rh(1)–O(1)–O(2)–Rh(2) unit is nonplanar, as it was found in all previously determined structures of binuclear μ -peroxo- μ -hydroxo complexes, and the dihedral angle is 62.8(5)°, which is close to the values being observed for dicobalt and dirhodium species [9] (62.2(5)° in $(\text{NH}_3)_4\text{Rh}(\text{O}_2, \text{OH})\text{Rh}(\text{NH}_3)_4^{3+}$ [10]). The coordination octahedra are distorted, bond angles are ranging from 82° to 97°, whilst bond distances are differing in the small range of 1.999 to 2.099 Å.

Experimental. – *Materials.* Δ, Δ -[(en)₂Rh(OH)₂Rh(en)₂](ClO₄)₄ was synthesized as described in [11]. Δ, Δ -[(en)₂Co(OH)₂Co(en)₂](NO₃)₄ was prepared from the chloride salt [21], as described in [22]. CF₃SO₃Na was prepared from CF₃SO₃H (3M Company) and Na₂CO₃. All other reagents were of anal. grade.

Instruments. A Zeiss DMR 21 spectrophotometer was used for all spectrophotometric measurements. Data are given with the molar extinction coefficient ϵ in l mol⁻¹ cm⁻¹ and the wavelength λ in nm. Crystal-diffraction data were collected with a CAD4 Enraf-Nonius diffractometer equipped with a fine focus Mo tube and a graphite monochromator to select MoK _{α} radiation.

Analyses. C, H, N, and S analyses were performed by the Microanalytical Laboratory at the H. C. Ørsted Institute, Copenhagen.

Preparations. Δ, Δ -[(en)₂Rh(O₂)(OH)Rh(en)₂](ClO₄)₃ (meso- μ -Peroxo- μ -hydroxobis[bis(ethylenediamine)-rhodium(III)] Perchlorate). A soln. of Δ, Δ -[(en)₂Rh(OH)₂Rh(en)₂](ClO₄)₄ (0.5 g, 0.569 mmol) in a mixture of 1M NaOH (0.56 ml) and 30% H₂O₂ (1.0 ml) was heated to 90 (±1)°. The color of the soln. changed from yellow to yellowish-brown during the first 3 min. Within the same period, a vigorous evolution of O₂ was also observed. After 4 min, the mixture (pH ~ 8) was cooled in ice and a sat. soln. of NaClO₄ (1.0 ml) was added. Pale yellow crystals of the perchlorate salt of **2** precipitated. After 10 min, the crystals were filtered off, washed with several portions of 96% EtOH and finally with Et₂O. The product was dried in the air. This gave 0.23 g (51%) of an almost pure perchlorate salt which was reprecipitated as follows: 0.2 g was dissolved at r.t. in H₂O (4 ml), and a sat. soln. of NaClO₄ (2 ml) was added to the filtered soln. The crystals were isolated as above (yield 0.16 g). Further reprecipitation did not change the spectrum, which was identical to that of the trifluoromethanesulfonate salt (see Table 1). Anal. calc. for [Rh₂(C₂N₂H₈)₄(O₂)(OH)](ClO₄)₃: C 12.11, H 4.19, N 14.12; found: C 12.30, H 4.16, N 14.20.

Caution: We have observed that this perchlorate *detonates* violently when exposed to a mechanical shock. It must, therefore, be handled with caution and should not be prepared in quantities larger than those described above.

A,A-[(*en*)₂Rh(O₂)(OH)Rh(*en*)₂](CF₃SO₃)₃ (meso-*μ*-Peroxo-*μ*-hydroxobis[bis(ethylenediamine)rhodium-(III)]trifluoromethane Sulfonate). *A,A*-[(*en*)₂Rh(OH)₂Rh(*en*)₂](ClO₄)₄ (1.0 g, 1.14 mmol) was reacted with 1M NaOH (1.14 ml) and 30% H₂O₂ (2 ml) as described above. The mixture was cooled to r.t. and then solid sodium trifluoromethanesulfonate (1.0 g) was added. The precipitate was filtered off, washed several times with 96% EtOH, once with Et₂O, and dried in the air. This gave 0.48 g (45%) of an almost pure trifluoromethanesulfonate salt which was reprecipitated as follows: 0.2 g was dissolved at r.t. in H₂O (6.0 ml), and solid sodium trifluoromethanesulfonate (0.8 g) was added to the filtered soln. The crystals were isolated as above (yield 0.15 g). Anal. calc. for [Rh₂(C₂N₂H₈)₄(O₂)(OH)](CF₃SO₃)₃: C 14.02, H 3.53, N 11.89, S 10.21; found: C 13.80, H 3.68, N 11.76, S 10.32.

Spectral data are given in Table 1. Reprecipitation at 0° gave a dihydrate. A soln. of the trifluoromethanesulfonate salt (0.25 g) in H₂O (5 ml) was cooled in ice and solid sodium trifluoromethanesulfonate (0.5 g) was then added. Crystals of the dihydrate separated and were collected as described above. Yield 0.2 g. Anal. calc. for [Rh₂(C₂N₂H₈)₄(O₂)(OH)](CF₃SO₃)₃·2 H₂O: C 13.50, H 3.81, N 11.45, S 9.83; found: C 13.45, H 3.69, N 11.55, S 10.0. The spectral data for the dihydrate in 1M NaClO₄ (ϵ, λ)_{max} = 5090, 289) agreed with those for the anh. salt, see Table 1. The crystals which were used in the X-ray determination were obtained by this method, but using a smaller amount of sodium trifluoromethanesulfonate.

A,A-[(*en*)₂Co(O₂OH)Co(*en*)₂](ClO₄)₃·H₂O (meso-*μ*-Peroxo-*μ*-hydroxobis[bis(ethylenediamine)cobalt-(III)] Triperchlorate Hydrate). *A,A*-[(*en*)₂Co(OH)₂Co(*en*)₂](NO₃)₄ (1.0 g, 1.56 mmol) was reacted at pH 6.3 with 30% H₂O₂ (5 ml) at r.t. The pH was maintained constant by addition of 1.0M NaOH by the application of a pH-stat instrument. A total amount of 1.6 ml of 1M NaOH was added. The soln. was kept at 15° for 24 h. The color changed slowly from deep violet to brown, indicating that a peroxo-bridged complex had been formed. Solid NaClO₄·H₂O (0.8 g, 5.7 mmol) was added, and crystals of *A,A*-[(*en*)₂Co(O₂)(OH)Co(*en*)₂](ClO₄)₃·H₂O separated (0.57 g, 51%). The crystals were identified by comparing unit cell parameters and space group of the overall structure [13] by Weissenberg photographs.

Table 2. Summary of Crystal Data, Intensity Collection, Structure, Solution, and Refinement

Formula	C ₁₁ H ₃₇ F ₉ N ₈ O ₁₄ Rh ₂ S ₃
Mol. wt.	978.45
Space group	P1
<i>a</i> [Å]	11.895(5)
<i>b</i> [Å]	12.491(4)
<i>c</i> [Å]	13.053(5)
α [°]	103.98(3)
β [°]	92.59(3)
γ [°]	119.52(6)
<i>Z</i> ; <i>V</i> [Å ³]	2; 1606.39
<i>D</i> _{calc.} [g cm ⁻³]	2.024
<i>F</i> ₀₀₀	980
Diffractometer	Enraf-Nonius CAD4
Radiation [Å]	MoK α (λ = 0.71069)
Scan type	$\theta/2\theta$
Reflections measured	$\pm h, \pm k, l$ (144 check reflections; intensity loss 10%)
θ_{max} [°]	23
Unique total data	4452
Data in refinement [<i>F</i> _o > 2 σ (<i>F</i> _o)]	3979
Atoms/asymmetric unit	84
No. of variables	371
Phasing technique	Patterson
<i>R</i>	0.0894
<i>R</i> _w	0.1014
$w = (\sigma^2(2F_o) + g(F_o)^2)^{-1}$	$g = 0.00035$

Table 3. Positional and Thermal Parameters of $C_{11}H_{37}F_9N_8O_{14}Rh_2S_3$ and their Standard Deviations

Atom	X/A	Y/B	Z/C	U ₁₁ or U	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Rh(1)	-0.0574(1)	0.6874(1)	0.2455(1)	0.0172(5)	0.0246(5)	0.0323(5)	0.0071(4)	0.0021(4)	0.0116(4)
Rh(2)	0.2065(1)	0.6502(1)	0.2005(1)	0.0171(5)	0.0284(5)	0.0362(5)	0.0071(4)	0.0010(4)	0.0129(4)
O(1)	-0.0654(7)	0.5452(7)	0.1289(6)	0.0282(40)	0.0289(37)	0.0396(43)	0.0020(33)	0.0008(33)	0.0189(33)
O(2)	0.0222(7)	0.5050(7)	0.1754(6)	0.0199(36)	0.0301(38)	0.0559(50)	0.0102(36)	0.0052(34)	0.0172(32)
O(3)	0.1428(7)	0.7719(6)	0.2653(6)	0.0188(36)	0.0256(37)	0.0543(49)	0.0080(35)	0.0028(34)	0.0119(31)
N(1)	-0.0439(9)	0.7966(9)	0.1433(8)	0.0373(53)	0.356(52)	0.0455(58)	0.0113(45)	-0.0003(45)	0.0231(45)
N(2)	-0.0378(9)	0.8463(9)	0.3632(7)	0.0440(55)	0.0343(48)	0.0364(53)	0.0040(42)	-0.0001(44)	0.0292(45)
N(3)	-0.2614(9)	0.5902(9)	0.2200(8)	0.0234(47)	0.0344(51)	0.0521(60)	0.0127(45)	0.0085(44)	0.0123(42)
N(4)	-0.0780(8)	0.5820(8)	0.3496(8)	0.0263(48)	0.0337(48)	0.0460(57)	0.0150(44)	0.0031(42)	0.0179(41)
N(5)	0.2423(9)	0.6171(9)	0.3443(8)	0.0302(51)	0.0481(57)	0.0394(55)	0.0047(46)	0.0023(43)	0.0258(47)
N(6)	0.2687(9)	0.5259(9)	0.1363(8)	0.0299(50)	0.0419(54)	0.0481(59)	0.0146(46)	0.0014(44)	0.0245(45)
N(7)	0.3927(9)	0.8142(9)	0.2188(8)	0.0238(48)	0.0473(57)	0.0454(58)	0.0155(47)	0.0008(43)	0.0176(44)
N(8)	0.1783(8)	0.6792(8)	0.0563(6)	0.0242(45)	0.0330(46)	0.0241(45)	0.0074(38)	0.0062(37)	0.0154(39)
C(1)	0.0209(12)	0.9364(11)	0.2129(10)	0.0568(79)	0.0313(60)	0.0470(72)	0.0181(55)	0.0156(62)	0.0231(59)
C(2)	-0.0469(13)	0.9371(11)	0.3079(10)	0.0578(81)	0.0411(67)	0.0528(78)	0.0142(60)	0.0118(65)	0.0345(65)
C(3)	-0.3050(12)	0.4772(14)	0.2633(12)	0.0276(64)	0.0764(94)	0.0695(92)	0.0412(79)	0.0109(63)	0.0222(66)
C(4)	-0.2144(12)	0.5205(13)	0.3722(11)	0.0362(69)	0.0651(85)	0.0585(84)	0.0276(70)	0.0144(63)	0.0231(65)
C(5)	0.2694(12)	0.5071(12)	0.3188(10)	0.0480(73)	0.0488(70)	0.0471(73)	0.0139(59)	-0.0073(59)	0.0331(62)
C(6)	0.3495(16)	0.5246(13)	0.2290(10)	0.0607(82)	0.719(87)	0.0482(76)	0.0201(67)	0.0044(64)	0.0558(76)
C(7)	0.3028(12)	0.7891(12)	0.0412(10)	0.0370(66)	0.0537(74)	0.0389(67)	0.0243(59)	-0.0029(55)	0.0162(59)
C(8)	0.3770(11)	0.8842(11)	0.1478(9)	0.0343(64)	0.0454(69)	0.0389(68)	0.0150(56)	-0.0033(54)	0.0128(56)
S(1)	0.9255(3)	0.2426(3)	0.3588(3)	0.0530(19)	0.0325(15)	0.0465(18)	0.0155(14)	0.0020(15)	0.0191(15)

S(2)	0.4008(3)	0.2906(3)	-0.0311(3)	0.0277(15)	0.0401(16)	0.0493(18)	0.0125(14)	0.0007(13)	0.0181(13)
S(3)	0.6490(3)	0.8160(5)	0.4810(4)	0.0297(18)	0.1145(34)	0.0793(28)	0.0557(26)	0.0164(18)	0.0288(21)
O(4)	0.9709(10)	0.3763(8)	0.3816(9)	0.0729(68)	0.0379(51)	0.1098(90)	0.0223(55)	0.0149(64)	0.0277(50)
O(5)	0.9362(12)	0.2024(9)	0.4502(8)	0.1044(84)	0.0509(55)	0.0499(58)	0.0136(47)	-0.0201(56)	0.0284(58)
O(6)	0.9692(11)	0.1916(9)	0.2673(8)	0.1003(84)	0.0622(62)	0.0612(63)	0.0238(52)	0.0189(59)	0.0461(63)
O(7)	0.6854(8)	0.6617(9)	0.0140(8)	0.0449(52)	0.0618(57)	0.0774(66)	0.0175(50)	0.0198(48)	0.0381(48)
O(8)	0.6019(11)	0.7616(10)	0.1412(8)	0.0859(76)	0.0787(71)	0.0584(64)	0.0119(55)	0.0149(57)	0.0532(64)
O(9)	0.4693(9)	0.6284(10)	-0.0335(10)	0.0403(55)	0.0624(62)	0.1046(86)	0.0169(60)	-0.0262(55)	0.0157(49)
O(10)	0.5319(10)	0.8072(10)	0.4394(9)	0.0486(59)	0.0799(73)	0.0849(77)	0.0108(61)	-0.0159(54)	0.0303(55)
O(11)	0.6707(18)	0.7238(23)	0.4072(13)	0.1659(164)	0.3079(262)	0.1208(127)	0.0732(153)	0.0674(122)	0.1950(194)
O(12)	0.7604(15)	0.9335(16)	0.5242(14)	0.1032(113)	0.1451(136)	0.1579(151)	0.1089(128)	-0.0461(105)	-0.0231(102)
C(9)	0.7528(29)	0.1645(15)	0.3082(14)	0.2415(268)	0.0422(90)	0.0397(93)	0.0044(74)	-0.0405(128)	0.0199(128)
C(10)	0.6734(14)	0.8470(14)	-0.0219(16)	0.0371(76)	0.0496(81)	0.1161(143)	0.0043(87)	0.0093(83)	0.0194(67)
C(11)	0.6144(14)	0.7516(15)	0.5865(14)	0.0387(79)	0.0618(93)	0.0891(116)	0.0162(84)	0.0275(80)	0.0109(71)
F(1)	0.6936(12)	0.0378(11)	0.2919(9)	0.1063(33)					
F(2)	0.6989(15)	0.2097(14)	0.3886(13)	0.1390(48)					
F(3)	0.7236(13)	0.1927(13)	0.2311(11)	0.1286(42)					
F(4)	0.6072(11)	0.9088(10)	-0.0090(9)	0.1031(33)					
F(5)	0.7955(12)	0.9358(11)	0.0389(9)	0.1102(35)					
F(6)	0.6815(14)	0.8130(13)	-0.1197(12)	0.1309(45)					
F(7)	0.7119(13)	0.7496(12)	0.6385(10)	0.1164(38)					
F(8)	0.5157(16)	0.6351(16)	0.5589(12)	0.1518(52)					
F(9)	0.5874(14)	0.8188(14)	0.6686(12)	0.1386(47)					
W(1)	-0.0005(8)	0.2772(7)	0.0802(6)	0.0438(19)					
W(2)	0.5679(22)	0.9175(21)	0.4491(17)	0.1825(78)					

Determination of pK_a for the μ -Hydrogenperoxo- μ -hydroxorhodium(III) Cation. The acid dissociation constant K_a for the hydrogenperoxo-bridged cation Δ, Δ -[(en)₂Rh(HO₂)(OH)Rh(en)₂]⁴⁺ was determined from spectroscopic measurements on solns. of Δ, Δ -[(en)₂Rh(O₂)(OH)Rh(en)₂](CF₃SO₃)₃ in 1M (Na,H)ClO₄ at 1.0° and 25°. The reversibility of the reaction with acid was shown as follows: A 3·10⁻⁴M soln. of Δ, Δ -[(en)₂Rh(O₂)(OH)Rh(en)₂](CF₃SO₃)₃ in 0.1M HClO₄, 0.9M NaClO₄ was kept at 0° for 14 s, and was then mixed with an equal volume of 0.2M NaOH, 0.9M NaClO₄. The UV spectrum of this soln. showed $(\epsilon, \lambda)_{\max} = (4800, 289)$, which is nearly the same as found for **2** in 0.1M NaOH, 0.9M NaClO₄. A similar result was obtained when base was added to the acidic soln. after 20 s.

The spectra of acidic solns. of **2** changed with time, and the molar absorbances at the time of dissolution, ϵ_0 , were, therefore, obtained by extrapolation. At 1.0°, ϵ_0 values at three different wavelengths (310, 300, and 290 nm) were obtained by linear extrapolations based on 2–3 absorption curves recorded within 1–4 min after dissolution. Such extrapolation led to a correction of about 1%. At 25°, the reaction with acid is fast ($t_{1/2} \approx 4$ min in 0.1M HClO₄) relative to the time required to obtain a full spectral curve (~ 1 min). At this temp., the absorbances were, therefore, measured at a constant wavelength, $\lambda = 290$ nm, and ϵ_0 values were calculated by linear extrapolations based upon absorbances measured within 20–50 s after dissolution. The corrections due to extrapolations were never greater than 10%. The absorbances ϵ_A of the deprotonated species were obtained from measurements in 1M NaClO₄. Spectral data for solns. with $[H^+] = 0.1, 0.2, \text{ and } 1.0M$ were almost identical, and were, therefore, assumed to correspond to the pure protonated species, ϵ_{AH} (see also *Table 1*).

The acid-dissociation constant was then calculated from the *Eqn. 8* using ϵ_0 values measured for solns. with $[HClO_4] = 0.001, 0.002, 0.005, \text{ and } 0.01M$ and with $[Dimer] \approx 2 \cdot 10^{-4}M$. This gave $K_a = 1.19(6) \cdot 10^{-3}M$ at 1.0°, and $K_a = 2.01(6) \cdot 10^{-3}M$ at 25°.

$$K_a = \left[\frac{[HClO_4]}{(\epsilon_0 - \epsilon_A)} - \frac{[Dimer]}{(\epsilon_{HA} - \epsilon_A)} \right] (\epsilon_{HA} - \epsilon_0) \quad (8)$$

X-Ray Structure Determination. Crystal data and details of data collection are given in *Table 2*. Unit cell parameters were determined from accurate centering of 25 independent strong reflections. No correction for absorption was applied. A three-dimensional sharpened *Patterson* map yielded the positions of the metal centres. Difference *Fourier* maps and subsequent least-squares refinements located the remaining atoms. H-atoms were not considered. The programs used were developed by *Sheldrick* [23] and by us. Scattering factors for Rh³⁺ and neutral atoms were those of *Cromer et al.* [24]. The trifluoromethanesulfonate anions are disordered, and F-atoms were not included in anisotropic refinement steps. Atomic positional and thermal parameters are given in *Table 3*, whilst selected bond distances and bond angles are given in *Table 4*. A full list of bond distances and bond angles as well as a list of observed and calculated structure amplitudes are available from *M.Z.*

Table 4. Selected Bond Distances and Bond Angles in the Cation

Bonds	Distance [Å]	Bonds	Angle [°]
Rh(1)–Rh(2)	3.448(3)	Rh(1)–μO(3)–Rh(2)	115.0(3)
Rh(1)–μO(1)	1.999(8)	Rh(1)–μO(3)–μO(2)	107.3(5)
Rh(1)–μO(3)	2.046(7)	Rh(2)–μO(2)–μO(1)	107.0(5)
Rh(1)–N(1)	2.085(12)	μO(1)–Rh(1)–μO(3)	85.7(3)
Rh(1)–N(2)	2.096(10)	μO(2)–Rh(2)–μO(3)	87.8(3)
Rh(1)–N(3)	2.073(9)	N(1)–Rh(1)–N(2)	83.2(4)
Rh(1)–N(4)	2.054(11)	N(1)–Rh(1)–N(3)	94.0(4)
Rh(2)–μO(2)	1.983(6)	N(2)–Rh(1)–N(3)	92.6(4)
Rh(2)–μO(3)	2.043(9)	N(5)–Rh(2)–N(6)	84.2(5)
Rh(2)–N(5)	2.085(11)	N(5)–Rh(2)–N(7)	97.0(4)
Rh(2)–N(6)	2.054(12)	N(6)–Rh(2)–N(7)	92.8(4)
Rh(2)–N(7)	2.099(8)	Rh(1)–μO(1)–μO(2)	62.80(5)
Rh(2)–N(8)	2.046(10)		
μO(1)–μO(2)	1.521(14)		

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