258. Synthesis and Crystal Structure of a Peroxo-Bridged Binuclear Rhodium(III) Complex and its Superoxo-Bridged Analogue

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Summary

The reaction of the ammonia diol $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]^{4+}$ with H_2O_2 yields among other products a peroxo-bridged dimeric species $[(NH_3)_4Rh(O_2)(OH)Rh(NH_3)_3(H_2O)](ClO_4)_3$. Its structure was determined by single-crystal X-ray diffraction. The crystals are monoclinic with space group $P2_1/n$ and lattice constants $a = 12.269(5)$ Å, $b = 10.769(4)$ Å, $c = 15.964(4)$ Å, $\beta = 107.17(3)°$. The dihedral angle of the RhOORh group in the bimetallic ring deviates by 62° from planarity. The peroxo-bridged complex was found to disproportionate in 1M $HClO_4$ and a red superoxo-bridged complex, $[(NH_3)_4Rh(O_2)(OH)Rh(NH_3)_3(H_2O)](NO_3)_4$, was isolated. Its structure was solved by single-crystal X-ray diffraction. The crystals are orthorhombic with space group $Pna2_1$ and lattice constants $a = 14.997(5)$ Å, $b = 11.952(4)$ Å, $c = 10.489(4)$ Å. The dihedral angle of the RhOORh group deviates by 7° from planarity.

Introduction. – Metal complexes containing peroxide or superoxide as ligands are of biochemical relevance as potential model systems for the superoxide dismutase enzymes, which, in organic tissue, catalyze the disproportionation of O_2^-. Superoxide dismutase enzymes are known to contain the metals Cu and Zn, Mn or Fe, and the redox chemistry and the function of these metal centers have been intensively studied [1–3]. Peroxo and superoxo complexes of Co(III) have been known since the end of the last century [4–6], and have since then been the subject of a very large number of preparative, kinetic, thermodynamic and spectroscopic studies [7–9]. Although Rh(III) analogues of many of the classical *Werner*-type complexes have been reported within the last couple of decades, there have been no reports of corresponding peroxide or superoxide Rh(III) complexes. From kinetic and thermodynamic points of view such Rh(III) complexes are expected to be more stable than the Co(III) complexes; Rh(III) is generally much more inert than Co(III), and decomposition into M(II) and O_2, which is a common route in Co(III) peroxo systems, is not so likely to occur with Rh(III) because of the enhanced stability of the oxidation state +3 relative to +2.

The apparent reduced tendency for Rh(III) to form peroxo or superoxo complexes is probably due to unfavorable kinetics of formation rather than thermodynamic instability. The formation of Co(III) peroxo complexes is generally achieved by oxidation of Co(II) with molecular oxygen in the presence of the appropriate ligands, but the transient existence of *e.g.* aqua and ammine Rh(II) complexes in aqueous solution clearly prohibits this method to be used to form peroxo Rh(III) complexes.

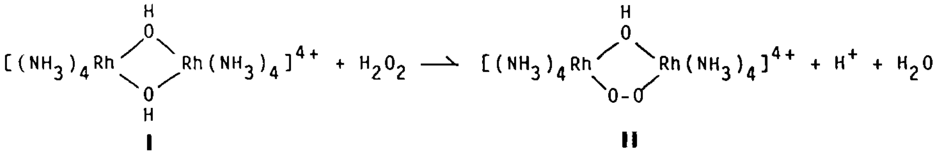
An alternative method would be to employ a Rh(III) complex as a precursor to be used in a substitution reaction with H_2O_2 (or HO_2^-). Following the Co(III) chemistry a suitable complex should be dimeric and contain labile ligands in appropriate positions for a bridging peroxide. The dimeric Rh(III) complexes $[N_4Rh(OH)_2RhN_4]^{4+}$ ($N_4 = (NH_3)_4$ or $(en)_2$) was recently shown to undergo a rapid acid- and base-catalyzed cleavage of one bridge with conservation of the other bridge [10] [11]. In the light of the substitution chemistry of analogous or similar complexes of Cr(III) [12–14] and Co(III) [7] [8] such Rh-dioles seemed to be good candidates for the pursuit of such a strategy.

Here, we report results obtained for the ammonia system and present the first examples of bridged peroxo and superoxo Rh(III) complexes.

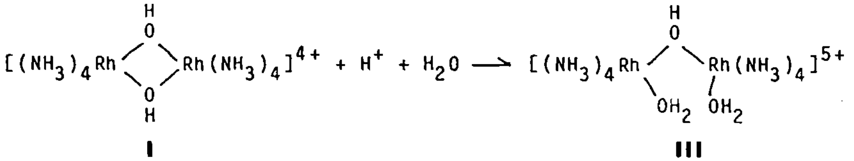
Results and Discussion. – The ammonia diol $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]^{4+}$ (**I**) was found to react with H_2O_2 at *ca.* 90°C in 10–20% aqueous H_2O_2. Different products, depending on the reaction times, were isolated and characterized. From the reaction in 10% H_2O_2 at 90°C a bridged peroxo complex **II** was isolated as a pure salt, which was analyzed for $[(NH_3)_4Rh(O_2)(OH)Rh(NH_3)_4](ClO_4)_3$. The yield was rather low (10%) and the proposed µ-peroxo-µ-hydroxo structure is at present tentative. A detailed report on this complex and its chemical and structural properties will appear in a forthcoming paper.

During the reaction between the diol **I** and H_2O_2, a vigorous evolution of O_2 was always observed in the early stage of the reaction (first 60 sec). Subsequent addition of H_2O_2 did not produce a similar effect. Also a drastic color change was observed during the initial stage: after approximately 20 sec the color of the reaction mixture changed from yellow to intense reddish-brown and again became bright yellow after 60 sec. These strongly colored intermediates are probably associated with the disproportionation of H_2O_2, but the nature of these intermediates is at present unknown.

As shown in *Eqn. 1* formation of **II** produces acid and the observation that the reaction mixture becomes basic (pH 8) implies that reaction (*1*) is accompanied by at least one other and acid-consuming reaction. The diol itself can react with acid [11],

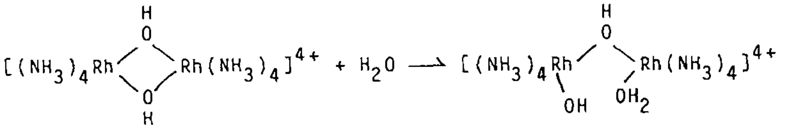


(1)



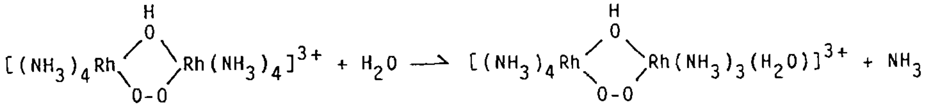
(2)

Eqn. 2, but since the product **III** has $\mathrm{p}K_{a1} = 3.4$ (1M $NaClO_4$, 25 °C) this reaction can not account for the observed increase in pH. Loss of NH_3 from **I** during the reaction can be ignored, as we found that when an aqueous solution of **I** was heated to 98 °C for 3 min, the dominant reaction was hydroxo-bridge cleavage giving **IV** *(Eqn. 3),* as described previously for room temperature [11], and loss of NH_3 was negligible. It is, therefore, assumed that the pH increase is due to loss of NH_3 from the peroxo-bridged complex **II** rather than from the diol **I** as shown in *Eqn. 4.* According to *Eqn. 1* and *4* the yield of **II** should decrease with increasing reaction time, and at the same time the yield of the asymmetrical peroxo-bridged complex **V**, should increase. This agreed with the experiment, samples of **V** as the perchlorate salt were isolated when the reaction with peroxide was performed at 92–93 °C for 6 min. This new peroxo-bridged complex was reprecipitated to give a pure fraction in a low yield (2%) which was analyzed as $[(NH_3)_4Rh(OH,O_2)Rh(NH_3)_3(H_2O)](ClO_4)_3$ (**V**). Its identity and the peroxo-bridged configuration were established by X-ray single-crystal structure analysis (see *Fig. 1* and *Table 1*).



I **IV**

(3)



(4)

II **V**

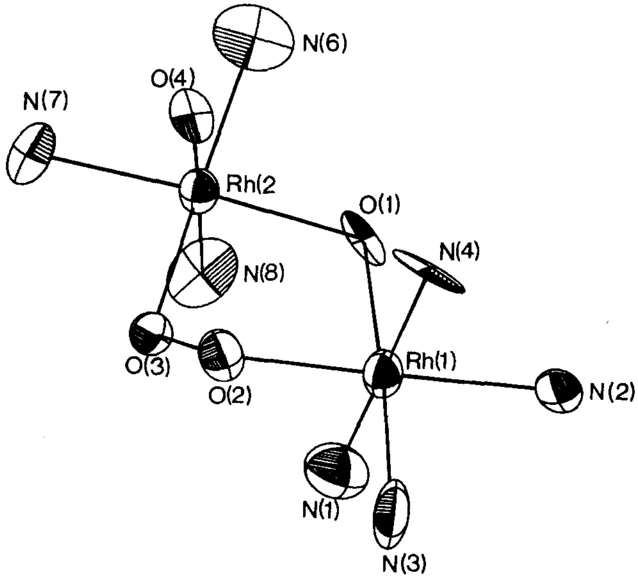


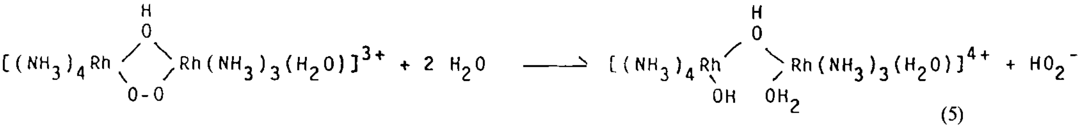
Fig. 1. *ORTEP drawing of structure* V

Table 1. *Bond Distances and Selected Bond Angles of* V *and* VII *and their Standard Deviations* (the numbering scheme is that of the *Figures*)

Atoms	Distance [Å]		Atoms	Angle [°]	
	V	VII		V	VII
O(2)–O(3)	1.489(23)	1.322(18)	Rh(1)–O(1)–Rh(2)	115.4(8)	113.7(3)
Rh(1)–O(1)	2.041(21)	2.034(18)	Rh(1)–O(2)–O(3)	110.1(10)	124.1(10)
Rh(1)–O(2)	1.982(16)	1.970(12)	Rh(2)–O(3)–O(2)	110.5(11)	118.7(10)
Rh(1)–N(1)	2.069(21)	2.177(22)	O(1)–Rh(1)–O(2)	87.7(7)	91.4(5)
Rh(1)–N(2)	2.102(18)	2.071(18)	O(1)–Rh(2)–O(3)	87.2(8)	91.6(5)
Rh(1)–N(3)	2.070(26)	2.007(18)	N(2)–Rh(1)–N(1)	93.2(8)	85.5(8)
Rh(1)–N(4)	2.102(22)	2.098(16)	N(2)–Rh(1)–N(3)	90.3(9)	95.0(7)
Rh(2)–O(1)	2.039(19)	2.039(19)	N(2)–Rh(1)–N(4)	89.6(8)	88.0(7)
Rh(2)–O(3)	1.975(20)	2.035(14)	N(6)–Rh(2)–O(4)	91.6(9)	92.0(6)
Rh(2)–O(4)	2.091(19)	2.055(15)	N(6)–Rh(2)–N(7)	90.9(11)	87.2(7)
Rh(2)–N(6)	2.119(26)	2.081(18)	N(6)–Rh(2)–N(8)	89.1(10)	85.3(6)
Rh(2)–N(7)	2.086(26)	2.135(19)			
Rh(2)–N(8)	2.053(23)	2.081(15)			

The first ligand field band of **V** is obscured by a very intense charge-transfer band $(\varepsilon, \lambda)_{max} = (4200, 286)$, as also observed in corresponding Co(III) species [7] [9] [15–17].

Reaction times longer than *ca.* 6 min did not increase the yield of **V** due to further decomposition. When the mixture was kept at 90 °C for 18 min, decomposition of **V** was almost complete and the reaction mixture contained several products of which a complex tentatively assigned as **VI** in *Eqn. 5* was isolated as a perchlorate salt.

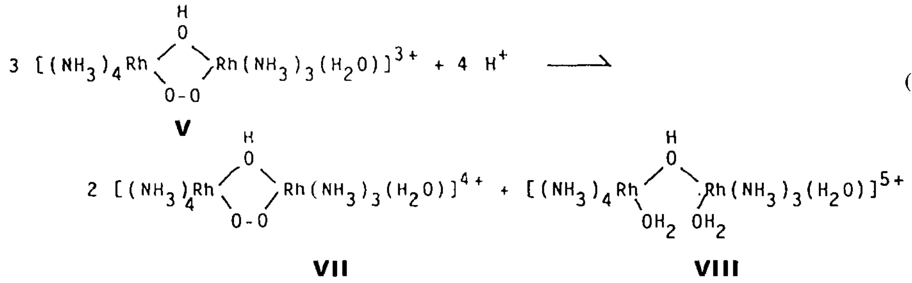


$$[(NH_3)_4Rh\overset{\overset{\text{H}}{\text{O}}}{\underset{\text{O-O}}{\diagup\diagdown}}Rh(NH_3)_3(H_2O)]^{3+} + 2\ H_2O \longrightarrow [(NH_3)_4Rh\overset{\overset{\text{H}}{\text{O}}}{\underset{\text{OH}\ \ \text{OH}_2}{\diagup\diagdown}}Rh(NH_3)_3(H_2O)]^{4+} + HO_2^- \qquad (5)$$

V **VI**

The formation of **VI** *(Eqn. 5)*, has been considered as a decomposition product of **V** but since the product solution does contain other yet unidentified complexes, it is quite possible that decomposition of **V** also occurs by reactions involving the cleavage of the hydroxo-bridge, which is the predominant route in the decomposition of µ-hydroxo-µ-peroxo-Co(III) complexes such as *e.g.* Δ,Δ-$[(en)_2Co(O_2,OH)Co(en)_2]^{3+}$ [9] [17]. In *Eqn. 5*, **VI** has been given as a singly-bridged cation, but a doubly-bridged structure is also in agreement with the present data. The UV spectrum of **VI** has $(\varepsilon, \lambda) = (268,326)_{max}$; $(497,270)_{sh}$ which shows that the peroxo group no longer is bound to Rh(III). The corresponding octaammine complex **IV** has $(\varepsilon, \lambda)_{max} = (381,338)$; $(432,275)_{sh}$ [11].

As mentioned above, **V** is decomposed in aqueous solution within minutes at 90 °C, but at 25 °C it is stable for hours at pH 7. In acid solution, **V**, within minutes, undergoes a disproportionation reaction producing superoxide coordinated to Rh(III) *(Eqn. 6)*. The rate of this disproportionation and also the yield of the red superoxide complex **VII** depended on the total concentration of dimer, and other reactions are obviously also taking place.



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The red superoxo complex **VII** was isolated as a perchlorate salt together with yellow crystals of a complex which in *Eqn. 6* tentatively has been formulated as **VIII**, *i.e.* the acid form of complex **VI.** Reprecipitation with HNO_3 of the mixture containing **VII** and **VIII** gave a red nitrate salt of $[(NH_3)_4Rh(OH)(O_2)Rh(NH_3)_3(H_2O)](NO_3)_4$ (**VII**) which was characterized by a single-crystal structure analysis (see *Fig. 2* and *Table 1*). The absorption spectrum of **VII** shows maximum at $\lambda = 504$ nm, ($\varepsilon = 685$). A similar and characteristic absorption band around 700 nm has been observed for the corresponding superoxide complexes of Co(III) [7] [9] [18].

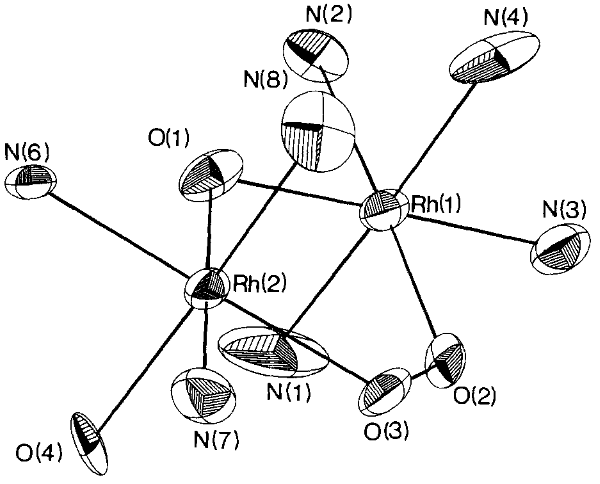
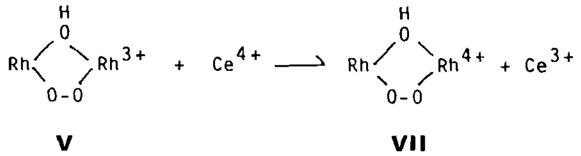


Fig. 2. *ORTEP drawing of structure* VII

Qualitative studies showed that **VII** could be obtained also by oxidation of **V** with Ce^{4+} *(Eqn. 7)*. The reaction is quantitative and very fast. ($t_{1/2} < 1$ sec for $[Ce^{4+}] \approx 10^{-2}$M and $[Rh] \approx 10^{-3}$M.) A similar rapid formation of superoxide complexes has been observed in the corresponding Co(III) chemistry, where *e.g.* $[(NH_3)_4Co(O_2,OH)Co(NH_3)_4]^{3+}$



(7)

Table 2. *Comparison of Bond Distances and Bond Angles in the Bimetallic Ring of Co(III)- and Rh(III)-μ-peroxo-μ-hydroxo- and μ-superoxo-μ-hydroxo Complexes and Comparison of Dihedral Angles in the M–O–O–M Unit* (the numbering scheme is that of the *Figures*)

Compound[a])	Bond distances [Å]	Bond angles [°]	Dihedral angles [°]
	(a) M(1)–O(1)	(f) M(1)–O(2)–O(3)	(1) M(1)–O(2)–O(3)–M(2)
	(b) M(1)–O(2)	(g) M(2)–O(3)–O(2)	
	(c) M(2)–O(1)	(h) M(1)–O(1)–M(2)	
	(d) M(2)–O(3)	(i) O(1)–M(1)–O(2)	
	(e) O(1)–O(2)	(k) O(1)–M(2)–O(3)	
Peroxo complexes			
$[(tren)Co(O_2,OH)Co(tren)]^{3+}$	(a) 1.970(23)	(f) 112.1(12)	(1) 60.7
	(b) 1.857(18)	(g) 109.4(14)	
	(c) 1.872(23)	(h) 117.9(12)	
	(d) 1.869(23)	(i) 85.5(9)	
	(e) 1.462(26)	(k) 87.9(10)	
rac-$[(en)_2Co(O_2,OH)Co(en)_2]^{3+}$	(a) 1.955	(f) 110.0	(1) 60.7
	(b) 1.860	(g) 111.6	
	(c) 1.943	(h) 114.4	
	(d) 1.865	(i) 88.7	
	(e) 1.465	(k) 88.7	
meso-$[(en)_2Co(O_2,OH)Co(en)_2]^{3+}$	(a) 1.934(10)	(f) 108.3(6)	(1) 64.5(5)
	(b) 1.880(8)	(g) 110.2(6)	
	(c) 1.919(8)	(h) 117.2(4)	
	(d) 1.866(10)	(i) 87.4(4)	
	(e) 1.460(13)	(k) 85.0(4)	
rac-$[(dmtad)Co(O_2,OH)Co(dmtad)]^{3+}$	(a) 1.987(19)	(f) 107.3(10)	(1) 67.9(6)
	(b) 1.843(15)	(g) 109.9(10)	
	(c) 1.934(19)	(h) 115.8(5)	
	(d) 1.946(19)	(i) 87.3(6)	
	(e) 1.429(20)	(k) 84.6(6)	
$[(NH_3)_5Rh(O_2,OH)Rh(NH_3)_4(OH_2)]^{3+}$	(a) 2.041(21)	(f) 110.1(10)	(1) 62.2(5)
	(b) 1.982(16)	(g) 110.5(11)	
	(c) 2.039(19)	(h) 115.4(8)	
	(d) 1.975(20)	(i) 87.7(7)	
	(e) 1.489(23)	(k) 87.2(8)	
Superoxo complexes			
rac-$[(en)_2Co(O_2,OH)Co(en)_2]^{4+}$	(a) 1.901	(f) 119.7	(1) 22.0
	(b) 1.872	(g) 120.0	
	(c) 1.917	(h) 117.4	
	(d) 1.875	(i) 90.1	
	(e) 1.339	(k) 89.7	
$[(NH_3)_4Rh(O_2,OH)Rh(NH_3)_3(OH_2)]^{4+}$	(a) 2.034(18)	(f) 124.1(10)	(1) 7.1
	(b) 1.970(12)	(g) 118.7(10)	
	(c) 2.039(19)	(h) 113.7(3)	
	(d) 2.035(14)	(i) 91.4(5)	
	(e) 1.322(18)	(k) 91.6(5)	

[a]) References see [9].

gives a superoxo complex with Ce^{4+} or other one-electron oxidants. Disproportionation reactions analogous to *Eqn. 7* have also been reported for some Co(III) complexes [9], but not for μ-hydroxo-μ-peroxo-Co(III) complexes, and in the case of *e.g.* $[(en)_2Co(O_2,OH)Co(en)_2]^{4+}$ the reaction only proceeds in the presence of a catalyst such as Cl^- [19].

The O–O distance of 1.489(23) Å marks **V** as a true peroxo complex and **VII** shows the characteristic O–O distance of the superoxo analogue (1.322(18)). The dihedral angle of the Rh–O–O–Rh group is 62° in the case of the peroxo compound which is in the range of the observed values of Co(III)complexes. The bimetallic ring in the μ-superoxodirhodium(III) compound is closer to planarity with a dihedral angle of 7°. As in Co compounds, the octahedra are somewhat distorted with bond angles N–Rh–N and N–Rh–O(4) between 85 and 95° and 87 and 93°, respectively. *Table 1* shows a comparison between μ-dioxygen-dicobalt(III) and μ-dioxygen-dirhodium(III) complexes.

Owing to the low yield in the synthesis of **V** and the cost of rhodium, only minor amounts of the complexes **V** and **VII** have been available, and this prevented further characterization of the compounds. To some extend the same kind of problem also arises with the corresponding octaammine complexes, although, as mentioned, these complexes can be made in a somewhat larger yield. Clearly, these preparative problems are essentially due to the side reactions involving hydrolysis of coordinated NH_3. Similar complications are less likely to occur in the corresponding bis(ethylenediamine) systems and this aspect is currently being explored.

Experimental. – *Preparative Methods.* $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4$ (**I**) was synthesized following the methods in [11] [20]. All other chemicals were of analytical grade.

*$[(NH_3)_4Rh(OH)(O_2)Rh(NH_3)_3(H_2O)](ClO_4)_3$ (Tetraammine-μ-hydroxo-μ-peroxo-*fac*-triammineaqua-dirhodium(III) Perchlorate* (**V**)). A soln. of $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4$ (1.0 g, 0.0012 mol) in a mixture of H_2O (2 ml) and 30% H_2O_2 (7 ml) was heated to ca. 95°C. The color of the soln. changed from yellow to brown within the first 20 sec and after *ca.* 1 min the color turned yellow again. During this time a vigorous evolution of O_2 was also observed. After 2 and 4 min, respectively, a further two portions of H_2O_2 (1 ml) were added. The yellow mixture was then cooled to *ca.* 30°, and fractionated precipitation by addition of solid $LiClO_4$ (2 g) gave 3 fractions. The most soluble fraction was reprecipitated from H_2O using solid $LiClO_4$, and this gave *ca.* 20 mg (2%) of a pure peroxo complex. Anal. calc. for $[Rh(NH_3)(H_2O)(O_2)(OH)](ClO_4)_4$: N 14.2, Cl 15.4; found: N 14.4, Cl 16.0. Spectral data in 1M $NaClO_4$: $(\varepsilon, \lambda)_{max} = (4200, 286)$; $(\varepsilon, \lambda)_{min} = (3000, 261)$.

*$[(H_2O)_2(NH_3)_3Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4$ (*fac*-Diaquatriammine-μ-hydroxo-tetramminehydroxo-dirhodium(III) Perchlorate* (**VI**). $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4$ (0.5 g, 0.00062 mol) was reacted with H_2O_2 as described above but the mixture was kept for 18 min at 90°. Addition of solid $LiClO_4$ (1 g) and cooling in ice gave a yellow precipitate, which was filtered off, washed with 96% EtOH and dried in the air. This crude product (0.2 g) was reprecipitated from H_2O (4 ml). After two further reprecipitations a small amount (60 mg, 12%) of an almost pure salt was obtained. Anal. calc. for $[Rh_2(NH_3)_7(OH)_2(H_2O)_2](ClO_4)_4$: N 12.4, Cl 17.9; found: N 12.8, Cl 17.7. Spectral data in 1M $NaClO_4$: $(\varepsilon, \lambda)_{max} = (268,326)$ and $(\varepsilon, \lambda)_{sh} = (496,270)$.

*$[(NH_3)_4Rh(OH)(O_2)Rh(NH_3)_3(H_2O)](NO_3)_4$ (Tetraammine-μ-hydroxo-μ-superoxo-*fac*-aquatriammine-dirhodium(III) Nitrate* (**VII**)). Crude perchlorate salt of the peroxo complex (*ca.* 10 mg) was dissolved in a few drops of 1M $HClO_4$. The color of the solution turned from yellow to red within minutes. After 1 h at r.t. a sat. soln. of $NaClO_4$ was added and a mixture of red and yellow crystals precipitated. This precipitate was dissolved in 1M HNO_3. The red soln. was left overnight at r.t., and a few red crystals of the nitrate salt separated. The crystals were characterized by an single-crystal X-ray structure analysis. The minor amounts available of this complex prohibited further characterizations, but spectral data for the cation, $(\varepsilon, \lambda)_{max} = (685,504)$, were obtained by measuring the VIS spectrum of a solution of the peroxo complex in the presence of a slight excess of Ce(IV) at pH ≈ 0.

Crystal Data and Data Collection. Crystallographic data of **V** ($Rh_2Cl_3O_{16}N_7H_{24}$) and **VII** ($Rh_2O_{16}N_{11}H_{24}$) are: monoclinic, space group $P2_1/n$, $a = 12.269(5)$ Å, $b = 10.769(4)$ Å, $c = 15.964(4)$ Å, $\beta = 107.17(3)°$, $D_{obs} = 2.28$, $D_{calc} = 2.276$ gcm^{-3} for $Z = 4$ and orthorhombic $Pna2_1$, $a = 14.997(5)$ Å, $b = 11.952(4)$ Å, $c = 10.489(4)$ Å, $D_{obs} = 2.26$, $D_{calc} = 2.262$ gcm^{-3} for $Z = 4$, respectively. Intensities of 1730 independent reflexions for **V** and 1863 for **VII** were collected ($\theta/2\theta$ scan) in the range of $1 < \theta < 27°$ with a *CAD4 Enraf-Nonius* diffractometer equipped with a fine focus Mo tube and a graphite monochromator to select MoK_α. No correction for absorption was applied.

Solution and Refinement of the Structure. The position of the Rh atoms were determined from a three-dimensional sharpened *Patterson* map. In **VII** (space group $Pna2_1$), the z positional parameter for one of the metals was fixed. Difference *Fourier* maps and subsequent least-squares refinements located the remaining atoms. According to the criterion $F_o > 2\sigma(F_o)$, 1289 reflections for **V** and 1649 reflexions for **VII** were used in the anisotropic refinement steps using unit weights. All parameters converged and the final R-indices are 0.066 for **V** and 0.040 for **VII** ($R = \Sigma||F_o| - |F_c||/|F_o|$) without considering H-atoms. Programs used were developed partly by *G.M. Sheldrick* (SHELX-76) [21] and partly by ourselves. Scattering factors for Rh^{3+} and neutral atoms were those of *Cromer et al.* [22].

Atomic positional and thermal parameters are sent to the Cambridge data base or are available from *M.Z.*

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REFERENCES

[1] *A.M. Michelson, J.M. McCord & I. Fridovich*, eds., 'Superoxide and Superoxide Dismutases', Academic Press, New York, 1977.

[2] *J.V. Baumeister & H.A.O. Hill*, eds., 'Chemical and Biochemical Aspects of Superoxide and Superoxide Dismutases', Elsevier/North Holland, New York, 1980.

[3] *A.G. Sykes*, Adv. Inorg. Bioinorg. Mechanisms *1*, 121 (1982).

[4] *E. Fremy*, Annalen *83*, 227 (1852).

[5] *A. Werner & A. Mylius*, Z. Anorg. Allg. Chem. *15*, 245 (1898).

[6] *A. Werner*, Annalen *375*, 1 (1910).

[7] *A.G. Sykes & J.A. Weil*, Prog. Inorg. Chem. *13*, 1 (1970).

[8] *A.G. Sykes*, Chem. Br. *10*, 170 (1974).

[9] *S. Fallab & P.R. Mitchell*, Adv. Inorg. Bioinorg. Mechanisms, submitted.

[10] *M. Hancock, B. Nielsen & J. Springborg*, Acta Chem. Scand., Ser. A *36*, 313 (1982).

[11] *F. Christensson & J. Springborg*, Acta Chem. Scand. (1984), submitted.

[12] *F. Christensson & J. Springborg*, Acta Chem. Scand., Ser. A *36*, 21 (1982).

[13] *J. Springborg & H. Toftlund*, Acta Chem. Scand., Ser. A *33*, 31 (1979).

[14] *J. Springborg*, Acta Chem. Scand. Ser. A *32*, 231 (1978).

[15] *G. McLendon & A.E. Martell*, Co-ord. Chem. Rev. *19*, 1 (1976).

[16] *A.B.P. Lever & H.B. Gray*, Acc. Chem. Res. *11*, 348 (1978).

[17] *S. Fallab, M. Zehnder & U. Thewalt*, Helv. Chim. Acta *63*, 1491 (1980).

[18] *V.M. Miskowski, B.D. Santarsiero, W.P. Schaefer, G.E. Ansok & H.B. Gray*, Inorg. Chem. *23*, 172 (1984).

[19] *R. Davies & A.G. Sykes*, J. Chem. Soc. (A) *1968*, 2840.

[20] *M.P. Hancock*, Acta Chem. Scand., Ser. A *33*, 499 (1979).

[21] *G.M. Sheldrick*, Göttingen, unveröffentlicht.

[22] *D.T. Cromer & J.B. Mann*, Acta Crystallogr., Sect. A *24*, 321 (1968).