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A Paramagnetic Oxygen Adduct Compound of Rhodium(III)

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Solutions of $[Rh(bpy)_2]^+$ produced by chemical[2a] or electrochemical reduction[2b,3] in acetonitrile are extremely sensitive to air; furthermore, the purple Rh(I) solid when isolated changes to a yellow-brown mixture upon exposure to air. The chemical redox studies of Martin et al.[2a] in water and the work of Miller and Oliver[4] suggest that the yellow-brown solution contains as the dominant product a diamagnetic Rh(III) compound, likely a $[Rh(bpy)_2(H_2O)_2]^{3+}$ species. However, we have observed that chlorine gas bubbled through an acetonitrile solution of $[Rh(bpy)_2]^+$ produces a deep red solution that gives a strong and persistent electron spin resonance signal at room and liquid nitrogen temperature.

Oxygen adduct compounds of Rh(I) with diphosphine ligands are reported by Vaska and co-workers[5] and Gray and co-workers,[6] but in all cases the materials produced are diamagnetic. Alternatively, rather than formation of an O_2 adduct with Rh(I), Rh(II) complexes can be produced by exposure to air. However, Rh(II) typically forms dimer species in solution as for $Rh_2(OAc)_4$ in water.[7,8] Examples of stable monomeric Rh(II) complexes are few—a phosphine adduct[9,10] of Rh whose ESR spectra has been reported and a unique square-planar complex of Rh(II) with the bidentate maleonitrile ligand.[11] Pulse radiolysis[12] in water solvent of a series of $[Rh(NH_3)_5X]^{n+}$ complexes, where X = Cl^-, Br^-, or H_2O and n = 2 or 3, produces a monomeric Rh(II) complex that is very reactive in water to ligand displacement and disproportion reactions.

In contrast, monomeric d^7 cobalt(II) compounds are known and a number of Co(II) compounds have been observed to produce paramagnetic oxygen adducts[13-15] in which the unpaired spin is localized on the oxygen. Such an oxygen species is best considered as a superoxide with the $Co^{III}\cdot O_2^-$ moiety then resulting from an intramolecular redox process.[14] Dimeric oxygen adduct compounds of cobalt(III)[16-20] containing two cobalt ions per oxygen molecule are well-known and can be formulated as containing oxygen as a peroxide, i.e., O_2^{2-}. Such materials when oxidized by a one-electron oxidizing agent as Cl_2 also produce a paramagnetic complex best formulated as containing a superoxide species, O_2^-.[19,20]

Therefore, we undertook characterization of the paramagnetic material resulting from the Cl_2 oxidation of the diamagnetic product produced by air oxidation of $[Rh(bpy)_2]^+$ to determine if Rh(II) or superoxo complexes had been produced. The synthesis, analysis, and spectral and some chemical properties of the brown diamagnetic precursor and the bright red paramagnetic complex are reported, and a simple reaction sequence is proposed to rationalize these data.

Experimental Section

Materials. The complexes were synthesized from $RhCl_3\cdot 3H_2O$ (Engelhard) and 2,2′-bipyridine (Aldrich) used as received. The acetonitrile (Fisher reagent grade) and tetraethylammonium perchlorate (Eastman White Label) were further purified and dried by methods reported previously.[2b]

Syntheses. Preparation of $[Rh(bpy)_3](ClO_4)_3\cdot 2H_2O$[21] and of $[Rh(bpy)_2]ClO_4\cdot 3H_2O$[1] have been described elsewhere. The diamagnetic rhodium dimer, I, was prepared as follows: 1.2 g of $[Rh(bpy)_2]ClO_4\cdot 3H_2O$ was dissolved in 50 mL of acetonitrile, and the solution was left in the presence of dry air for 24 h while it turned completely from purple-violet as it was initially to a yellow-brown color. (*Caution*! Too rapid exposure to air or pure O_2 results in a fire and occasionally an explosion.) After air evaporation, the solution was decanted from the yellow insoluble Rh(III) complex which was discarded. This process was repeated until no more yellow solid was produced from the solution. The brown solution remaining was then slowly evaporated to dryness to obtain ~0.2 g of the brown compound (I). This compound (I) was further purified on a polyamide column using acetonitrile as eluent. Analysis indicated some residual impurity.

Anal. (Galbraith Laboratories, Knoxville, Tenn.) Calcd for $[Rh_2(bpy)_4(CH_3CN)_2][ClO_4]_4$: C, 40.31; H, 2.90; N, 10.69; Cl, 10.82; O, 19.53; Rh, 15.71. Found: C, 41.60; H, 3.50; N, 9.63; Cl, 11.79; O, 21.23.

The red paramagnetic rhodium dimer (II) was prepared by one of the following methods.

A. Chemical Preparation. One-tenth gram of I dissolved in acetonitrile was treated with chlorine gas in the presence of air for 10 min, forming a deep red solution. After the acetonitrile was evaporated, a red crystalline compound (II) was obtained. This material (II) is sensitive to traces of water and base. It was further purified by bidimensional TLC using acetonitrile eluent. Some decomposition occurred as a result of the water in the plate substrate.

Anal. (Galbraith Laboratories, Knoxville, Tenn.) Calcd for $[Rh_2(bpy)_4Cl_2O_2][ClO_4]_3$: C, 39.00; H, 2.60; N, 9.10; Cl, 14.40; O, 18.18; Rh, 16.71. Found: C, 38.84; H, 2.99; N, 9.29; Cl, 14.08; O, 20.96.

Attempts to obtain I and II from $[Rh(bpy)_2]^+$ materials produced by reduction of $[Rh(bpy)_2Cl_2]X$ (where X^- = Cl^-, NO_3^-, or BF_4^-) were unsuccessful.

B. Electrochemical Preparation. A 5×10^{-3} M $[Rh(bpy)_3](ClO_4)_2\cdot 2H_2O$ solution in acetonitrile (supporting electrolyte 2.5×10^{-1} M) was completely electrolyzed at −1.2 V, where both cyclic voltammetry[3] and coulometric measurements (n = 1.9 electrons) indicated the formation of $[Rh(bpy)_2]^+$. This solution left in dry air turns from deep purple-violet to yellow-brown. Subsequently, Cl_2 gas was bubbled through the solution for 10 min, producing a bright red solution. The ESR spectrum is identical with that obtained from the red complex (in acetonitrile) prepared chemically.

Results

Neither the solution of the starting material $[Rh(bpy)_2]^+$ nor the solution of the brown rhodium dimer, I, gave an ESR signal at room or liquid nitrogen temperatures.

The red rhodium dimer, II, obtained from either the chemical or the electrochemical preparation gave a signal at room temperature and an anisotropic spectrum at 77 K (Figure 1). Pure solid samples of II gave g factors identical with those of the solution. Solution samples allowed to stand in air give in addition to the spectrum of II a superimposed spectrum (IIa) due to a second species (Figure 1). Subsequent addition of water to dry samples of II verified that IIa results from reaction of water with II. Addition of large quantities of H_2O, NH_3, or pyridine causes destruction of II and loss of the paramagnetism. The dry red paramagnetic complex, II, is stable in solution or as a solid indefinitely since the characteristic ESR signal can be measured after a period of months.

The experimental **g** tensor values are tabulated in Table I along with g_{iso} calculated from eq 1. The analysis of the 77

$$g_{iso} = {}^1/_3(g_1 + g_2 + g_3) \qquad (1)$$

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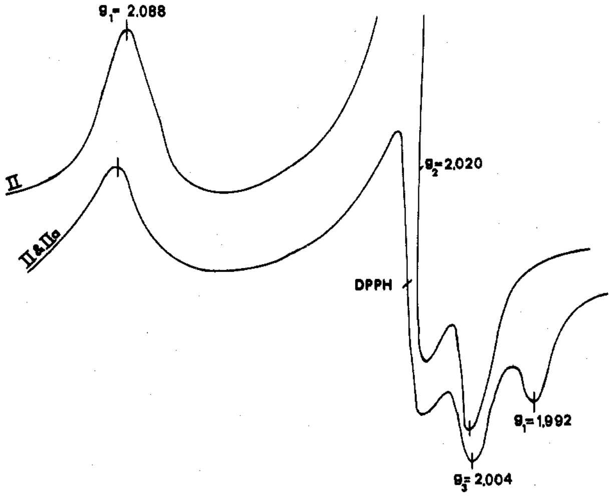

Figure 1. ESR spectra of rhodium–oxygen adducts.

Table I. g Tensor Components for Superoxo Complexes

Complex[a]	g_1	g_2	g_3	g_{iso} Calcd	g_{iso} Exptl
II	2.088_8	2.020_9	2.004_5	2.038_1	2.040_3
IIa	2.088_8	2.020_9	1.992_6	2.034_1	2.032_8
$[Co(en)_2]_2O_2^{5+}$	2.079	2.023	2.010	2.037	
$Co(acacen)H_2O{\cdot}O_2$	2.087_8	1.996_6	1.966_6	2.027_0	

[a] en = ethylenediimine, acacen = *N*, *N'*-ethylenebis(acetylacetonimine).

K spectra was accomplished using the method of Kneubuhl.[22]

Temperature-dependent ESR (25–150 °C) indicates that the signal remains strong until 135 °C where it disappeared completely and irreversibly. To verify this result, the red paramagnetic rhodium dimer (II) was slowly heated in a differential scanning calorimetry apparatus where a thermal transition was found at 135 °C. The yellow-brown solid remaining after heating was identified as I by redissolving it in aerated acetonitrile and treating with Cl_2 gas to produce a paramagnetic red solid having the ESR signal characteristic of II. This paramagnetic solution upon evaporation to dryness and heating to 135 °C again gave the diamagnetic brown solid which upon treatment with Cl_2 again gave the red solid (II). This cycle (Figure 2) was repeated three to four times with a moderate loss of the ESR intensity of the paramagnetic II material.

Magnetic susceptibility measurements of the red paramagnetic dimer (II) at room temperature gave $\mu_{eff} = 1.80$ corresponding to one unpaired electron.

Discussion

The characterization of the two materials (I and II) is primarily concerned with three questions: (1) Are the materials O_2 adducts or simple oxidation products? (2) What are the formal oxidation states of the materials? (3) Are the materials monomeric or dimeric?

The elemental analysis of the brown diamagnetic solid (I) is best fit by the empirical formula $[Rh(bpy)_2][ClO_4]_2$; therefore the material apparently is not an O_2 or O_2^{2-} adduct but does contain Rh(II). The O_2^- species in monomeric Co(III) adducts has an IR absorption in the ~1120-cm^{-1} region;[13] however, here ClO_4^- anion absorption overlaps this region. The remainder of the spectrum is characteristic of the bpy absorption found in $[Rh(bpy)_3]^{3+}$ and $[Rh(bpy)_2Cl_2]^+$. The electronic absorption spectra show broad structureless visible spectra and characteristic UV spectra observed for bpy complexes. Further, the luminescence which is typical of Rh(III) complexes could not be detected for this material. Both ESR and magnetic susceptibility data indicate that the substance has no unpaired electrons as expected for *dimeric* Rh(II).

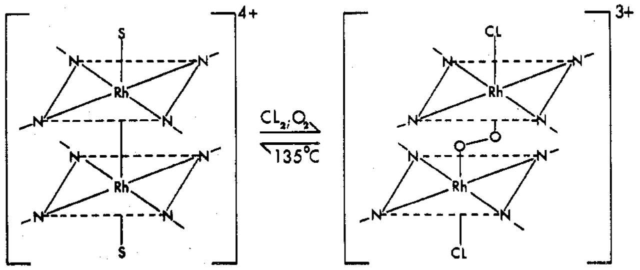

Figure 2. Role of Cl_2 and O_2 in production of superoxo species (S = CH_3CN or Cl^-).

The IR spectrum of the red paramagnetic solid (II) produced by Cl_2 oxidation was also of limited use because of the presence of ClO_4^- anions. (The hygroscopic character of both materials and the attendant slow decomposition of the red material by H_2O precluded Cl^- ion exchange of these materials.) Electronic absorption spectra are similar to those of the brown precursor with the absorption in the visible at slightly longer wavelengths. Again, that emission was not observed for this red material implies the absence of the common Rh(III) species. The magnetic susceptibility of the red material (II) indicates one unpaired electron per two Rh ions and the ESR spectra at room and liquid nitrogen temperature indicate $S = {}^1/_2$ and gives values for (g_{soln}), g_z, g_x, and g_y almost identical with those reported[14,23] for monomeric and dimeric $Co^{III}{\cdot}O_2^-$ adducts (Table I). Moreover, Addison and Gillard[24] have reported the isolation of superoxo dimers of Rh(III) having the general formula $[ClL_4Rh{\cdot}O_2{\cdot}RhL_4Cl]Y_3$ with L = pyridine or γ-picoline and Y = anion. An analogous species with H_2O substituting for Cl^- is also reported. The species having Cl^- ligands are reported to give a single-line solution resonance at $g = 2.019$, somewhat lower than that reported here. There, as in our case, the small magnitude of the rhodium nuclear moment for ^{103}Rh (100% abundant) precludes observation of hyperfine splitting.

The elemental analysis data here indicate an empirical formula of $[Rh(bpy)_2Cl]_2O_2[ClO_4]_3$. Therefore, the red material is identified as a dimeric superoxo, O_2^- adduct of Rh(III). The sensitivity of the complex to base (H_2O, pyridine, and NH_3 all slowly decompose the complex) suggests a square-planar orientation of the bpy ligands analogous to the structure of the monomeric Co(III) complex and is consistent with the pseudo-square-planar structure of the $[Rh(bpy)_2{}^+]$ species postulated earlier.[3] Recently, Endicott and co-workers[12] have produced by pulsed radiolysis a transient species that they identify as an O_2^- adduct of Rh(III), i.e., $[O_2Rh(NH_3)_4H_2O]^{2+}$ therefore suggesting that the formation of $Rh^{III}{\cdot}O_2^-$ adducts may be a general phenomenon.

The anisotropic character of the *g* factor implies that the oxygen–oxygen bond is not symmetrically arranged relative to the plane of the bpy ligands. Hence, the so-called bent-adduct structure[14] is likely rather than the symmetric end-to-end or side-on bonding of the O_2 molecule to the Rh ions. Indeed, identification of g_1, the largest of the tensor components, as g_z, the tensor component having the direction perpendicular to the bpy planes, is consistent with the interpretation of the spectrum for species IIa. Displacement of Cl^- by H_2O would only be expected to modify the tensor component perpendicular to the bpy plane.

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Registry No. I, 66482-85-7; II, 66610-90-0; $[Rh(bpy)_2]ClO_4{\cdot}3H_2O$, 52382-28-2; $[Rh(bpy)_3](ClO_4)_3$, 28018-83-9.

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^{1}H and ^{31}P Nuclear Magnetic Resonance Spectroscopy of Substituted Phosphinito and Phosphito Complexes of Platinum(II). Analysis of the ^{31}P Spectrum of an AA′BB′-AA′BB′X Spin System Showing Second-Order Effects in Coupling with ^{195}Pt[1]

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Dimethyl phosphite and diphenylphosphinous acid can exist in tautomeric forms where the phosphorus is either tricoordinate or tetracoordinate. In the presence of metal ions, coordination can occur via oxygen or phosphorus atoms giving the ligand ambidentate character. Both ^{1}H NMR spectroscopy and ^{31}P NMR spectroscopy have been used to investigate the coordination of metal ions to these compounds.[2,3] With platinum metal ions such as Pt(II), coordination occurs through phosphorus, and the kinetically inert complexes can be readily isolated in a pure state. This paper reports and discusses the ^{1}H and ^{31}P NMR spectra of the series of complexes $Pt[OPR_2]_2[HOPR_2]_2$ (R = OMe, OPh, Ph),[4,5] $PtX[OPR_2][HOPR_2]L$ (X = H, R = Ph, L = $PMePh_2$; X = Cl, R = OMe, L = PEt_3, PPh_3; X = Cl, R = OPh, L = PEt_3),[5-7] and $Pt[OPR_2]_2[L\text{-}L]$ (R = OMe, L-L = dppe, diars).[5,8] Finally we include NMR spectral work on complexes having BF_2 or a second metal ion coordinated through the oxygens. Details of the electronic and EPR spectra of these complexes have been previously published[9] but not our work on the ^{1}H and ^{31}P NMR spectra of these substituted phosphinito or phosphito complexes.

The ^{31}P NMR data have been measured on a Fourier transform instrument with broad-band proton decoupling. This technique allows unambiguous assignments for the chemical shifts of the separate inequivalent nuclei and also for the coupling constants $^1J(\text{PPt})$ and $^2J(\text{PPt}P)$. In an earlier study of the ^{1}H and ^{31}P NMR spectra of some of these compounds using continuous-wave instrumentation, it was possible to resolve and assign some of these values, but the use of broad-band proton decoupling has allowed complete analysis of the ^{31}P NMR spectrum of a compound of type $[\{Pt[OP(OMe)_2]_2dppe\}_2Zn][ClO_4]_2$ to be achieved for the first time. The spectrum is a composite of an AA′BB′ spin system at two-thirds of the total intensity and an AA′BB′X (X = ^{195}Pt) spin system contributing the additional one-third. The analysis has allowed evaluation of the chemical shift and coupling constant data to be made and has verified that second-order effects due to coupling with ^{195}Pt must be taken into consideration when such spectra are analyzed.

Figure 1. ^{1}H NMR spectrum of $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$.

Results and Discussion

^{1}H NMR Spectra. The compound $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$ has been prepared by Troitskaya et al. from the hydrolysis of trimethyl phosphite in the presence of salts of tetrachloroplatinate(II).[4a,b] The complex is a diprotic acid which shows two inflections in a conductivity titration against added base after the addition of first 1 and then 2 equiv of base.[9] The protons can be considered to be symmetrically bonded between paris of oxygens, and the ^{1}H NMR spectrum shows a symmetric pattern centered 3.60 ppm downfield of Me_4Si (Figure 1). The pattern is complex because of coupling to ^{31}P and ^{195}Pt and also because of virtual coupling between $^3J(\text{POC}H)$ and $^2J(P\text{Pt}P)$.

Complexes $PtCl[OP(OMe)_2][HOP(OMe)_2]L$ (L = PEt_3, PPh_3) show separate resonances for methoxy protons on the dimethyl phosphito-*P* group trans to chloride or phosphine. The low-field line at $\delta = 3.720$ in the triethylphosphine complex has been assigned to the dimethyl phosphite trans to the phosphine,[5,10] with the high-field line at $\delta = 3.570$ being the dimethyl phosphite ligand trans to chloride.[11] Addition of triethylamine to a solution of the compound $PtCl[OP(OMe)_2][HOP(OMe)_2]PEt_3$ causes progressive shift of the methoxy resonances to a limiting pair of $\delta = 3.685$ and 3.645. These shifts do not change on lowering the temperature to −50 °C and represent an upfield shift from the free acid for the

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