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Dioxygen Complexes of Rhodium Porphyrins

Sir:

A previous communication reported on the preparation of a paramagnetic ($S = 1/2$) complex formulated as rhodium(II) tetraphenylporphyrin (Rh^{II}TPP).[1] The report that this apparently low spin (d^7) rhodium(II) complex failed to form a dioxygen complex seemed anomalous in view of the fact that dioxygen complex formation is a general feature of low spin d^7 cobalt(II) complexes such as Co^{II}TPP.[2-5] Furthermore, the limited observations available on authentic Rh(II) species such as $Rh(NH_3)_4^{2+}$ indicates that dioxygen complex formation is an important feature of Rh(II) chemistry.[6] We report herein on the reaction of $(RhOEP)_2$ (OEP = octaethylporphyrin) with molecular oxygen to form RhOEP(O_2) and on a reexamination of the complex previously formulated as Rh^{II}TPP.

$(RhOEP)_2$ has recently been prepared from the hydrido complex RhOEP(H).[7] We have modified this procedure by recognizing that RhOEP(H) can be easily photolyzed in toluene solution to quantitatively produce $(RhOEP)_2$ and H_2. $(RhOEP)_2$ reacts rapidly with NO to form RhOEP(NO) (ν_{NO} 1630 cm^{-1}) in analogy to cobalt(II) porphyrins (ν_{NO}(CoTPP(NO)) 1690 cm^{-1}).[2,8] When dry oxygen is allowed to slowly diffuse into a cold toluene solution (−80 °C) of $(RhOEP)_2$, electronic spectral changes occur (Figure 1) accompanied by the appearance of an EPR spectrum ($\langle g \rangle = 2.032$). Freezing this toluene solution (−160 °C) results in an EPR spectrum with three g values ($g_1 = 2.100$, $g_2 = 2.010$, $g_3 = 1.988$) characteristic of an end-on coordinated dioxygen species similar to HO_2 and CoTPP(O_2)[2,3] (Figure 2). The dioxygen complex is formulated as RhOEP(O_2) and described as a Rh(III) complex. RhOEP(O_2) forms 1:1 complexes with donor molecules such as trialkylphosphines and phosphites as evidenced by the ^{31}P hyperfine splitting in the EPR (Figure 2). These EPR observations on RhOEP(O_2) species closely parallel results for CoTPP(O_2) complexes[2,9] (Table I, Figure 2).

Table I. EPR Parameters for Dioxygen Complexes of Rhodium(II) and Cobalt(II) Porphyrins[a]

complex	g_1	g_2	g_3	$\langle g \rangle$
RhOEP(O_2)	2.100	2.010	1.988	2.030
RhTPP(O_2)	2.084	2.025	1.993	2.033
CoTPP(O_2)(pyridine)[6b,c]	2.072	2.003	2.003	2.026
RhOEP(O_2)(piperidine)	2.094	2.010	1.996	2.031
RhOEP[$(BuO)_3P$](O_2)	2.084 (22)[c]	2.004 (22)[c]	2.000 (24)[d]	2.032 (23.7)[d]
CoTPP[$(BuO)_3P$](O_2)[e]				2.016 (31.4)[d]

[a] g values are ±0.001. [b] Reference 3. [c] Reference 6. [d] Values in parentheses are the ^{31}P hyperfine coupling constants in gauss. [e] Reference 9.

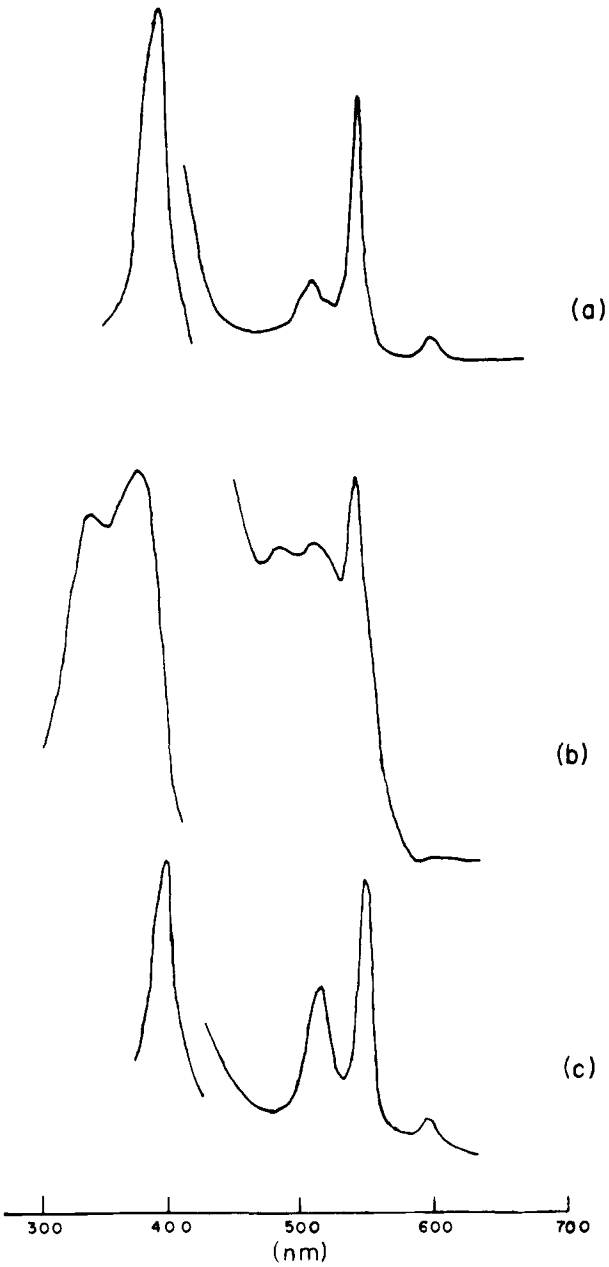

Figure 1. Electronic spectra in toluene solution: (a) RhOEP(H), (b) $(RhOEP)_2$, (c) RhOEP(O_2).

When toluene is pumped off at low temperatures (−20 °C) from a solution of RhOEP(O_2), the resulting solid is predominantly RhOEP(O_2). IR spectra of this solid shows a new band centered at 1075 cm^{-1} which, although partially obscured by ligand bands, is tentatively assigned to the ν_{O-O} stretching frequency in RhOEP(O_2). The ν_{O-O} stretching frequency in an analogous cobalt(II)-dioxygen complex appears at 1137 cm^{-1}.[10]

When solutions of RhOEP(O_2) are warmed to 20 °C the EPR signal diminishes in intensity and eventually disappears. The presence of donor molecules accelerates this process. The resulting diamagnetic complex has electronic and ^1H NMR spectra characteristic of a Rh^{III}OEP species and is tentatively formulated as the μ-peroxo complex $(RhOEP)_2O_2$. Bridging peroxo complexes of cobalt(III) and rhodium(III) have been characterized previously.[11,12] The ν_{O-O} band was not observed in the IR of this μ-peroxo complex which is consistent with a centrosymmetric bridging peroxide.[13]

The EPR g values for RhOEP(O_2) are virtually identical

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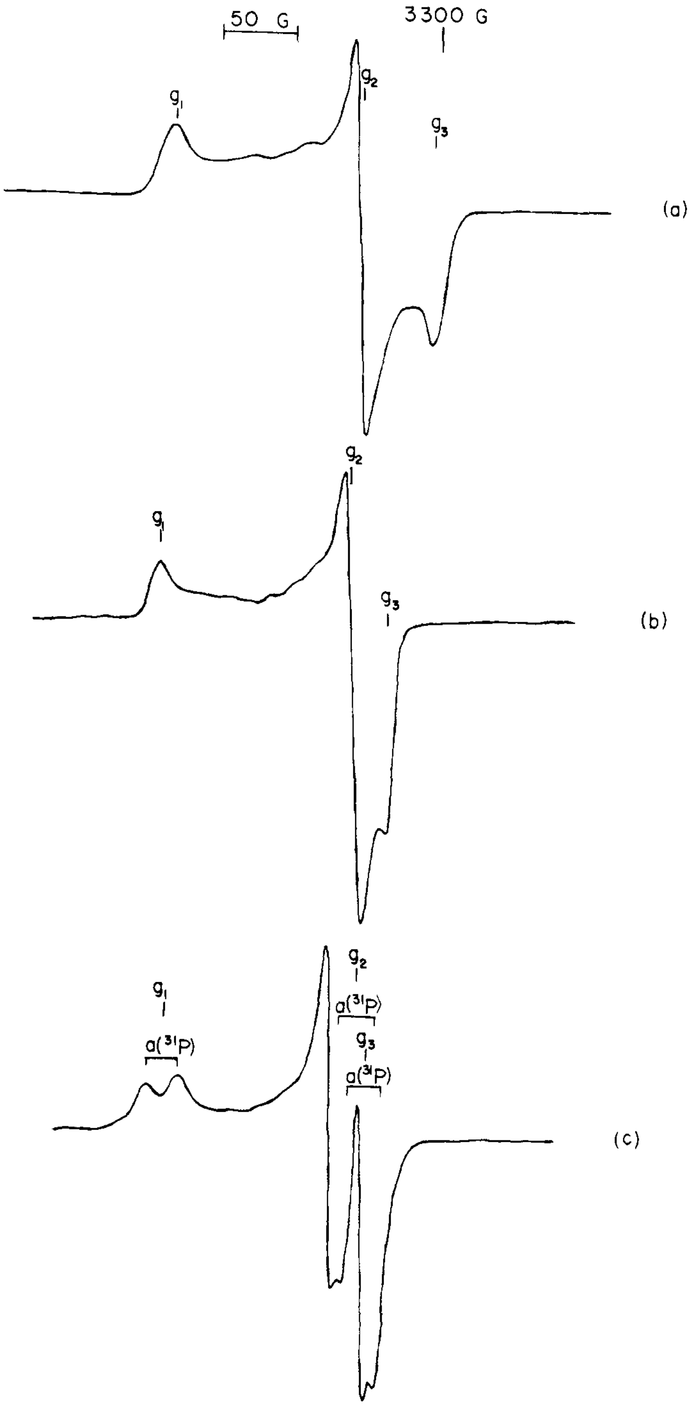

Figure 2. EPR spectra for dioxygen complexes of RhOEP in toluene glass (−160 °C): (a) RhOEP(O_2), (b) RhOEP(O_2) (piperidine), (c) RhOEP(O_2)[P($OBu)_3$].

with those reported for the complex previously formulated as $Rh^{II}TPP$ (Table I), suggesting that this species is actually the dioxygen complex, RhTPP(O_2). Authentic Rh(II) species with effective D_{4h} symmetry have substantially larger g values ($g_{\parallel} \sim 2.0$, $g_{\perp} \sim 2.3$: $\langle g \rangle \sim 2.2$) associated with the $(d_{xy}{}^2d_{xz,yz}{}^4)d_{z^2}{}^1$ electron configuration.[14,15] Heating a solid sample of the compound that we formulate as RhTPP(O_2) at 150 °C in high vacuum results in sublimation of a diamagnetic RhTPP compound. This species readily reacts with NO to form RhTPP(NO) (ν_{NO} 1658 cm^{-1}) and reacts with O_2 in the presence of donors to regenerate the EPR spectrum that we associate with RhTPP(O_2) complexes. The diamagnetic RhTPP species has NMR and electronic spectral properties as well as reactivity patterns consistent with a $Rh^{II}TPP$ dimer $(RhTPP)_2$. We are presently attempting to grow crystals of RhTPP(O_2) and $(RhTPP)_2$ suitable for X-ray structure determinations.

Although no monomeric rhodium(II) porphyrin species has been directly observed, the Rh–Rh bonding in $(RhOEP)_2$ and its reactivity with NO and O_2 are indicative of a half-occupied d_{z^2} in $Rh^{II}OEP$. The free-radical-like reactivity of the rhodium(II) porphyrin unit is similar to that recognized for other low spin d^7 complexes such as $[Co(CN)_5]^{3-}$ [16] and $Rh(NH_3)_4{}^{2+}$.[6] The reactivity patterns for cobalt(II) and rhodium(II) porphyrins are closely related; however, increased thermal stability of the rhodium(II)-dioxygen complexes and the unique metal-metal bonding are manifestations of the enhanced covalent bonding ability of the second transition series metal.

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Cyclopropanation of Olefins with a Stable, Iron-Containing Methylene Transfer Reagent[1]

Sir:

A common synthetic transformation is the conversion of olefins into cyclopropanes. The importance of this conversion stems from the occurrence of cyclopropane rings in many natural products and from the utility of cyclopropanes as synthetic intermediates leading to other systems.[2] A disadvantage of many of the previously reported methods for the cyclopropanation of olefins is that the species required for methylene transfer are often quite unstable and cannot be isolated easily if at all. During the past decade, transition metal-carbene complexes have been studied extensively.[3] Although these species have structures that suggest that they may behave as carbene sources of possible use in cyclopropa-