plexes, a situation also seen with $\mathrm{TCVPDM^-}$,[8] owing to the intense visible absorption of those species.[1,9] However, for TCVDMA·TNF, spectra in ethanol solution and in KBr pellets reveal absorption at wavelengths >750 nm not due to either component of the complex and assigned to the tail of a charge-transfer absorption band. A further attempt to observe a charge-transfer maximum in TCVDMA·TNF was made. In 0.5-mm-path-length cells, a 10^{-3} M solution of TCVDMA in ethanol or chloroform gave a level base line. Portionwise solution of TNF in the sample cell gave new absorbance in both cases between 500 and 530 nm, with maxima at 517 nm in ethanol and 502.5 and 527.5 nm in chloroform attributed to charge-transfer absorption.[14] Charge-transfer absorption between DMA and TCVDMA was observed as follows. In chloroform solution, 10^{-3} M in TCVDMA, a "window" in the absorption spectrum is apparent between 350 and 400 nm. Portionwise addition of DMA up to a concentration of 10^{-2} M in this solution reveals new absorption with absorbance increasing from 0.04 at 390 nm to 0.44 at 350 nm; however, no maximum was observed in this region. The new absorption, which we assign to charge-transfer absorption in both DMA·4TCVDMA and TCVDMA·TNF, is at energies expected[15] for molecular species with the energy levels and redox potentials listed in Table II.

In summary, we have demonstrated the π-amphoteric character of TCVDMA by its formation of solid complexes with TNF where it functions as a donor and with DMA where it functions as the acceptor in a solid complex of rare 1:4 stoichiometry. New absorption attributed to complex formation has been observed for each of the new complexes. A potential outgrowth of this work might be the use of π-amphoteric molecules to form new classes of complexes with three interacting components.[3] Our attempts to use TCVDMA to form three-component complexes with DMA and TNF have led only to the isolation of mixtures of the two-component complexes of these compounds to date.

Acknowledgments. The authors thank G. T. Fekete for X-ray powder diffraction patterns of the materials discussed herein and K. Fuller and K. Graham for typing the manuscript.

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Oxygenation of Cobalt(II) Carboranylporphyrinates: Solid-State, Nonaqueous, and Aqueous Solutions

Sir:

Oxygenation studies[1] of cobalt(II) porphyrinate complexes have ranged from simple porphyrins[2-7] like $\mathrm{L{\cdot}Co^{II}\{TPP\}}$[8] to porphyrins with more elaborate peripheral substitution such as the elegant "picket fence" cobalt(II) porphyrinate, $\mathrm{L{\cdot}Co^{II}\{TpivPP\}}$ of Collman and co-workers.[9] We report here the reaction of certain cobalt(II) carboranylporphyrinate complexes with molecular oxygen in the solid state, in solution in organic solvents, and in aqueous solution.

The crystalline porphyrin $\mathrm{MeIm{\cdot}Co^{II}\{TpivPP\}}$ reversibly binds O_2 with $P_{1/2}{}^{O_2} = 8.1$ kPa.[9] Although no solid-state $P_{1/2}{}^{O_2}$ values were determined for the porphyrins described here, the EPR spectra provide good estimates of the extent of oxygenation. The tetra-meso-substituted porphyrins $\mathrm{ar{\cdot}Co^{II}\{P(CH_2C_2B_{10}H_{10}Me)_4\}}$[10] (**1**), $\mathrm{ar{\cdot}Co^{II}\{P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4\}}$[11] (**2**), $\mathrm{\alpha^4{\cdot}Co^{II}\{P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4\}}$[12] (**3**), $\mathrm{ar{\cdot}Co^{II}\{P(C_6H_4NHCOCH_2C_2B_9H_{11}{\cdot}pipH)_4\}}$[13] (**4**), and $\mathrm{\alpha^4{\cdot}Co^{II}\{P(C_6H_4NHCOCH_2C_2B_9H_{11}{\cdot}pipH)_4\}}$[13] (**5**) were prepared by reaction of the free base[13b] with anhydrous $CoCl_2$ and 2,6-lutidine as proton scavenger[14] in THF and identified by elemental analysis[15] and/or visible spectra and EPR. The pentametalloporphyrin $\mathrm{ar{\cdot}Co^{II}{\cdot}\{P[C_6H_4NHCOCH_2C_2B_9H_{10}Rh^{III}(H)(PPh_3)_2]_4\}}$[16] (**6**) was prepared in very good yield by reaction of **4** with 4 equiv of $\mathrm{(Ph_3P)_3RhCl}$[17] in refluxing EtOH.

The solid-state oxygenation of **1–4** and **6** was investigated after preparation of the five-coordinate MeIm complexes under N_2 and determination of the EPR spectrum of the deoxy species ($g \approx 2.3$) at room temperature. After evacuation the sample was exposed to ~100 kPa of O_2 for 6-24 h at ~22 °C before the EPR spectrum was recorded again. During this time the deoxy signal diminishes and the oxy signal ($g \approx 2.0$) increases in intensity.[18] Figure 1 shows the EPR spectra of MeIm·**1** and the MeIm·**6**, respectively, under ~100 kPa of O_2. The figures show that the majority of the cobalt sites are oxygenated under these conditions and both porphyrins have a similar extent of oxygenation even though the peripheral substituents of **6** are many times larger than those of **1.** The atropisomeric purity seems to have relatively little effect on the extent of oxygenation with **3**·MeIm having only a slightly higher affinity for O_2 than **2.** In contrast, no reaction was detectable by EPR when crystalline $\mathrm{MeIm{\cdot}Co^{II}\{TPP\}}$ was exposed to ~100 kPa of O_2. The oxygenation reactions are reversible (high vacuum, ~50 °C, 12 h) except in the case of **6** which had EPR absorptions remaining in the $g = 2$ region after the deoxygenation treatment. From these observations we conclude that an important factor in the reversible oxygenation of solid cobalt(II)[18b] porphyrinates is the ease of access of O_2 to the cobalt site with the bulk and orientation of the peripheral protection apparently having little effect on the extent of oxygenation.

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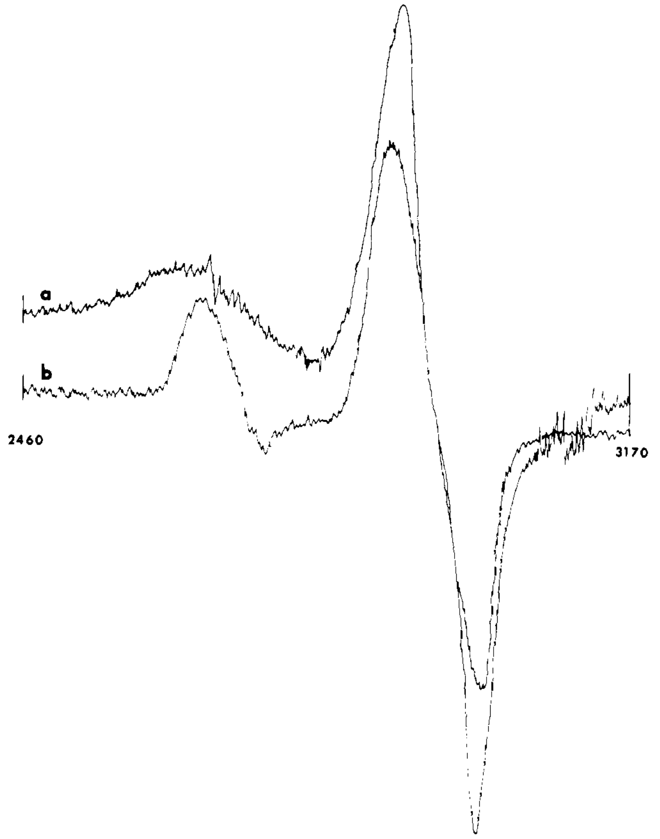

Figure 1. The 9.145-GHz EPR spectra of (a) MeIm·**1** and (b) MeIm·**6**; solid-state samples under ~100 kPa of O_2 at 22 °C. The sweep is from 2460 to 3170 G.

In contrast to the solid-state results, the reactions of carboranylporphyrinate complexes with molecular oxygen in solution are very sensitive to the nature of the peripheral substitution. Previously reported $\mathrm{L\cdot Co^{II}P + O_2}$ reactions in organic solvents range from essentially no oxygenation (e.g., $\mathrm{L\cdot Co^{II}\{TPP\}}$ derivatives[7]) to mostly oxygenated (e.g., $\mathrm{L\cdot Co^{II}TpivPP}$, $P_{1/2}^{O_2}$ = 18.6 kPa in PhMe[9]). The porphyrin with the least peripheral protection (**1**), when dissolved in the presence of excess MeIm or TrIm, shows behavior similar to that of $\mathrm{L\cdot Co^{II}\{TPP\}}$ derivatives,[2] i.e., no reaction with O_2 at room temperature.

Dilute solutions of TrIm·**3** reversibly bind O_2 at room temperature in THF in the presence of excess TrIm. The 530-nm absorption (deoxy) is rapidly replaced by the 550-nm absorption (oxy) when solutions are exposed to ~100 kPa of O_2 and can be reversed by purging the solution with N_2.[19] Exposure of ~10^{-3} M solutions of **3** in 2-MeTHF with excess TrIm to ~100 kPa of O_2 for 10 min at room temperature yields an EPR spectrum that shows only the signal of oxy adduct when examined in glassy 2-MeTHF at −160 °C. Preliminary equilibrium studies indicate the $P_{1/2}^{O_2}$ of TrIm·**3** is ~25 kPa in PhMe solution.

The piperidine degradation of the carborane cages of $\alpha^4\text{-}\mathrm{H_2\{P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4\}}$ gives a good yield of $\alpha^4\text{-}\mathrm{H_2\{P(C_6H_4NHCOCH_2C_2B_9H_{11}\cdot pipH)_4\}}$ (**7**), which gives **5** upon metalation with $CoCl_2$. The EPR spectra of TrIm·**5** and TrIm·**5**·O_2 (Figures 2a and 2b, respectively) under conditions similar to the oxygenation of **3** (excess TrIm, ~10^{-3} M in 2-MeTHF, 100 kPa of O_2 for 10 min) shows only the spectrum of oxy adduct. When the EPR sample is warmed to room temperature and degassed by the freeze–thaw technique, the sample shows only the deoxy signal demonstrating reversibility (Figure 2c). However, in contrast to the oxygenation of **3**, the exposure of THF solutions of **5**·TrIm to O_2 results in insignificant changes in the visible spectrum at room temperature.

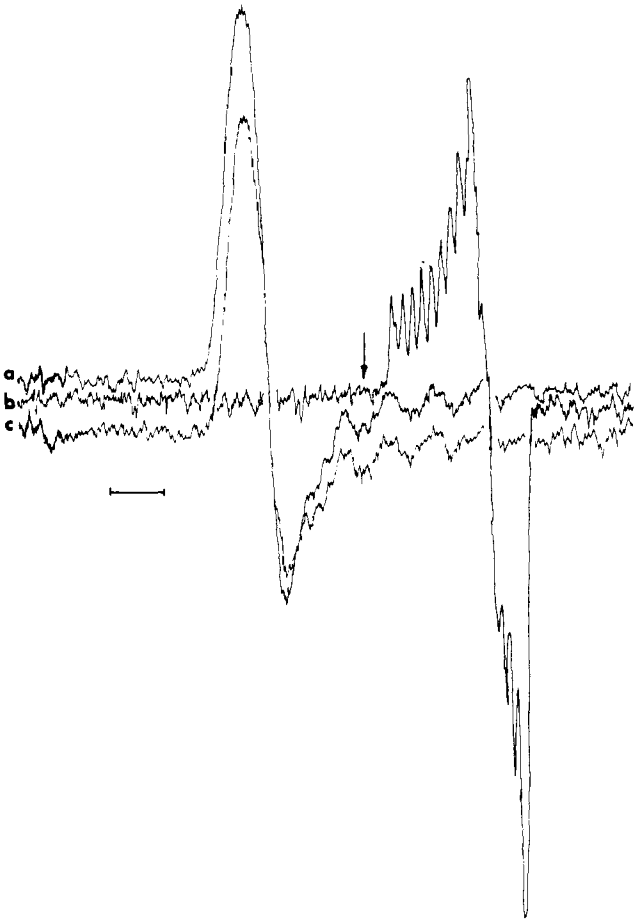

Figure 2. The EPR spectra of TrIm·**5** in 2-MeTHF glasses at −160 °C: (a) deoxy, (b) oxy (100 kPa for 10 min), (c) after freeze–thaw degassing. The field marker is at 3000 G; a 100-G unit is shown.

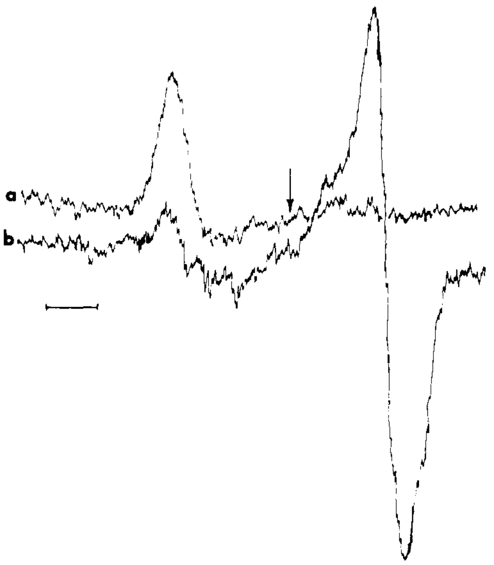

Figure 3. The EPR spectra of PVIm·**5** in 4:1 H_2O–glycerin at −160 °C: (a) deoxy, (b) oxy (100 kPa for 10 min). The field marker is at 3000 G; a 100-G unit is shown.

The oxygenation of **5** also was studied in aqueous solutions. Solid **5** is only slightly soluble in pure water, but appreciable amounts may be dissolved when very concentrated acetone solutions of **5** are added to water (total acetone concentration, ~5%). Bulky, water-soluble 1-polyvinylimidazole (1-PVIm) was the axial ligand in the aqueous oxygenation experiments.[20,21]

The EPR spectrum of **5** in 0.01 M 1-PVIm-glycerin[22] (4:1) at −160 °C is shown under N_2 (Figure 3a) and after exposure to 100 kPa of O_2 at room temperature for 10 min (Figure 3b). Although the resolution is very poor in H_2O compared with the glasses obtained from 2-MeTHF, the important features of the spectra are clear. We assign the absorption at $g \approx 2$ to the oxy adduct of PVIm·Co{α^4-$P(C_6H_4NHCOCH_2C_2B_9H_{11}\cdot pipH)_4$}. Since little oxygenation would be expected to take place after the solution is frozen (4:1 H_2O-glycerin mp −6 °C which would be depressed further by the ~5% acetone present), the EPR at −160 °C should reflect the *approximate* relative amounts of oxy:deoxy present[23] at room temperature assuming that the K_{eq} for oxygenation is not too strongly dependent on T. The EPR samples can be thawed and refrozen to give the same spectrum showing that the oxy adduct does not rapidly oxidize (to Co(III)) upon warming to room temperature. Removing the O_2 from the system regenerates the deoxy Co(II) EPR spectrum. After several hours at room temperature the solutions are EPR silent suggesting oxidation to diamagnetic Co(III) species. Again the room temperature visible spectrum shows no change upon exposure to O_2;[24] thus there is no direct evidence of oxygenation at room temperature.

The apparent oxygenation of **5** under these conditions in aqueous solutions casts some doubt on the premise[25] that metalloporphyrinates must have a hydrophobic environment in order to undergo oxygenation. Note that the cobalt atom in **5** binds O_2 in preference to H_2O[26] even though $[O_2] \approx 10^{-5}[H_2O]$ in these solutions and the hydrophobic environment is at best very local. This situation may not be true for a similar iron(II) porphyrinate; iron porphyrinates have a much greater affinity than cobalt porphyrinates for a sixth ligand in the axial position. A previous report of reversible oxygen binding by a water-soluble, polymer-bound iron porphyrinate[27] has been questioned by other workers.[28]

The apparently reduced O_2 affinity of **5** in solution might be related to a lower local solubility in the polar binding pocket of the cage-degraded porphyrinate than the nonpolar pocket of the undegraded porphyrinate. Dioxygen is more soluble in nonpolar than polar solvents.[29] The fact that the EPR shows complete oxygenation at low temperature is consistent with the expected increased solubility at lower temperatures.

As shown here carboranylporphyrins are versatile and useful ligands for the investigation of metalloporphyrinate oxygenation reactions. Starting from the basic ligand, such properties as solubility and extent of oxygenation can be altered by suitable modification of the carboranyl cages while keeping the immediate environment of the porphyrinate core approximately constant.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(8) Abbreviations used are TPP = tetraphenylporphyrinate, Tpiv = tetrapivalimidophenylporphyrinate, MeIm = 1-methylimidazole, TrIm = 1-triphenylmethylimidazole, ar = atropisomerically random, $\alpha^4 = \alpha\alpha\alpha\alpha$ atropisomer (~C_{4v}) of a porphyrin, P = tetra-meso-substituted porphyrinate nucleus, THF = tetrahydrofuran, 2-MeTHF = 2-methyltetrahydrofuran, pipH = piperidinium cation.

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(10) Calcd for $C_{36}H_{68}N_4B_{40}Co$: C, 41.26; H, 6.49; N, 5.34; B, 41.30. Found: C, 41.24; H, 6.59; N, 5.22; B, 41.17. Visible (THF): 530 nm (note that the B band appeared in all $Co^{II}P$'s reported here at ~415 nm). For EPR see Figure 1.

(11) Calcd for $C_{60}H_{80}N_8O_4B_{40}Co\cdot THF$: C, 49.90; H, 5.72; N, 7.28; B, 28.09. Found: C, 49.49; H, 6.33; N, 6.91; B, 27.97. Visible (THF): 530 nm. EPR: for **1**·MeIm (solid), $g = 2.3$.

(12) Visible (acetone): 530 nm. EPR: for **3**·MeIm (solid), $g = 2.3$.

(13) (a) Visible (acetone): for **4** and **5**, 530 nm. (b) See R. C. Haushalter and R. W. Rudolph, *J. Am. Chem. Soc.*, **100**, 4628 (1978).

(14) See ref 9 for a discussion of this metalation technique.

(15) Spang Microanalytical Laboratory, Eagle Harbor, Mich.

(16) Calcd for $C_{204}H_{196}N_8O_4B_{36}P_8Rh_4Co$: C, 62.28; H, 5.08; N, 2.85; B, 9.89; Rh, 10.46; Co, 1.50. Found: C, 61.24; H, 5.27; N, 2.36; B, 9.48; Rh, 9.99; Co, 1.67. Visible (THF): 530 nm. IR (KBr): ν_{BH} 2520, ν_{NH}(amide) 3370, ν_{CO} 1681, ν_{CH}(PhH) 3052. ^1H NMR: although the porphyrin signals were broadened and shifted by the Co(II) center making assignment difficult, the Ph_3P signals were observed at δ ~7.3 and the hydride at −6.5.

(17) T. E. Paxson and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 4674 (1974).

(18) (a) The measured *g* values are typical for $Co^{II}P$ complexes; see ref 7 for example. (b) See ref 1, p 149, and references therein for a discussion of diffusion of O_2 into solid Co(II)–Schiff base complexes.

(19) These visible spectrum changes are similar to those reported in ref 9.

(20) In these oxygenation studies, smaller 1-R-imidazoles such as 1-MeIm did not prevent oxidation, presumably owing to coordination on the hindered side of the porphyrin thus allowing coordination of O_2 on the unprotected porphyrin face and subsequent oxidation.

(21) The concentration of the polymer was calculated as moles of imidazole present. This polymer was a gift from Professor Overberger of this department.

(22) If pure water solutions are frozen, often no EPR signal can be observed, presumably owing to aggregation of the paramagnetic species with the resultant dipolar coupling greatly broadening the signals. Addition of glycerin minimizes this affect. Even with glycerin present, no signals are observed if the sample is frozen too slowly.

(23) The fact that the EPR of **9** shows both the deoxy and oxy species while TrIm·**5**·O_2 shows only the oxy species may be due to one or more of the following: (a) the solution was not as cold when it froze (thus, the extent of oxygenation was not as great); (b) H_2O is competing with O_2 for the axial site on the cobalt; (c) 1-PVIm is less effective as an axial ligand than a monomeric imidazole.

(24) J. P. Collman et al., *J. Am. Chem. Soc.*, **96**, 6800 (1974), reported manometric O_2 uptakes corresponding to oxygenation of 50% of the Co(II) sites in their porphyrin accompanied by only minor visible absorption spectrum changes.

(25) Reference 1, p 149; ref 1, p 160.

(26) EPR measurements show the odd electron in the deoxy cobalt d_{z^2} orbitals is delocalized into the π^*-type orbital of O_2 when the oxy adduct forms. H_2O has no similar MO available for delocalization. The ^{59}Co superhyperfine splittings observed here for the deoxy and oxy forms of either TrIm·**3** or TrIm·**5** are ~83 and 15 G, respectively. These are typical values (ref **1**, p 151).

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(28) H. R. Allcock, P. P. Greigger, J. E. Gardner, and J. L. Schmutz, *J. Am. Chem. Soc.*, **101**, 606 (1979).

(29) Solubilities of O_2 in solvents of decreasing polarity follow (millimolar at 25 °C): H_2O, 1.23; EtOH, 8.32; acetone, 12.12; *n*-perfluoroheptane, 23.7. From "Matheson Gas Data Book", Matheson Gas Products, Hasbrouck Heights, N.J. 07604.

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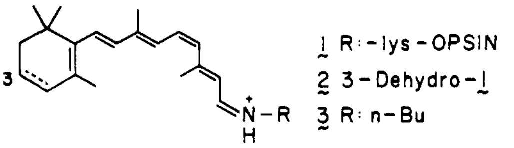
Hydroretinals and Hydrorhodopsins[1]

Sir:

In the visual pigments rhodopsins,[2,3] the chromophore 11-*cis*-retinal is bound to the ϵ-amino of a lysine moiety of the apoprotein opsin through a protonated Schiff base (SBH^+) **1**.[4]



The absorption maximum of SBH^+ formed from 11-*cis*-retinal and *n*-$BuNH_2$ (3) is at 440 nm in the leveling solvent metha-

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