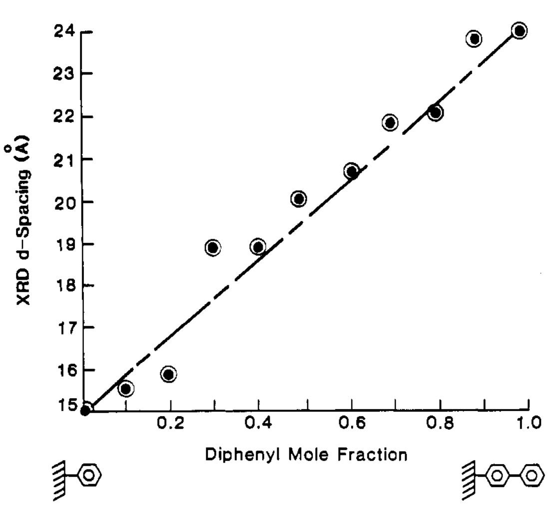

Figure 4. Dependence of the layer–layer spacing on compositional variation.

of a particularly homogeneous size distribution, there were not apparent any trends paralleling the surface area variation.

Figure 4 presents the X-ray-diffraction-determined interlayer distances for the series. Clearly, for the 0.3–0.8 biphenyl mole fraction compositions there is apparent a linear dependence with molar ratio of the groups. This observation is not consistent with the picture given in Figure 2. According to that view, one would expect to see an extended region of structure having the biphenyl–biphenyl distance (24 Å), which might drop to the biphenyl–phenyl distance (ca. 19.5 Å) and there be maintained until collapse to the phenyl–phenyl distance as some low biphenyl mole fraction is reached. A more fitting explanation of the XRD data, as well as the modest density diminution in the intermediate compositional region, is that strain imposed by the incipient voids forces the biphenyl groups to bend away from their normal orientation in an effort to better accommodate the space allowed, thus resulting in a continuously decreasing interlayer distance. Density should be somewhat lower than expected for close-packed phases, due to ineffective space filling (see Figure 5), and one might even expect some increase in surface area resulting from such porosity. At the extreme compositions 0.1, 0.2, and 0.9 there is some evidence of discontinuous interlayer dilation presumably arising from abutment or "roof collapse" effects.

In the tetravalent phosphonates there is permitted approximately 24 Å^2 of cross-sectional area per site on the basal surface. Since the area required for a phenyl ring is about 18 Å^2, there does appear to be room for the suggested bending away from a strictly perpendicular orientation.[4] In addition, there is likely some flexibility in the inorganic framework that could assist in the redirection of the organic groups yet maintain the lamellar structure.

There is a phenomenon well-known to clay mineralogists called "interstratification" in which mixed phases occur as randomly staged substances.[5] Whereas each individual layer is of a pure phase, they stack upon one another willy-nilly, yielding broad averaged *d* spacings. While such a corresponding situation could be occurring in the present case, it is considered less likely than the explanation offered above since no variations in density would be expected. On the other hand, the remarkable linearity seen in Figure 4 seems less consistent with the rationale presented.

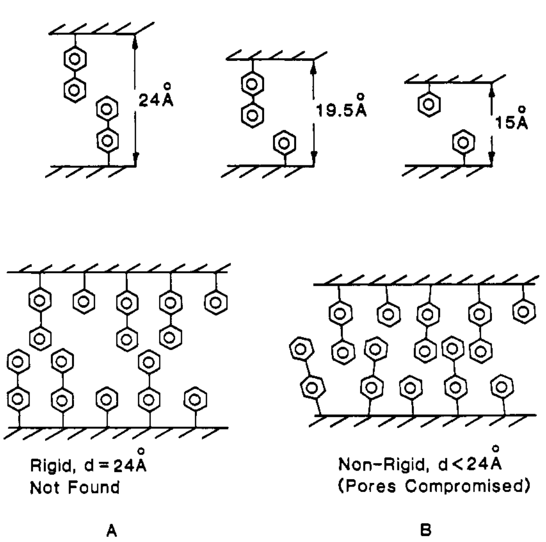

Figure 5. Alternative structures of an intermediate and end members of the series: (top) pure-phase biphenyl, ordered phenyl–biphenyl, and phenyl compounds; (bottom) situation for the propped structure (A) and situation for the bending of biphenyl groups, which compromises pores (B).

Regardless of which of the two situations is in actuality operating—partial interdigitation or interstratification of pure-phase layers—the data do show that it is possible to prepare mixed-component compounds of differing groups within the interlayer region but that such an approach is not satisfactory for inclusion of significant microporosity.

Registry No. $Th(O_3P\text{-}C_6H_5)_2$, 75406-79-0; $Th(O_3P\text{-}C_6H_4\text{-}C_6H_5)_2$, 83947-44-8; $Th(O_3P\text{-}C_6H_5)(O_3P\text{-}C_6H_4\text{-}C_6H_5)$, 83947-45-9.

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[4] In the single-component compounds there is not enough room for any significant "interdigitation". This is borne out by the fact that the interlayer distances are just what would be expected for the bilayered, noninterpenetrating structure.

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Iron Benzoquinone Dioxime Complexes. Electronic Effects on Axial Ligation to Ferrous Dioximes

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The ability of a macrocyclic ligand to "tune" the chemistry of the metal is a recurring theme in metalloporphyrins and related complexes. When substituents do not conjugate directly with the macrocycle π system, the substituent effects are typically small. For example, replacing methyl[1] by phenyl[2] in bis(glyoxime) ($Fe(DMGH)_2$ vs. $Fe(DPGH)_2$) or in tetraimine systems[3] ($Fe(Me_4[14]tetraeneN_4)$) (FeTIM) vs. $Fe(Ph_4[14]tetraeneN_4)$ results in minor spectral shifts (less than 50 nm) and changes in axial ligation (spanning about one order of magnitude). The spectra and axial ligation to iron porphyrins vary only slightly for proto-, meso-, deutero-, diacetyl-,[4] and tetraphenylporphyrin[5] and somewhat more for octa-

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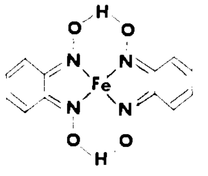
methyltetrabenzoporphyrin[6]. Reduction of double bonds not directly involved in the great inner ring of the porphyrin, as in chlorins or bacteriochlorins, does not seem to markedly alter CO bonding.[7]

More dramatic effects may be anticipated when the substituent interacts strongly with the macrocycle π system via direct conjugation. The binding of CO should be especially sensitive to these effects. We report here the synthesis, spectra, and reactions of new iron(II) complexes of benzoquinone dioxime (**1**) (BQD, 3,5-cyclohexadiene-1,2-dione dioxime)



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containing 1-methylimidazole (MeIm), pyridine (py), benzyl isocyanide (BzNC), and carbon monoxide as axial ligands where the direct conjugation of the hexadiene system to the dioxime chromophore results in bathochromic shifts up to 200 nm in visible bands and a 10^4 increase in CO lability.

Previous studies of metal complexes of benzoquinone dioxime have been largely limited to square-planar derivatives of Ni, Pd, and Pt.[8,9] A limited description of a square-planar iron complex has been reported.[10]

Experimental Section

Ferrous acetate was prepared from iron powder and acetic acid and stored under nitrogen. Benzoquinone dioxime was prepared by borohydride reduction of benzofurazan oxide.[11,12] All procedures were carried out under nitrogen.

$Fe(BQD)_2(MeIm)_2$. Ferrous acetate (0.9 g) and benzoquinone dioxime (1.1 g) were dissolved in a degassed solution of 2 mL of MeIm and 50 mL of methanol. The mixture was stirred for 30 min, and the dark precipitate was filtered, washed with methanol (containing a few drops of MeIm) and petroleum ether, and dried in vacuo; yield 1.8 g. $Fe(BQD)_2(py)_2$ was prepared similarly.

$Fe(BQD)_2(MeIm)(BzNC)$. $Fe(BQD)_2(MeIm)_2$ (0.5 g) was dissolved in chloroform containing benzyl isocyanide (0.15 g). The solution was filtered and concentrated, and precipitation was induced by addition of petroleum ether. The dark solid was filtered, washed with petroleum ether, and dried in vacuo: yield 0.4 g; $\nu_{NC} = 2170$ cm^{-1}.

$Fe(BQD)_2(BzNC)_2$. Ferrous acetate (0.45 g), benzoquinone dioxime (0.6 g), and benzyl isocyanide (1.0 g) were dissolved in 25 mL of absolute ethanol. The solution was stirred for 30 min and then filtered. Petroleum ether was added to the filtrate, and the solution was left to stand at −10 °C overnight. The dark precipitate was removed by filtration, washed with petroleum ether, and dried in vacuo: yield 0.2 g; $\nu_{NC} = 2184$ cm^{-1}. NMR ($CDCl_3$): δ 4.65 (4 H), CH_2 of BzNC; 6.5 (4 H), half of AA'BB' multiplet of BQD; 7.2 (14 H), overlap of aromatic BzNC plus other half of AA'BB' multiplet.

All complexes gave satisfactory elemental analyses (C, H, N).

Kinetics. Solutions of the carbonyl complexes were generated in situ by dissolving a few milligrams of $Fe(BQD)_2L_2$ (L = MeIm or py) in chloroform (trap distilled on a vacuum line) and letting them stand for several hours under 1 atm of CO. Excess L (0.1 mL) was then added to the thermostated solutions and the rate of reaction followed by visible spectroscopy. Pseudo-first-order rate constants (k_{obsd}) were obtained from log plots linear over 3 half-lives. Rates were invariant to a 10-fold change in concentration of added ligand, identifying k_{obsd} with the rate constant for CO dissociation from the complex.

Table I. Visible Spectral Data

complex	color[a]	λ_{max}, nm	λ_{max}, nm[b]
$Fe(BQD)_2(CH_3Im)_2$	green	744, 440	531
$Fe(BQD)_2(py)_2$	green	704, 420, 375	508, 417
$Fe(BQD)_2(CH_3Im)(CO)$	yel-brn	485, 400	385
$Fe(BQD)_2(py)(CO)$	yel-brn	484, 400	389, 350
$Fe(BQD)_2(CH_3Im)(BzNC)$	purple	582, 420	445
$Fe(BQD)_2(BzNC)_2$	orange	504, 402	392

[a] Color of a dilute chloroform solution. All of the solids are essentially black. [b] For the analogous $Fe(DMGH)_2$ complex.[1]

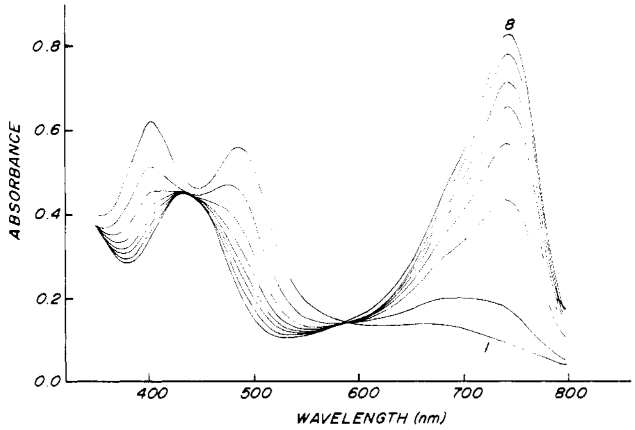

Figure 1. Spectrum of $Fe(BQD)_2(MeIm)(CO)$ prepared by dissolution of $Fe(BQD)_2(MeIm)_2$ in CO-saturated $CHCl_3$(1). Spectra 2–8 are those taken with increasing time after addition of excess MeIm.

Results and Discussion

Spectral data for the $Fe(BQD)_2$ complexes are given in Table I along with corresponding data for the $Fe(DMGH)_2$ analogues. The long-wavelength band is assigned to a charge-transfer transition by analogy with the case for the $Fe(DMGH)_2$ complexes and its shift with variations in axial ligands is similar to that for the $Fe(DMGH)_2$ system. The much lower energy of this transition in the BQD complexes is consistent with a lowering of the π^* level of the dioxime moiety as a result of conjugation with the hexadiene group.

IR data for carbonyl and isocyanide derivatives are consistent with significantly reduced axial π-donor character in the BQD complexes. ν_{CO} for $Fe(BQD)_2(MeIm)(CO)$ is at 2028 cm^{-1} in $CHCl_3$ solution, compared with 1978 cm^{-1} for the $Fe(DMGH)_2(MeIm)(CO)$ complex,[1] and ν_{NC} is higher in $Fe(BQD)_2(MeIm)(BzNC)_2$ and $Fe(BQD)_2(BzNC)_2$ (2170 and 2184 cm^{-1}, respectively) compared to that for the DMGH analogues (2141 and 2167 cm^{-1}, respectively).[1] The reduced axial π-donor character of iron could result because of greater π-back-donation to the lower energy π^* BQD orbitals cited above.

Reactions. The general pattern of reactivity of the BQD complexes parallels that of the DMGH systems described previously.[1] Reactions were studied in chloroform solution by visible spectroscopy. The kinetics are indicative of a dissociative mechanism. Methylimidazole in $Fe(BQD)_2(MeIm)_2$ is replaced rapidly ($k = 1.0 \times 10^{-2}$ s^{-1} at 0 °C) by CO (eq 1) or isocyanides, giving $Fe(BQD)_2(MeIm)$, X = CO or

$$Fe(BQD)_2(MeIm)_2 + CO \rightarrow Fe(BQD)_2(MeIm)(CO) + MeIm \quad (1)$$

BzNC. Replacement of BzNC by MeIm in $Fe(BQD)_2(MeIm)(BzNC)$ or $Fe(BQD)_2(BzNC)_2$ is thermally slow. Attempts to study the kinetics of these reactions at higher temperatures resulted in extensive decomposition. BzNC is readily photodissociated, giving $Fe(BQD)_2(MeIm)_2$ cleanly in the presence of excess MeIm. With sunlight, the photosubstitution reaction is far more efficient in the BQD com-

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Table II. Kinetic Data for CO Dissociation

complex	k_{-CO}, s^{-1}	T, °C	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)
$Fe(BQD)_2(MeIm)(CO)$[a]	1.9×10^{-2}	25	23	10
	3.5×10^{-3}	15		
	4.8×10^{-4}	0		
$Fe(BQD)_2(py)(CO)$[a]	2.4×10^{-2}	15	...	...
$Fe(DMGH)_2(MeIm)(CO)$[b]	3.7×10^{-6}	25	27[e]	6
$Fe(DMGH)_2(py)(CO)$[c]	1.1×10^{-5}	25	28[e]	14
$Fe(DPGH)_2(py)(CO)$[d]	2.5×10^{-5}	25	26[e]	7
$Fe(Pc)(MeIm)(CO)$[f]	2.0×10^{-2}	25	24	10
$Fe(DHD)(MeIm)(CO)$[g]	2.8×10^{-2}	20		

[a] In chloroform. [b] MeIm = 1-methylimidazole.[1] [c] py = pyridine.[1] [d] In chlorobenzene.[2] [e] Activation parameters recalculated by a least-squares method differ slightly from those given in ref 1. The $\Delta S^{\ddagger}$ reported in ref 2 is in error. [f] Pc = phthalocyanine; in toluene.[18] [g] DHD = deuteroporphyrin dimethyl ester; in benzene.[19]

plexes owing to a better overlap between the absorbance of BQD complexes and the solar spectrum. The ability to markedly shift the spectrum of these derivatives while retaining the essential photochemistry of the FeN_4 unit gives one a "wavelength-tunable" photochromic system based on BzNC or CO photosubstitution reaction.[13]

A delabilizing effect of BzNC and CO is observed on MeIm lability. The reaction

$$Fe(BQD)_2(MeIm)(BzNC) + BzNC \rightarrow Fe(BQD)_2(BzNC)_2 + MeIm \quad (2)$$

is slow even at elevated temperatures. Reaction of $Fe(BQD)_2(MeIm)(CO)$ with BzNC proceeds according to eq 3 at a rate identical with that of the reaction with MeIm.

$$Fe(BQD)_2(MeIm)(CO) + BzNC \rightarrow Fe(BQD)_2(MeIm)(BzNC) + CO \quad (3)$$

Clean isosbestic points are observed with no evidence for formation of $Fe(BQD)_2(BzNC)_2$, which would result from a mechanism involving MeIm loss trans to CO.[17] This indicates that MeIm dissociation trans to CO is slower than 10^{-4} s^{-1} at 25 °C. Thus MeIm is at least 10^3 times more inert trans to CO or BzNC than trans to MeIm. This trans-delabilizing effect of CO and BzNC has been observed previously in hemes and other iron macrocycles.[14-17]

Kinetic data for the carbonyl complexes were obtained on samples prepared in situ. We have been unable to isolate pure solid samples owing to the facile reversibility of CO binding and the much greater solubility of the carbonyl derivatives. Attempts to precipitate carbonyl complexes invariably give the starting $Fe(BQD)_2(MeIm)_2$ as product. $Fe(BQD)_2(MeIm)(CO)$ is considered well characterized in solution on the basis of visible spectra, ν_{CO}, and the clean conversion to $Fe(BQD)_2(MeIm)_2$ and $Fe(BQD)_2(MeIm)(BzNC)$.

Kinetic data for CO replacement by MeIm (the reverse of eq 1) are summarized in Table II along with comparable data for dimethyl- and diphenylglyoxime analogues. The BQD complexes are nearly 10^4 times more labile toward CO loss than the DMGH or DPGH complexes. To verify that the result is not due to the differences in solvents, we have measured the rate of decarbonylation of $Fe(DMGH)_2(MeIm)(CO)$ in $CHCl_3$ and it is not significantly different from that reported in toluene previously. As in the DMGH system CO is seen to be about 10 times more labile trans to py than trans to MeIm.

The $Fe(BQD)_2$ complexes are structurally and electronically so different from iron porphyrins and phthalocyanines that detailed comparisons with these complexes are unwarranted. We note, however, that the lability of CO in $Fe(BQD)_2(MeIm)(CO)$ is virtually identical with that in corresponding iron phthalocyanine[18] and iron porphyrin[19] complexes. While it is possible to obtain "heme-like" CO lability in these complexes, the lability of MeIm in $Fe(BQD)_2(MeIm)_2$ ($k_{-MeIm} = 1.0 \times 10^{-2}$ s^{-1} at 0 °C in $CHCl_3$) is only about one order of magnitude faster than that of $Fe(DMGH)_2(MeIm)_2$ ($k_{-MeIm} = 6.9 \times 10^{-4}$ s^{-1} at 10 °C in $CHCl_3$) and is still significantly slower than that of iron porphyrins ($k_{-MeIm} = 1500$ s^{-1} for $Fe(TPP)(MeIm)_2$ at 25 °C in toluene).[21] The porphyrins have a special mechanism for labilization of σ donors, which we have discussed elsewhere.[16,17,19]

Structural data for $Ni(DMGH)_2$[21] and $Ni(BQD)_2$[8] show surprisingly little effect of the hexadiene substituent on the metrical details of the dioxime group. This result is, however, consistent with our observations that large differences between the $Fe(DMGH)_2$ and $Fe(BQD)_2$ complexes occur primarily in properties where the dioxime π^* level is important: visible spectra, ν_{CO} and ν_{NC}, lability of CO.

Acknowledgment. Financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. $Fe(BQD)_2(MeIm)_2$, 83947-66-4; $Fe(BQD)_2(MeIm)(BNC)$, 83947-67-5; $Fe(BQD)_2(BNC)_2$, 83947-68-6; $Fe(BQD)_2(py)_2$, 83947-69-7; $Fe(BQD)_2(MeIm)(CO)$, 83947-70-0; $Fe(BQD)_2(py)(CO)$, 83966-22-7.

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