

reference data can be expected, although the model has potential for considerable refinement, for example, by the use of expressions for the energy integrals better than the simple Hückel approximations. Some of our preliminary work suggests that the agreement with SCF results is good for the close clusters.

TSH theory is not limited to the boranes or even to the first-row elements. It is of particular value in dealing with

transition-metal clusters, since it greatly reduces the number of orbitals to be considered at one time. It should be possible to use the theory to model many different types of metal cluster in the same sort of way as we have used it here to model the main types of borane cluster.

**Acknowledgment.** M.J.A. thanks the Science and Engineering Research Council for financial support.

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## Synthesis and Mössbauer Spectroscopic Studies of Carbonyl Derivatives of (Phthalocyaninato)iron(II)

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Received October 8, 1981

The monocarbonyl complexes of (phthalocyaninato)iron(II), FePc(CO)L, where L = *N,N*-diethylacetamide, pyridine, piperidine, hexamethylphosphoramide, and triphenylphosphine oxide, have been prepared and characterized, as has the dicarbonyl compound FePc(CO)<sub>2</sub>, which was isolated after exposing FePc in a hydrocarbon solvent to a high pressure of CO. The Mössbauer spectroscopic parameters,  $\Delta E_Q$  and  $\delta$ , both decrease upon replacement of an axial ligand of the bisadducts, FePcL<sub>2</sub>, by CO to give FePc(CO)L. These changes are consistent with a decrease in mean axial bond distances upon carbonylation and a concomitant increase in *s*-electron density along the *z* axis. The electronic basis of these structural modifications requires consideration of both *cis* and *trans* effects.

### Introduction

(Phthalocyaninato)iron(II), FePc,<sup>2</sup> has been studied extensively as a model for the heme group.<sup>3</sup> Complexes containing the FePc moiety, unlike ferrous porphyrins, do not undergo reversible 1:1 O<sub>2</sub> binding;<sup>4</sup> however, both classes bind CO reversibly. Solution studies have considered the reaction of FePc with CO in Me<sub>2</sub>SO,<sup>5</sup> in concentrated sulfuric acid,<sup>6</sup> and in the presence of nitrogen Lewis bases.<sup>7</sup> Our groups have reported independently the isolation of the carbonyl complexes FePc(CO)L, where L = nitrogen-,<sup>8</sup> oxygen-, and sulfur-donor<sup>9,10</sup> ligands, and the solid-state structure of the dimethylformamide adduct FePc(CO)DMF<sup>10</sup> has been determined. This paper describes the synthesis and properties of several additional monocarbonyl complexes, together with the new dicarbonyl derivative, FePc(CO)<sub>2</sub>, and then discusses the bonding in these compounds as investigated by Mössbauer spectroscopy.

The Mössbauer technique provides a useful probe for the electronic structure of the central metal, and several reports have attempted to correlate Mössbauer parameters with the

$\sigma$ - and  $\pi$ -bonding characteristics of metalloporphyrin complexes.<sup>11</sup> The large decrease in both isomer shift  $\delta$  and quadrupole splitting  $\Delta E_Q$ , observed upon replacement by CO of an amine ligand in the diamine complexes FePL<sub>2</sub> (P = dianion of a porphyrin or phthalocyanine ligand), to give the monocarbonyl derivatives FeP(CO)L, has attracted considerable attention.<sup>10-14</sup>

The preliminary reports on the Mössbauer spectra of FeP(CO)L complexes<sup>10,13</sup> attributed the changes in  $\delta$  and  $\Delta E_Q$  to two different causes: (1) a substantial *cis* effect, whereby carbonylation causes pronounced changes in the Fe-P bonding,<sup>13</sup> and (2) a significant *trans* effect relating changes in the Mössbauer spectroscopic parameters to the nature of the ligand *trans* to CO.<sup>10</sup> In this paper we will use the expanded data base of the phthalocyaninato complexes to consider these arguments in more detail.

### Experimental Section

**Syntheses.** Unless otherwise stated, all operations were carried out under an atmosphere of prepurified argon or nitrogen. Solvents were purified by conventional methods prior to use.

The syntheses of FePc<sup>9,10</sup> and some of the carbonyl adducts FePc(CO)L<sup>8,10</sup> were carried out as reported earlier. Only the preparations of the new complexes are described here. Occlusion of solvent in the crystals of these materials is a characteristic that has been noted previously.<sup>10</sup>

**Preparation of FePc(CO)DEA.** FePc (1.24 g, 2.2 mmol) suspended in DEA (20 mL) was stirred under an atmosphere of CO for about 10 h. The violet microcrystalline solid was filtered from the blue solution and dried in vacuo (1.34 g, 74% yield). Anal. Calcd for FePc(CO)DEA-DEA: C, 65.4; H, 5.1; N, 17.0. Found: C, 65.5; H, 5.0; N, 17.3.

The solid compound is stable in air, soluble in DEA with a deep blue color, and slightly soluble in acetone, dichloromethane, and

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- (2) Abbreviations: Pc, TPP, OEP = the dianions of phthalocyanine, tetraphenylporphyrin, and octaethylporphyrin, respectively; DEA, *N,N*-diethylacetamide; DMF, *N,N*-dimethylformamide; Me<sub>2</sub>SO, dimethyl sulfoxide; HMPT, hexamethylphosphoramide; *n*-PrNH<sub>2</sub>, *n*-propylamine; pip, piperidine; py, pyridine; THF, tetrahydrofuran; THT, tetrahydrothiophene.
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ethanol. A control gas volumetric experiment showed that FePc in DEA at 25 °C absorbs CO in a 1:1 ratio at 1 atm (CO:Fe molar ratio found = 1.02).

**Preparation of FePc(CO)py.** FePc (1.05 g, 1.85 mmol) suspended in 80 mL of CCl<sub>4</sub> was stirred with pyridine (0.15 mL, 1.86 mmol) under an atmosphere of CO for about 20 h. The resulting suspension was filtered and the microcrystalline violet solid dried in vacuo for about 10 min (1.54 g, 85% yield). The compound is stable in air for limited periods of time, with no formation of the aquocarbonyl derivative<sup>9</sup> upon exposure of a Nujol mull sample to air. Anal. Calcd for FePc(CO)py·2CCl<sub>4</sub>: C, 48.9; H, 2.1; N, 12.8. Found: C, 48.1; H, 2.3; N, 12.5.

**Preparation of FePc(CO)pip.** FePc (1.33 g, 2.3 mmol) was stirred with piperidine (0.23 mL, 2.3 mmol) and CCl<sub>4</sub> (100 mL) at room temperature for about 10 h under an atmosphere of CO. After removal of about 70 mL of solvent under reduced pressure, hexane (30 mL) was added to the resulting suspension. The violet microcrystalline complex was recovered by filtration and dried for about 10 min in vacuo (0.42 g, 18.4% yield). Anal. Calcd for FePc(CO)pip·2CCl<sub>4</sub>: C, 48.6; H, 2.7; N, 12.7. Found: C, 49.5; H, 3.0; N, 12.3.

**Preparation of FePc(CO)[OP(NMe<sub>2</sub>)<sub>3</sub>].** FePc (1.12 g, 1.97 mmol) was stirred with CCl<sub>4</sub> (30 mL) and hexamethylphosphoramide (HMPT) (5 mL) at room temperature for about 4 h under an atmosphere of CO. The violet microcrystalline complex was recovered by filtration and dried in vacuo for about 20 min (1.91 g, 94% yield). The air-stable complex dissolves in HMPT to give a blue color. A gas volumetric experiment at 25 °C showed that FePc in HMPT absorbed CO to a CO:Fe ratio of 0.94. Anal. Calcd for FePc(CO)HMPT·HMPT·0.5CCl<sub>4</sub>: C, 53.0; H, 5.1; N, 19.0; CO, 2.71. Found: C, 52.6; H, 5.3; N, 18.8; CO, 2.76.

**Preparation of FePc(CO)(OPPh<sub>3</sub>).** FePc (0.762 g, 1.3 mmol) was stirred for about 15 h under an atmosphere of CO with CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and the phosphine oxide (4.6 g, 16.5 mmol). The resulting violet microcrystalline solid was filtered, washed with CH<sub>2</sub>Cl<sub>2</sub>, and dried for 3 h in vacuo (0.53 g, 46% yield). The air-stable compound is slightly soluble in CH<sub>2</sub>Cl<sub>2</sub> and acetone. Anal. Calcd for FePc(CO)(OPPh<sub>3</sub>): C, 70.1; H, 3.6; N, 12.8. Found: C, 70.9; H, 3.4; N, 13.1.

**Preparation of FePc(CO)<sub>2</sub>.** A suspension of FePc (2.07 g, 3.6 mmol) in heptane (15 mL) was prepared in a glass vial. This was introduced into a stainless-steel autoclave which was then pressurized at 70 atm with predried CO and heated at 100–110 °C for 2 days. The blue violet solid was filtered and dried briefly in vacuo (2.54 g). The compound was isolated in a mixture with the aquocarbonyl complex FePc(CO)H<sub>2</sub>O, from which it can be distinguished easily by IR in the carbonyl stretching region, and by Mössbauer spectrometry. Anal. Calcd for FePc(CO)<sub>2</sub>·0.67FePc(CO)H<sub>2</sub>O·1.5C<sub>7</sub>H<sub>16</sub>: CO, 6.31; Fe, 7.73. Found: CO, 6.0; Fe, 7.5. The presence of lattice heptane in the mixture was ascertained by IR after the solid was dried in vacuo for 1 h at room temperature.

The dicarbonyl derivative is characterized by a strong IR absorption at 2057 cm<sup>-1</sup>. On exposure to air, the ν(CO) vibration of the aquocarbonyl at 1997 cm<sup>-1</sup> becomes more intense while the intensity of the 2057-cm<sup>-1</sup> band decreases.

**Physical Measurements.** IR spectra were measured with a Perkin-Elmer 283 instrument on Nujol mulls under rigorous exclusion of air and moisture.

**Electronic spectra** of the carbonyl adducts of FePc with THF, DMF, and DEA were measured as solutions with the ligands as neat liquids with a Varian 635D spectrophotometer. The solutions were prepared under an atmosphere of CO; under these conditions gas volumetric measurements establish that a substantially complete carbonylation of the iron complex has occurred. This was confirmed by the absence, or by the very low intensity, of a band at ~420 nm, attributable<sup>7</sup> to FePcL<sub>2</sub>. A band formed at ~660 nm due to FePc(CO)L species is largely unaffected by the change in L. For L = THF, HMPT, DMF, and DEA, λ<sub>max</sub> = 660, 662, 662, and 659 nm, respectively.

**Mössbauer spectra** were measured in both the Pisa and Vancouver laboratories. In Pisa, room-temperature spectra were measured with an Elron Elscint AME-30 spectrometer equipped with a <sup>57</sup>Co(Pd) source. The absorber was constructed as a plastic sample holder filled with 200–300 mg of the substance and sealed with an epoxy resin under an atmosphere of prepurified CO. The chemical stability of the substance in the sample holder was established by repeating the spectral measurement several days after the first spectral data had been collected. Formation of the aquocarbonyl derivative, as monitored

by its typical ΔE<sub>Q</sub> parameter, was sometimes observed over long periods of time (several weeks), probably due to water diffusion through the plastic walls of the container. The spectra were optimized by a least-squares analysis with the assumption of Lorentzian line shapes. For this purpose, a Fortran IV conversationally running program was used, based on the iterative method of Gauss-Newton, modified by Hartley for fitting nonlinear functions.<sup>15</sup> As a criterion of goodness of fit, the χ<sup>2</sup>, as defined by Ruby,<sup>16</sup> was calculated for each spectrum.

Spectra recorded in Vancouver employed a <sup>57</sup>Co(Rh) source. The spectrometers and data reduction procedures used have been described.<sup>17</sup> Samples of the complexes were loaded, in a CO-atmosphere glovebox, into nylon cells which were then sealed with epoxy resin. The Doppler velocity scale was calibrated with a metallic iron foil absorber. Mössbauer spectra for six of the complexes were measured in both laboratories, and in each case isomer shift and quadrupole splitting values agreed to within ±0.02 mm s<sup>-1</sup>.

## Results and Discussion

**Synthetic Approach.** The preparation of the carbonyl derivatives was carried out by treating FePc with CO and the ligand L in an inert solvent (when L = py, pip) or without any additional solvent in neat L (DEA, HMPT) (eq 1). The



presence of an inert solvent, usually CCl<sub>4</sub> (or *sym*-tetrachloroethane), is necessary when the formation of the bisadduct FePcL<sub>2</sub> competes with that of the carbonyl complex. It was noted earlier<sup>18</sup> that no stable bisadducts with oxygen-containing ligands such as THF, DMF, acetone, water, methanol, and ethyl acetate could be isolated. The stability of the bisadducts of DEA, HMPT, and OPPh<sub>3</sub> must be low also, as the carbonyl adduct could be prepared in the presence of a large excess of these ligands. Furthermore, gas volumetric measurements of CO uptake in neat DEA and HMPT indicated a quantitative formation of FePc(CO)L, similar to that found earlier<sup>9,10</sup> for carbonylation reactions in THF, DMF, and other oxygen-containing donor solvents. No solid bisadducts of FePc with oxygen-donor ligands have been prepared directly from FePc and such ligands; even in the FePc(Me<sub>2</sub>SO)<sub>2</sub> complex, Me<sub>2</sub>SO is sulfur bonded to iron.<sup>18</sup>

The bisadducts of FePc with nitrogen-donor ligands are well authenticated, both in solution and in the solid state.<sup>18–23</sup> Analogous complexes with other group 5 ligands such as PBu<sub>3</sub> and P(OR)<sub>3</sub> have been described,<sup>24</sup> and group 4 donor-atom ligands such as isocyanide<sup>25</sup> and cyanide<sup>26</sup> are also known to give FePcL<sub>2</sub> derivatives.

Data reported previously<sup>13</sup> for FePc(CO)pip in fact refer to FePc(CO)(MeOH). Precipitation of the piperidine complex occurs on addition of hexane after toluene solutions of FePc(pip)<sub>2</sub> are reacted with CO, but addition of methanol<sup>8</sup>

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Table I. Mössbauer and IR Data for FePc(CO)L Complexes at Room Temperature<sup>a</sup>

L	$\Delta E_Q$ , mm s <sup>-1</sup>	$\delta$ , <sup>b</sup> mm s <sup>-1</sup>	$\nu_{CO}$ , cm <sup>-1</sup>	
			Nujol	soln
THF	1.82	0.36	1975	1995 <sup>c</sup>
H <sub>2</sub> O	1.75	0.37	1997	
OPPh <sub>3</sub>	1.69	0.36	1975	
HMPT	1.60	0.36	1984	1988 <sup>d</sup>
Me <sub>2</sub> SO	1.56	0.36	1980	1995 <sup>e</sup>
DMF	1.56	0.35	1966	
MeOH	1.56	0.37	1995	
THT	1.55	0.38	1997	2002 <sup>c</sup>
DEA	1.45	0.35	1982	
pip	1.27	0.37	1992	
py	1.19	0.37	2000	
<i>n</i> -PrNH <sub>2</sub>	1.11	0.36	1992	2005 <sup>d</sup>
NH <sub>3</sub>	1.02	0.38	2006	
CO	0.82	0.36	2057	

<sup>a</sup> Comparative  $\Delta E_Q$  (mm s<sup>-1</sup>) data for FePcL<sub>2</sub> complexes:<sup>10</sup> L = py, 2.01; pip, 2.22; Me<sub>2</sub>SO, 2.08; THT, 2.20; *n*-PrNH<sub>2</sub>, 1.97.  
<sup>b</sup> With respect to sodium nitroprusside. <sup>c</sup> THF. <sup>d</sup> CH<sub>2</sub>Cl<sub>2</sub>.  
<sup>e</sup> CH<sub>2</sub>Cl<sub>2</sub>-heptane.

results in precipitation of the methanol complex. (However, stirring a suspension of FePc(CO)pip in methanol gives no replacement of the amine.) The earlier measurements had been done on a methanol-precipitated product.

Trans dicarbonyls of tetraphenylporphyrin complexes of Fe(II),<sup>27</sup> Ru(II),<sup>28</sup> and Os(II)<sup>29</sup> have all been isolated; the Fe(II) and Ru(II) systems readily lose CO upon standing and during the preparation of samples for IR studies.<sup>27,28</sup> A corresponding dicarbonyl of Fe(II) with a naturally-occurring porphyrin has also been detected spectroscopically, and again the second CO molecule is bound very weakly.<sup>30</sup> In view of these results, the isolation of the FePc(CO)<sub>2</sub> complex in the present work is particularly interesting. The dicarbonyl was formed in admixture with the aquo complex FePc(CO)H<sub>2</sub>O by reaction of FePc in heptane with anhydrous CO under pressure. Samples of the dicarbonyl with analytical purity of 60% could be obtained, the limiting factor presumably being the presence of trace moisture:



The monocarbonyl complexes FePc(CO)L, where L = DMF, THF, and Me<sub>2</sub>SO, are similarly moisture sensitive, while the other complexes listed in Table I exhibit no spectroscopic changes at least on limited exposure to air.

The FePc(CO)<sub>2</sub> complex has a characteristic high  $\nu(\text{CO})$  band at 2057 cm<sup>-1</sup>, comparable with the 1970–2050-cm<sup>-1</sup> range observed for the dicarbonyls of the iron subgroup porphyrins,<sup>27–29</sup> the high values resulting from competitive  $\pi$  bonding between trans-CO groups. The higher  $\nu(\text{CO})$  value of the phthalocyanine dicarbonyl compared to that of Fe(T-PP)(CO)<sub>2</sub> (2042 cm<sup>-1</sup>) possibly reflects the better  $\pi$ -acceptor properties of phthalocyanines vs. porphyrins.<sup>31</sup> The Mössbauer data for FePc(CO)<sub>2</sub> (Figure 1D, Table I) show  $\delta = 0.36$  mm s<sup>-1</sup>, typical of all the FePc(CO)L complexes, but a  $|\Delta E_Q|$  value of 0.82 mm s<sup>-1</sup>, the lowest found for any of the carbonyl complexes (vide infra).

**Mössbauer Spectra.** Figure 1 shows some representative spectra, and the Mössbauer spectroscopic parameters, together

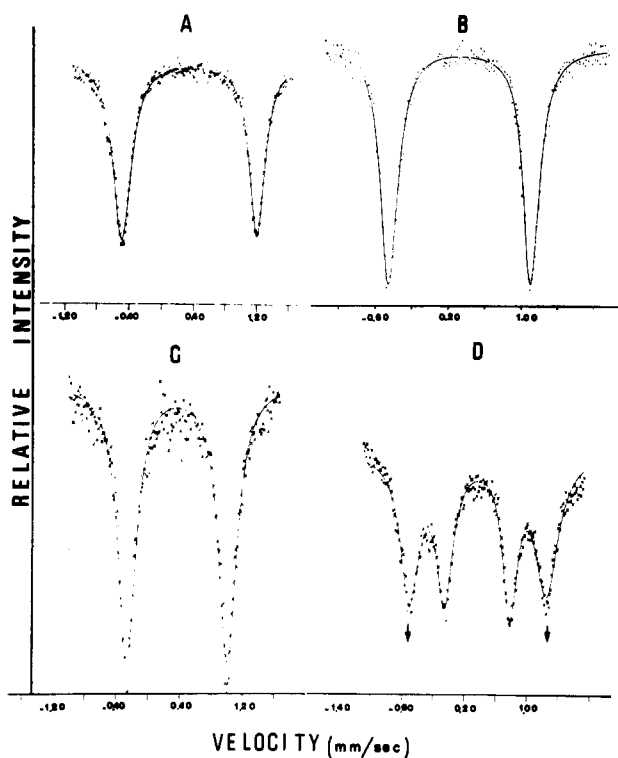


Figure 1. Mössbauer spectra of (A) FePc(CO)OPPh<sub>3</sub>, (B) FePc(CO)DMF, (C) FePc(CO)pip, and (D) FePc(CO)H<sub>2</sub>O + FePc(CO)<sub>2</sub>. In spectrum D the arrows indicate the aquocarbonyl complex.

with the carbonyl stretching frequencies, are reported in Table I.

For the FePcL<sub>2</sub> complexes (L = N- or S-donor ligand), the isomer shift ( $\delta$ ) values lie between 0.50 and 0.54 mm s<sup>-1</sup>, while the quadrupole splittings ( $\Delta E_Q$ ) are in the 1.97–2.34 mm s<sup>-1</sup> range.<sup>10,11</sup> The instability of the bisadducts with O-donor ligands precludes acquisition of Mössbauer data for such species. Carbonylation results in substantial decreases in both  $\delta$  (0.35–0.38 mm s<sup>-1</sup>) and  $\Delta E_Q$  (1.02–1.82 mm s<sup>-1</sup>). For the FePc(CO)L species,  $\delta$  is virtually independent of L, in contrast to the wide variation in  $\Delta E_Q$  values.

For the FePc(CO)(MeOH) complex (vide supra), the principal component of the electric field gradient (EFG),  $V_{zz}$ , has been shown<sup>13</sup> to be positive, with the asymmetry parameter  $\eta \approx 0$ . Positive EFG's have been observed similarly for FePcL<sub>2</sub> (L = py, pip)<sup>13,21</sup> and for a number of Fe(N<sub>4</sub>)L<sub>2</sub> and Fe(N<sub>4</sub>)(CO)L complexes, where N<sub>4</sub> represents a porphyrin or bis(dioxime) system.<sup>13,32–36</sup> Structural data available for these species<sup>37–40</sup> show that the Fe–N(equatorial) bond lengths are always shorter than the iron–axial ligand bonds. The positive  $V_{zz}$  values imply more metal character in bonds involving the iron  $d_{x^2-y^2}$  orbital, compared to bonding orbitals formed from the  $d_{z^2}$  orbital (see eq 4 below). Since metal–N(Pc) bonds are significantly shorter<sup>10</sup> than the corresponding metal–N(porphyrin) bonds, it is reasonable to expect that  $V_{zz}$

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will be positive for all of the FePc(CO)L complexes discussed here. The essentially axial symmetry is consistent with the linear Fe-C-O moiety found for both FePc(CO)DMF·DMF<sup>10</sup> and Fe(TPP)(CO)py.<sup>37</sup>

The EFG in these complexes arises mainly from an imbalance of electron densities in the iron 3d valence orbitals.<sup>41</sup> If lattice contributions are ignored, the quadrupole splitting is given by eq 3 with  $V_{zz} = eq_{\text{val}}$  and  $\eta = (V_{xx} - V_{yy})/V_{zz}$ . Ac-

$$\Delta E_Q = \frac{1}{2}eQV_{zz}(1 + \eta^2/3)^{1/2} \quad (3)$$

ording to the usual treatment,<sup>42</sup> the valence contribution to the EFG,  $q_{\text{val}}$ , can be expressed in terms of the effective populations  $n_i$  of the various iron 3d orbitals (eq 4) where R

$$q_{\text{val}} = \frac{4}{7}(1 - R)\langle r^{-3} \rangle [n_{x^2-y^2} + n_{xy} - n_{z^2} - \frac{1}{2}(n_{xz} + n_{yz})] \quad (4)$$

is a Sternheimer antishielding factor and  $\langle r^{-3} \rangle$  the expectation value of  $r^{-3}$  for the radial part of the 3d wave function. (A more realistic approach would be to weight each of the  $n_i$  in eq 4 by its own  $\langle r_i^{-3} \rangle$  value since in the presence of bonding interactions the radial extents of the various 3d orbitals will differ.) As  $d_{xy}$  is a nonbonding orbital it can be ignored. One then sees that to decrease  $|\Delta E_Q|$  there must be either an enhanced electron density in those iron orbitals that contribute negatively to  $q_{\text{val}}$  ( $d_{z^2}$ ,  $d_{xz}$ ,  $d_{yz}$ ), a diminished electron density in the  $d_{x^2-y^2}$  orbital, or both. The isomer shift will decrease both with an increase in ligand  $\rightarrow$  iron  $\sigma$  donation and iron  $\rightarrow$  ligand  $\pi$  back-donation.

To explain the decrease in  $|\Delta E_Q|$  observed upon replacement of an axial ligand L by CO, we shall begin with the reasonable assumption that CO is a weaker  $\sigma$  donor and stronger  $\pi$  acceptor than L. A decrease in axial ligand  $\sigma$  donation should decrease  $n_{z^2}$ , while an increase in Fe  $\rightarrow$  CO  $\pi$  donation will decrease  $n_{xz}$  and  $n_{yz}$ . Both these effects would result in an increase in  $|\Delta E_Q|$ , contrary to what is observed. In previous reports we independently proposed two alternative explanations for this apparent anomaly.<sup>10,13</sup>

The first argument<sup>13</sup> was based on the premise that CO cannot be so much stronger a  $\sigma$  donor (increasing  $n_{z^2}$ ) compared to a (non- $\pi$ -bonding) ligand such as piperidine as to overcome the iron  $d_x$  depletion due to Fe  $\rightarrow$  CO back-bonding and still produce a lowering in  $\Delta E_Q$  of  $>0.9$  mm s<sup>-1</sup>. We therefore concluded that carbonylation must be accompanied by a substantial cis effect, whereby there is an increase in Pc  $\rightarrow$  Fe  $\pi$  donation in compensation for Fe  $\rightarrow$  CO back-bonding, as well as a concurrent decrease in Pc  $\rightarrow$  Fe  $\sigma$  donation. The existence of such a cis effect is supported by the substantial differences in asymmetry parameters (as well as  $|\Delta E_Q|$  values) observed recently between carbonylamine and diamine complexes of bis(dioximato)iron(II).<sup>36</sup>

An alternative explanation was based on the observation<sup>10</sup> that the Fe-N(equatorial) bond lengths in FePc(CO)·DMF·DMF are similar to the corresponding bond distances in FePc(4-Mepy)<sub>2</sub> and FePc, and this was taken to imply that there had been little change in the iron-phthalocyanine bonding. Such reasoning suggested that reduction of the  $d_x$ -electron population on iron must be more than compensated by a strong  $\pi$  component from either CO or L. Consequently strong  $\sigma$  donors trans to CO should tend to decrease  $|\Delta E_Q|$ , and the opposite should be true for weak  $\pi$  donors. The large number of FePc(CO)L complexes whose Mössbauer parameters are reported here permits a more thorough evaluation of this trans-effect proposal.

The parameters used for comparing the  $\sigma$ -bonding properties of the various ligands are the  $pK_a$  values and the related proton affinities (PA) (the negative enthalpies for the gas phase re-

Table II. Comparison of the  $\Delta E_Q$  Values of FePc(CO)L Complexes with Proton Affinities (PA),  $pK_a$  Values, and Donor Numbers (DN) for Uncoordinated L

L	PA, kcal mol <sup>-1</sup>	$pK_a$	DN, kcal mol <sup>-1</sup>	$\Delta E_Q$ , mm s <sup>-1</sup>	ref <sup>d</sup>
THF		-2.02 <sup>b</sup>	20.0 <sup>c</sup>	1.82	10
H <sub>2</sub> O	164 <sup>e</sup>	-2.0 <sup>e</sup>	18.0 <sup>c</sup>	1.75	10
O <sup>t</sup> Ph <sub>3</sub>			31.0 <sup>d</sup>	1.69	
HMPT			38.8 <sup>c</sup>	1.60	
Me <sub>2</sub> SO		0.0 <sup>b</sup>	29.8 <sup>c</sup>	1.56	10
DMF		0.0 <sup>b</sup>	26.6 <sup>c</sup>	1.56	10
MeOH	180 <sup>e</sup>	-1.98 <sup>e</sup>	19.1 <sup>c</sup>	1.56	10
THT				1.55	10
DEA			32.2 <sup>c</sup>	1.45	
pip	228 <sup>e</sup>	11.12 <sup>f</sup>		1.27	
py	225 <sup>e</sup>	5.25 <sup>f</sup>	33.1 <sup>c</sup>	1.19	
n-PrNH <sub>2</sub>	222.3 <sup>g</sup>	10.89 <sup>h</sup>	55.5 <sup>c</sup>	1.11	
NH <sub>3</sub>	207.0 <sup>e</sup>	9.24 <sup>f</sup>	59.0 <sup>c</sup>	1.02	

<sup>a</sup> This work unless otherwise noted. <sup>b</sup> Collumeau, A. *Bull. Soc. Chim. Fr.* 1968, 5087. <sup>c</sup> Gutmann, V. *Chem. Tech.* 1977, 255.

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<sup>g</sup> Aue, D. H.; Webb, H. M.; Bowers, M. R. *Ibid.* 1972, 94, 4726.

<sup>h</sup> Jencks, W. P.; Gilchrist, M. *Ibid.* 1968, 90, 2622.

action  $\text{BH}^+ \rightarrow \text{B} + \text{H}^+$ ) and the donor numbers (DN), these being defined<sup>43</sup> as the negative  $\Delta H$  values for the reaction between  $\text{SbCl}_5$  and the donor in 1,2-dichloroethane. Table II includes a comparison of these parameters with the  $\Delta E_Q$  data. Although no linear correlation is evident, there is a general trend to lower  $\Delta E_Q$  values with increasing  $\sigma$ -donor strength of L.

Carbonyl stretching frequencies are often used as a measure of the electron density on a metal, lower  $\nu(\text{CO})$  values corresponding to higher metal  $d_x \rightarrow \text{CO} \pi^*$  electron transfer. In the present instance there is a general increase of  $\nu(\text{CO})$  as  $\Delta E_Q$  decreases (Table I). An increase in  $\nu(\text{CO})$  (1890–1902 cm<sup>-1</sup>) in the sequence DMF < THF < MeOH < py for some osmium(II) complexes, Os(OEP)(CO)L, has been explained<sup>44</sup> in terms of a decrease in L  $\rightarrow$  metal  $\pi$  donation, DMF > THF > MeOH > py. If a  $\pi$ -donating ligand alters the energy of the iron  $d_x$  orbitals so as to facilitate  $\pi$ -electron transfer to CO, this would still result in lower  $n_{xz}$ ,  $n_{yz}$  population and hence increase  $\Delta E_Q$  concurrent with a decrease in  $\nu(\text{CO})$ . Presumably for strong  $\sigma$ -donor but non- $\pi$ -bonding ligands such as NH<sub>3</sub>, whose complexes give high carbonyl stretching frequencies, the matching of the  $d_x$  and CO  $\pi^*$  orbitals is inappropriate.

The nonlinear correlations of ligand properties with  $\Delta E_Q$  values indicate not surprisingly that bonding interactions are complex within these highly delocalized systems. Some trans effects can be rationalized for ligands with extreme bonding requirements (e.g., DMF, a strong  $\pi$  donor; NH<sub>3</sub>, a strong  $\sigma$  donor), but for the majority of the carbonyl adducts there will be a complex mixture of  $\sigma$ - and  $\pi$ -bonding effects which cannot be separated by means of Mössbauer spectroscopy. A qualitative trend apparent from Table I is that  $\Delta E_Q$  decreases overall as the axial donor-ligand atom changes from O (or S) to N to C.

Thus the trans effect, while probably modulating the magnitude of the changes in the Mössbauer parameters, cannot be solely responsible for the observed trends in  $\Delta E_Q$ . Although the cis effect described above gains considerable support from the asymmetry parameter data determined for bis(dioximato)iron(II) complexes, it is similarly unlikely to be the only factor.

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Since similar decreases in  $\delta$  and  $\Delta E_Q$  reported for the FePc derivatives are observed for a wide range of iron(II)-macrocyclic complexes<sup>10,13,14,36</sup> for which the relative orbital energies and hence bonding characteristics should vary, we shall turn our attention to some structural data for these compounds.

In all cases for which structural data are available,<sup>37-40</sup> carbonylation results in a longer Fe-L(axial) bond length, but the Fe-C(O) bond distance is sufficiently short to cause a decrease in the sum of the axial bond lengths relative to the bis(L) adducts. Such a shortening of the mean axial bonds will increase the electron density near iron along the  $z$  axis and result in a decrease in  $\Delta E_Q$ . If this electron density has appreciable  $s$  character,  $\delta$  will also decrease. We suggest that these overall structural changes, irrespective of the  $\sigma$ - and  $\pi$ -bonding characteristics of the ligands, dominate the changes in Mössbauer parameters.

No structural data are available for dicarbonyl complexes nor has the sign of the EFG been determined in such a species

(although it is probably positive). This limits the present discussion of FePc(CO)<sub>2</sub> which gives one of the lowest  $|\Delta E_Q|$  values yet reported for a (phthalocyaninato)iron(II) complex. It is tempting to suggest that this results from a significant demand on the Pc  $\pi$  system, but further analysis awaits a detailed investigation of Fe(TPP)(CO)<sub>2</sub>.

**Acknowledgment.** The authors wish to thank the National Research Council of Italy and the Natural Sciences and Engineering Research Council of Canada for support of this work and the Scuola Normale Superiore of Pisa for a postdoctoral fellowship to G.P.

**Registry No.** FePc(CO)(DEA), 80720-96-3; FePc(CO)(py), 61395-36-6; FePc(CO)(pip), 68949-32-6; FePc(CO)(HMPT), 80737-35-5; FePc(CO)(OPPh<sub>3</sub>), 80737-36-6; FePc(CO)<sub>2</sub>, 80737-37-7; FePc(CO)(H<sub>2</sub>O), 74335-17-4; FePc(CO)(Me<sub>2</sub>SO), 58384-96-6; FePc(CO)(DMF), 71744-40-6; FePc(CO)(MeOH), 74325-92-1; FePc(CO)(THT), 80737-38-8; FePc(CO)(*n*-Pr-NH<sub>2</sub>), 71851-41-7; FePc(CO)(NH<sub>3</sub>), 71807-13-1; FePc(CO)(THF), 71744-41-7; FePc, 132-16-1.

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## Mössbauer Effect and Magnetic Investigation of the $S = 3/2 \leftrightarrow S = 1/2$ Spin Crossover in [Fe(salen)NO] and the $S = 3/2$ State in [Fe(5-Cl-salen)NO]

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Received April 9, 1981

The magnetic properties of quartet or doublet electronic ground states of the iron Schiff base complex [*N,N'*-ethylenebis(salicylideneiminato)]iron nitrosyl and its 5-chloro derivative have been studied by Mössbauer, magnetic susceptibility, and EPR methods with sample temperatures in the range 4–300 K. Near 175 K, the Mössbauer spectra of [Fe(salen)NO] clearly reflect the  $S = 3/2 \leftrightarrow S = 1/2$  transition detected by susceptibility studies reported previously by Earnshaw et al. Fluctuation rates between the two states are slow on the Mössbauer time scale, and a superposition of two spectra is seen near  $T_c = 175 \pm 3$  K. The high-temperature, intermediate-spin rate state has  $\Delta E_Q = 0.352 \pm 0.003$  and  $\delta E = 0.440 \pm 0.003$  mm/s at 275 K. The low-temperature, low-spin state has  $\Delta E_Q = 1.950 \pm 0.005$  and  $\delta E = 0.281 \pm 0.001$  mm/s at 4.2 K. The Mössbauer pattern of intermediate-spin [Fe(5-Cl-salen)NO] is a slightly asymmetric quadrupole doublet at all temperatures. At 77 K, the parameters are  $\Delta E_Q = 0.575 \pm 0.003$  and  $\delta E = 0.654 \pm 0.003$  mm/s. Intermediate-spin states of polycrystalline samples of [Fe(salen)NO] or its derivative show broad EPR spectra corresponding to a range of  $g$  factors from  $\sim 4$  to  $\sim 2$ . These values are consistent with Kramers levels from an  $S = 3/2$  term. The low-temperature  $S = 1/2$  state of [Fe(salen)NO] is characterized by an axial  $g$  tensor with  $g_{\perp} = 2.036 \pm 0.001$  and  $g_{\parallel} = 2.133 \pm 0.001$ . At the lowest temperatures available,  $T \leq 10$  K, the effective moment of [Fe(salen)NO] decreased sharply from the low-spin value. Also, in [Fe(5-Cl-salen)NO], the moment decreased from  $\sim 4 \mu_B$  for  $T \geq 120$  K to  $\sim 1 \mu_B$  at 4 K. These results, together with Mössbauer data, are consistent with short range antiferromagnetic interactions in these lattices.

The magnetic properties of the mononitrosyl adduct of [*N,N'*-ethylenebis(salicylideneiminato)]iron(II) are of interest because this material exhibits a relatively rare  $S = 3/2 \leftrightarrow S = 1/2$  spin crossover near 175 K.<sup>1,2</sup> This property was originally reported by Earnshaw and co-workers,<sup>1</sup> who also showed that the crossover is modulated by substitution in the salen macrocycle. The earlier studies reported susceptibility data above 80 K, but a detailed magnetic study of this material, including Mössbauer resonance and EPR properties, has been lacking and is the subject of this report.

As is typical of transition-metal complexes displaying spin-crossover phenomena, the higher spin state (with larger atomic volume) is favored at high temperatures. Thus [Fe(salen)NO] has an intermediate spin,  $S = 3/2$ , state above 175 K and is characterized by an  $S = 1/2$  state below this tem-

perature. The transition occurs over a temperature interval of a few degrees at most. By contrast, the 5-Cl derivative retains a moment characteristic of the  $S = 3/2$  state at all temperatures above 50 K and below this shows evidence of antiferromagnetic interactions.

The X-ray crystal structure of [Fe(salen)NO] at 98 and 296 K has recently been reported.<sup>3</sup> This work has shown only marginally significant structural changes above and below the transition temperature. Both forms have a disordered nitrosyl group, and the FeNO group has a bent geometry. The average Fe-N-O angle is  $147^\circ$  above the transition and  $127^\circ$  below the transition. At the latter temperature, the iron atom is

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