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CARBONYL DERIVATIVES OF PHTHALOCYANINATOIRON(II), ESPECIALLY THOSE CONTAINING GROUP VI AXIAL DONOR ATOMS. CRYSTAL AND MOLECULAR STRUCTURE OF CARBONYL(*N*,*N*-DIMETHYLFORMAMIDE)PHTHALOCYANINATO-IRON(II) AND MÖSSBAUER STUDIES OF SOME OF THE PRODUCTS *

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Summary

The carbonyl adduct of phthalocyaninatoiron(II), FePc, with *N*,*N*-dimethylformamide (DMF) as axial ligand, FePc(CO)DMF, was prepared by the reaction of iron carbonyls, $Fe(CO)_5$ or $Fe_2(CO)_9$, with *o*-phthalonitrile in DMF as solvent. Several carbonyl adducts of FePc of general formula FePc(CO)L are reported, with L being a ligand with oxygen, sulphur and nitrogen donor atoms (L = tetrahydrofuran, H_2O, CH_3OH, dimethylsulphoxide, tetrahydrothiophene, ammonia, n-propylamine, diethylamine, triethylamine). The crystal and molecular structure of FePc(CO)DMF · DMF was investigated by X-ray diffraction methods. The compound has a monoclinic unit cell and space group $P2_1/n$, a 9.86(1), b 17.35(3), c 19.79(4) Å, β 87.9(2)°, $Z = 4$, U 3383 Å^3, D_c 1.458 g cm^{-3}. The iron atom is hexacoordinated to the four inner nitrogen atoms of the

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macrocycle, to carbon monoxide (Fe—C distance 1.72(2) Å) and to DMF (Fe—O distance 2.07(1) Å). The extra DMF occupies lattice sites. All of the compounds reported in this paper are substantially diamagnetic. Mössbauer spectra show typical isomer shift parameters for the bis-adducts and for the carbonyl adducts, substantially independent of the nature of the axial ligand. The quadrupole splitting parameter of the carbonyl adducts is strongly affected by the nature of the axial ligand.

Introduction

Phthalocyaninatoiron(II), FePc, has been studied extensively in the past, mainly as a model for the haem group [1]. Solution studies have appeared in which the interaction between FePc and carbon monoxide in dimethylsulphoxide [2], in concentrated sulphuric acid [3] and in the presence of nitrogen bases [4] has been investigated. A paper has appeared [5] concerning the solid state isolation of carbonyl derivatives of FePc with nitrogen bases as presumed axial ligands. Taube has also reported [6] the carbonyl adduct of FePc with aniline as additional ligand. No studies have appeared in the literature in which oxygen or sulphur containing ligands had been shown to interact with FePc in combination with CO to yield stable solid adducts of the type FePc(CO)L.

We now report the isolation and characterisation of such solid carbonyl derivatives of phthalocyaninatoiron(II). In addition we describe the crystal and molecular structure of FePc(CO)DMF and we report the Mössbauer spectra of several compounds belonging to the $FePcL_2$ and FePc(CO)L classes (L = ligand containing O or S as donor atom). No metal—phthalocyaninato carbonyl derivatives had been characterised earlier by X-ray diffraction methods. Preliminary accounts of this work have already appeared [7—9].

Experimental

Unless otherwise stated, all of the operations described in this paper were carried out under an atmosphere of prepurified argon or nitrogen. Solvents were carefully purified by conventional methods prior to use.

IR spectra were measured with a Perkin-Elmer 283 instrument on solutions or nujol mulls of the complexes prepared under rigorous exclusion of air and moisture. Magnetic susceptibilities were measured with a magnetic balance equipped for the Faraday method and calibrated with $CuSO_4 \cdot 5\ H_2O$.

Mössbauer spectra were measured at room temperature with an Elron-Elscint AME-30 spectrometer equipped with a ^{57}Co in 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 nitrogen. 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. The spectra were optimised by a least-squares analysis assuming Lorentzian line shapes. For this purpose, A Fortran IV conversationally running programme was used, based on the iterative method of Gauss-Newton, modified by Hartley for fitting non-linear functions [10]. As a criterion of goodness of fit, the χ^2, as defined by Ruby [11], was calculated for each spectrum.

Preparations of FePc(CO)DMF. In a 100 ml flask equipped with a reflux condenser and a nitrogen inlet, $Fe(CO)_5$ (14.2 g, 72.5 mmol) was introduced together with *o*-phthalonitrile (37.7 g, 294 mmol) and dimethylformamide (309 ml). The mixture was stirred and heated to 130—135° C for about 80 h. During this time the gas evolved was measured by the amount of water displaced in a gasometer and found to correspond to 4.2 moles per mole of iron. Finally the reaction mixture was cooled to room temperature and kept overnight under an atmosphere of carbon monoxide. The reaction mixture was then filtered under carbon monoxide and the microcrystalline solid so obtained was dried in vacuo to give a 60% yield of crude product. This was recrystallised from dimethylformamide under carbon monoxide by heating at 100—105° C and then cooling the filtered solution down to about —10° C. The resulting crystalline product was filtered under carbon monoxide and dried in vacuo for about 20 min. Product I with the analysis shown in Table 1 was so obtained. The yield of recrystallisation was 67% and the overall yield of recrystallised product was therefore about 40%. More prolonged drying in vacuo resulted in the isolation of products of composition FePc(CO)DMF · x DMF, with $x < 1$. For example, drying the compound for 48 h at room temperature gave a product of composition FePc(CO)DMF · 0.5 DMF. Anal. Found: C, 63.59; H, 4.15; Fe, 7.88; N, 18.90. $C_{37.5}H_{26.5}FeN_{9.5}O_{2.5}$ calcd.: C, 63.79; H, 3.78; Fe, 7.91; N, 18.84%.

The DMF-CO adduct released CO quantitatively when treated with pyridine at room temperature: this reaction, carried out in a gasvolumetric equipment, was used for the analytical determination of the CO content (see Table 1). The DMF-CO adduct is a red-violet crystalline solid, moderately soluble in DMF with a typical blue colour (the solubility is about 3 g/l), and very little soluble in aromatic hydrocarbons. The solid crystalline substance is stable to air and moisture for several hours and is indefinitely stable in an atmosphere of dry carbon monoxide, nitrogen or argon, with no sign of CO loss; it is characterised by a strong infrared carbonyl absorption at 1972 cm^{-1} (see Table 1). The mulls for this measurement must be prepared under a dry atmosphere of argon or nitrogen. Exposure of the mull to air at the humidity level of the laboratory resulted in the fast decrease of the intensity of the 1972 cm^{-1} band and in the appearance of a new carbonyl band at higher frequency, due to the formation of the aquo-carbonyl complex (vide infra). This phenomenon was suppressed or took place at a drastically lower rate when the nujol mull was exposed to air pre-dried over P_4O_{10}.

The DMF-CO adduct has a strong tendency to retain lattice solvent. The presence of additional DMF with respect to the expected formula FePc(CO)-DMF was shown by direct gravimetric and spectrophotometric (IR) determination of the liquid collected in a cold trap (ca. —80° C) upon thermal decomposition of the compound at about 100° C/ca. 5×10^{-2} mmHg (vide infra). Washing the compound with toluene followed by filtration and drying in vacuo resulted in the displacement of some lattice DMF by the aromatic hydrocarbon, as shown by spectrophotometric (IR) determination of the volatile products obtained upon thermal decomposition of the new solid isolated. The preparation

TABLE 1

ANALYTICAL AND INFRARED DATA OF CARBONYLPHTHALOCYANONATOIRON(II) COMPLEXES

Compound	Formula	Analysis, Found (Calcd)(%)					ν(CO)(cm^{-1})	
		C	H	N	CO	Other	Nujol	Solution
FePc(CO)DMF · DMF [a], (I)	$C_{39}H_{30}FeN_{10}O_3$	62.95	4.02	18.88	3.78	Fe: 7.87	1972	
		(63.08)	(4.07)	(18.86)	(3.77)	(7.52)		
FePc(CO)THF · 0.75THF [b], (II)	$C_{40}H_{30}FeN_8O_{2.75}$	66.63	4.26	15.50			1975	1995 [d]
		(66.49)	(4.18)	(15.51)				
FePc(CO)H_2O · 0.3Me_2CO, (IIIa)	$C_{33.9}H_{19.8}FeN_8O_{2.3}$	64.40	3.18	17.83	4.20		1997	
		(64.44)	(3.16)	(17.73)	(4.43)			
FePc(CO)H_2O · 0.3MeCN, (IIIb)	$C_{33.6}H_{18.9}FeN_{8.3}O_2$	64.33	2.99	18.52				
		(64.39)	(3.04)	(18.55)				
FePc(CO)H_2O · 0.6H_2O, (IIIc)	$C_{33}H_{19.2}FeN_8O_{2.6}$	63.07	3.05	17.59				
		(63.40)	(3.09)	(17.92)				
FePc(CO)MeOH · 0.7CH_2Cl_2, (IVa)	$C_{34.7}H_{21.4}Cl_{1.4}FeN_8$	60.58	3.40	16.30				
		(60.59)	(3.14)	(16.29)				
FePc(CO)MeOH, (IVb)	$C_{34}H_{20}FeN_8O_2$	64.04	3.31	17.55			1995	
		(64.98)	(3.21)	(17.83)				
FePc(CO)DMSO · 0.2CH_2Cl_2, (Va)	$C_{35.2}H_{22.4}Cl_{0.4}FeN_8O_2S$	61.50	4.46	16.69		S: 4.67	1980	1995 [e]
		(61.14)	(3.27)	(16.20)		(4.64)		
FePc(CO)DMSO · 0.7DMSO, (Vb)	$C_{36.4}H_{26.2}FeN_8O_{2.7}S_{2.7}$	60.17	3.59	15.60		S: 7.03		
		(59.95)	(3.62)	(15.37)		(7.47)		
[FePc(CO)THT]$_{0.7}$ · [FePc(THT)$_2$]$_{0.3}$, [c] (VI)	$C_{37.9}H_{26.4}FeN_8O_{0.7}S_{1.3}$	65.58	3.92	15.93		S: 6.16	1997	2002 [f]
		(64.79)	(3.79)	(15.95)		(5.93)		
FePc(CO)NH_3 · 0.35CCl_4, (VII)	$C_{33.35}H_{19}Cl_{1.4}FeN_9O$	60.21	2.94	18.30			2008	
		(60.03)	(2.87)	(18.89)				
FePc(CO)(n-$C_3H_7NH_2$) · 0.1CH_2Cl_2, (VIIIa)	$C_{36.1}H_{25.2}Cl_{0.2}FeN_9O$	65.53	5.10	17.91			2005	2002 [g]
		(63.30)	(3.83)	(18.99)				
FePc(CO)(n-$C_3H_7NH_2$) · 0.5 CCl_4, (VIIIb)	$C_{36.5}H_{25}Cl_2FeN_9O$	59.14	3.55	16.91				2005 [h]
		(59.86)	(3.44)	(17.21)				
FePc(CO)Et_2NH · 1.1 CCl_4, (IX)	$C_{38.1}H_{27}Cl_{4.4}FeN_9O$	54.57	2.97	15.51			1993	
		(54.56)	(3.24)	(15.03)				
FePc(CO)Et_3N · 0.9 CCl_4, (X)	$C_{39.9}H_{31}Cl_{3.6}FeN_9O$	57.26	3.34	15.59			1973	
		(57.32)	(3.74)	(15.08)				

[a] DMF = *N,N*-dimethylformamide. [b] THF = tetrahydrofuran. [c] THT = tetrahydrothiophene. [d] In tetrahydrofuran solution. [e] In a dichloromethane—n-hexane mixture. [f] In a dichloromethane—n-heptane mixture. [g] In dichloromethane solution. [h] In CCl_4 solution.

of the DMF-CO adduct was also carried out by treating $Fe_2(CO)_9$ (5.53 g, 15.2 mmol) with phthalonitrile (15.9 g, 124 mmol) in DMF (75 ml) under conditions substantially similar to those used for the reaction with $Fe(CO)_5$. A 58% yield of FePc(CO)DMF · x DMF was obtained spectroscopically (IR) identical with the product prepared from $Fe(CO)_5$ and analytically consistent with it.

Infrared spectrum (Nujol mull) for a product of composition FePc(CO) DMF · 0.4 DMF: 1972vs, 1925vw, 1685ms, 1654s, 1615w, 1512ms, 1425m, 1332s, 1290m, 1260w, 1167m, 1121s, 1096s, 1075mw, 1070mw, 1005w, 910m, 785mw, 778w, 770w, 753m, 738ms, 727w, 686w, 657vw, 640w, 581vw, 575w, 523(sh), 512w and 435vw cm^{-1}.

Thermal decomposition of FePc(CO)DMF to FePc. Recrystallised FePc(CO)-DMF · DMF was heated in a Schlenk tube connected to a vacuum line (ca. 5×10^{-2} mmHg) through a cold trap (ca. —80° C). At about 80° C a sudden increase of the residual pressure was noted, due to loss of carbon monoxide. After 12 h heating at about 100° C, the content of the cold trap was found to consist of spectroscopically (IR) pure DMF in the expected amount. The solid residue was found to be analytically and magnetically (χ_M^{corr} 5740 $\times 10^{-6}$ cgsu, diamagnetic correction = —429 $\times 10^{-6}$ cgsu, corresponding to a magnetic moment of 3.68 BM) pure phthalocyaninatoiron(II). The IR spectrum corresponded to a mixture of α- and β-FePc [1,12].

Preparation of FePc(CO)THF. FePc (1.04 g, 1.84 mmol), obtained by thermal decomposition of FePc(CO)DMF · DMF, was suspended in 50 ml THF under an atmosphere of carbon monoxide and heated at reflux temperature for about 30 min; the mixture was then filtered and slowly cooled down to room temperature. The blue solution was ice-cooled and the solid obtained was collected by filtration, dried in vacuo (55% yield) and analysed, giving the results shown in Table 1. The THF content was determined by weight after thermal (ca. 100°C/5 $\times 10^{-2}$ mmHg) decomposition of the red-violet solid for 12 h. The CO-DMF adduct (0.323 g) was treated with THF (20 ml) in a gasvolumetric apparatus: no significant gas evolution was observed. Another sample of the CO-DMF adduct (0.052 mmol) in 5 ml THF under CO at atmospheric pressure had a band at 1680 cm^{-1}, characteristic of uncoordinated DMF, and a band at 1995 cm^{-1} for coordinated CO (see Table 1). Infrared spectrum (Nujol mull): 1975vs, 1930vw, 1650vw(br), 1610w, 1590vw, 1510s, 1505(sh), 1422ms, 1330s, 1288ms, 1200w(br), 1165ms, 1120vs, 1095s, 1075m, 1066mw, 1040w, 1001w, 980vw, 946vw, 940vw, 910m, 879mw, 874(sh), 780m, 752ms, 734vs, 692vw, 640w, 575mw, 522w, 511w, and 435vw cm^{-1}.

Preparation of FePc(CO)H_2O (III). FePc (0.600 g, 1.05 mmol) was suspended in 5 ml of a 0.25 M solution of H_2O in acetone (H_2O : Fe molar ratio = 1.2) and treated with carbon monoxide at room temperature for about 4 h. The liquid was then eliminated from the blue-green suspension, partly by suction and finally by evaporation under reduced pressure. The solid resulting from this operation was collected, sealed under carbon monoxide (82% yield) and analysed, giving the results in Table 1 for product IIIa. χ_M^{corr} 280 $\times 10^{-6}$ cgsu (diamagnetic correction —450 $\times 10^{-6}$ cgsu), corresponding to an apparent μ_{eff} of 0.81 BM. Infrared spectrum (Nujol mull), IIIa: *3570*w(sh), 2006(sh), 1997vs, 1705w, *1620*(sh), 1610mw, 1590w, 1510s, 1420m, 1330ms, 1288ms, 1183w, 1168m, 1121m, 1111m, 1101mw, 1090ms, 1074w, 1065mw, 1000vw, 955(sh), 949vw, 938vw, 910mw, 860w, 778w, 770w, 751ms, 729s, 720(sh), 636w, 574w, 515w(br), and 434w cm^{-1} (bands due to water are in italics). For the absorptions in the carbonyl stretching region, see the Results and discussion section. The presence of presumably lattice acetone in the solid carbonyl derivative was evidenced by a band at 1705 cm^{-1}. Furthermore, the aquo-carbonyl complex was heated for 10 h under reduced pressure (ca. 5×10^{-2} mmHg); loss of CO was noted at about 50° C. The temperature was then raised to 110—120° C and maintained at this level for about 10 h. The volatile products collected in the cold trap were shown by their IR spectrum between germanium windows to be an acetone-water mixture of composition similar to that expected on the basis of the elemental analysis. The deuterated compound, prepared as specified above with D_2O instead of H_2O, had an identical IR spectrum with the exception of the 3570 cm^{-1} band which was shifted to 2650 cm^{-1} ($\nu(OH)/\nu(OD) = 1.35$) and of the 1620 cm^{-1} band which was shifted to a region covered by ligand vibrations. Preliminary gasvolumetric measurements showed that no significant absorption of CO by sublimed FePc took place in dry acetone as solvent. Only addition of H_2O (H_2O : Fe molar ratio = 2) resulted in the fast absorption of CO in the expected amount. The CO-H_2O adducts was also obtained similarly with acetonitrile as solvent. The analytical results are in Table 1 for IIIb. A preliminary gasvolumetric experiment showed that sublimed FePc showed a small (CO : Fe molar ratio = 0.12) and scarcely chemically significant absorption of CO in neat MeCN at 20.2° C.

In another experiment, the CO-DMF adduct (1.975 g, 2.9 mmol) was treated with 59 mmol of H_2O and 100 ml acetonitrile (H_2O : Fe molar ratio = 20) under a CO atmosphere while stirred for 7 h. The suspension was then filtered and the solid dried in vacuo (95% yield). The analytical results for this product are those presented in Table 1 for IIIc.

The aquo-carbonyl derivative was also obtained as a precipitate by displacing the THF ligand from FePc(CO)THF when the latter was treated with one equivalent of water dissolved in acetonitrile.

All of the aquo-carbonyl complexes obtained by the procedures specified above were violet solids, characterised by a strong carbonyl absorption just below 2000 cm^{-1} (see Table 1), accompanied by an usually weak shoulder just above 2000 cm^{-1}. No change in the IR spectrum was observed upon exposure of the Nujol mull to air.

Preparation of FePc(CO)MeOH (IV). FePc (1.009 g, 1.77 mmol) in dichloromethane (50 ml) was treated with methanol (5 ml) and stirred for 7 h under an atmosphere of CO. The violet microcrystalline solid was filtered in vacuo (95% yield). The analytical results for this product are those reported in Table 1 for IV a. χ_M^{corr} 870 $\times 10^{-6}$ cgsu, diamagnetic correction —460 $\times 10^{-6}$ cgsu, corresponding to an apparent μ_{eff} of 1.43 BM.

The CO-MeOH adduct was also prepared in methanol as reaction medium. FePc (0.688 g, 1.20 mmol) was suspended in dry methanol (20 ml) under an atmosphere of argon. Introduction of CO resulted in a fast change of the colour and morphology of the solid. After 7 h stirring the blue-violet solid was collected by filtration and dried in vacuo (91% yield). The analytical results are those presented in Table 1 for IVb. A preliminary gasvolumetric measurement showed that 0.253 g of FePc (0.445 mmol) suspended in methanol (20 ml) absorbed 0.431 mmol of CO at 15.3°C and atmospheric pressure, corresponding to a CO : Fe molar ratio of 0.97. Infrared spectrum (Nujol mull), IVb: 2000(sh), 1995vs, 1980(sh), 1610w, 1590vw, 1510s, 1421mw, 1330ms, 1288m, 1162mw, 1112ms, 1090s, 1065mw, 1030s, 952w, 910mw, 860vw, 778mw, 769w, 750mw, 729s, 636w, 575w, 514w, 507w and 435w cm^{-1}.

Preparation of FePc(CO)DMSO (V). FePc (1.15 mmol) was suspended in 80 ml dichloromethane and treated with dimethylsulphoxide (0.29 ml, 4.08 mmol) under an atmosphere of carbon monoxide. After 12 h stirring the suspension was filtered. To the solution, n-heptane (20 ml) was added; after evaporation of most of the CH_2Cl_2 under reduced pressure, the resulting suspension was filtered and the solid compound was dried in vacuo (44.4% yield). The analytical results are reported in Table 1 for Va. χ_M^{corr} 490 × 10^{-6} cgsu (diamagnetic correction —520 × 10^{-6} cgsu), corresponding to an apparent μ_{eff} of 1.07 BM. Infrared spectrum (Nujol mull): 1982s, 1610vw, 1590vw, 1510ms, 1422mw, 1330ms, 1290m, 1265vw, 1168m, 1122ms, 1098ms, 1070mw, 1030vw, 996w, 950w, 910w, 780w, 750mw, 732ms, 640vw, 573w, 510w, and 435vw, cm^{-1}.

The carbonyl stretching absorption at 1980 cm^{-1} was strongly affected by exposing the mull to air, as previously described for the CO-DMF and the CO-THF adducts.

The CO-DMSO adduct was also prepared starting from $FePc(DMSO)_2 \cdot 2\,DMSO$ [13]. The latter compound (0.937 g, 1.07 mmol) was suspended in dichloromethane (20 ml) and treated with CO at atmospheric pressure. After 4 h stirring, the suspension was filtered and the solution was cooled down to about —80°C. The solid so obtained was collected by filtration and dried in a stream of carbon monoxide (8% yield). The analytical results are those reported in Table 1 for Vb.

In a gasvolumetric experiment FePc (0.216 g, 0.38 mmol) in DMSO (99 ml) at 27.5°C was found to absorb 0.125 mmol of CO at atmospheric pressure, corresponding to a CO : Fe molar ratio of 0.33. The gas absorption was found to be substantially complete in 8 h and conditions of constant volume were maintained for at least 5 h. At the end of the experiment, filtration confirmed the homogeneity of the system.

Preparation of FePc(CO)THT (THT = tetrahydrothiophene), in admixture with $FePc(THT)_2$ (VI). FePc (1.616 g, 2.8 mmol) was suspended in dichloromethane (100 ml) and treated with THT (5.7 mmol, THT : Fe molar ratio = 2.03) under an atmosphere of carbon monoxide. After 12 h stirring the reaction mixture was filtered. n-Heptane (20 ml) was added to the solution; after evaporation of most of the dichloromethane under reduced pressure, the resulting suspension was filtered and the red-violet solid was dried in vacuo (48% yield). The analytical results are given in Table 1. The Mössbauer spectrum (vide infra), the gasvolumetric analysis of the CO content and the gravimetric determination of the THT (IR) collected in a cold (ca. —80°C) trap by thermal (100—120°C) decomposition of the product were all consistent with the formulation given. χ_M^{corr} 680 × 10^{-6} cgsu (diamagnetic correction —520 × 10^{-6} cgsu), corresponding to an apparent μ_{eff} of 1.24 BM.

A gasvolumetric experiment showed that FePc absorbed 0.18 mmol of CO in neat THT at 16.8°C. Infrared spectrum (Nujol mull): 1997s, 1610vw, 1590vw, 1510s, 1421m, 1330ms, 1287m, 1161s, 1120s, 1090s, 1070ms, 1001vw, 909w, 778w, 749m, 731ms, 572w and 510vw cm^{-1}.

Preparation of FePc(CO)NH$_3$ (VII). FePc (1.22 g, 2.15 mmol) was suspended in CCl$_4$ (50 ml) and treated with 2.15 mmol of dry ammonia. The reaction flask was then connected intermittently with a carbon monoxide line and the reaction mixture was stirred for 15 h. The red-violet solid was filtered and dried briefly in vacuo (91% yield). The elemental analysis is given in Table 1, for the product presumably containing lattice CCl$_4$. The infrared spectrum (Nujol mull): 3320w, 3240w, 2008s, 1997(sh), 1650w(br), 1610w, 1590vw, 1508m, 1420mw, 1332m, 1287mw, 1230w, 1160mw, 1115s, 1088ms, 1065mw, 1000mw, 950vw, 910mw, 870vw, 780(sh), 775m, 768w, 750ms, 730s, 635vw, 570w, 510vw, 490vw and 435vw cm^{-1}.

The presence of CCl$_4$ was ascertained by thermal decomposition in vacuo and IR analysis of the liquid collected in the cold trap.

Preparation of FePc(CO)n-C$_3$H$_7$NH$_2$ (VIII). FePc (1.438 g, 2.53 mmol) was suspended in dichloromethane (50 ml) and treated with n-propylamine (10.1 mmol, n-propylamine : Fe molar ratio = 4.04). After 15 h stirring under carbon monoxide, the resulting suspension was evaporated to dryness under reduced pressure. By a second filtration under CO, the carbonyl adduct was isolated and dried in vacuo (15% yield). The analytical results for the violet microcrystalline adduct containing some presumably lattice dichloromethane are given in Table 1 for VIIIa. Infrared spectrum (Nujol mull): 2005m, 1650w(br), 1610vw, 1590w, 1505m, 1420mw, 1330m, 1285mw, 1260vw, 1160ms, 1115s, 1905s, 1068mw, 1000vw, 910w, 780w, 775mw, 750m, 730ms, and 570vw cm^{-1}.

The carbonyl adduct was also prepared with CCl$_4$ as reaction medium with a amine : Fe molar ratio = 1.0. In this case, the product labelled VIIIb in Table 1 was obtained.

Preparation of FePc(CO)NH(C$_2$H$_5$)$_2$ (IX). FePc (1.212 g, 2.13 mmol) in CCl$_4$ (30 ml) was treated with 0.156 g (2.14 mmol) diethylamine under an atmosphere of carbon monoxide. The intensely blue suspension was stirred for 20 h, then filtered and the violet microcrystalline solid compound was dried in vacuo (76% yield). The analysis is given in Table 1. Infrared spectrum (Nujol mull): 1993s, 1610w, 1590vw, 1505ms, 1420m, 1332ms, 1285ms, 1165m, 1157(sh), 1120vs, 1093s, 1058m, 1002vw, 982vw, 950vw, 910mw, 878vw, 785(sh), 771ms, 751s, 732s, 724s, 640w, 573w, 510w and 437w cm^{-1}.

Preparation of FePc(CO)N(C$_2$H$_5$)$_3$ (X). FePc (1.138 g, 2.00 mmol) in CCl$_4$ (30 ml) was treated with 0.203 g (2.01 mmol) of triethylamine under an atmosphere of carbon monoxide. After 20 h stirring, the suspension was filtered and the violet microcrystalline solid was dried briefly in vacuo (71% yield). The analytical results are given in Table 1. Infrared spectrum (Nujol mull): 1973s, 1610w, 1590vw, 1514ms, 1425m, 1335ms, 1290m, 1205vw, 1165m, 1120vs, 1095m, 1087m, 1075m, 1040vw, 1005vw, 955vw, 950vw, 910m, 880w, 785s, 755s, 735vs, 643w, 576w, 515w and 438w cm^{-1}.

FePc(CO)DMF · DMF. Crystal data and data collection. The preparation of single crystals of the CO adducts reported in this paper was attempted in some cases and found to be a difficult task, successful only with the CO-DMF adduct. After several unsuccessful attempts, the following procedure was found to lead to the crystals finally used for the X-ray investigation. FePc (0.28 g) was introduced in a glass vial together with DMF (20 ml) and heated (100—105°C) in a stainless-steel autoclave in the presence of CO (15 atm) for 24 h. The autoclave was then cooled to room temperature gradually, the gas was vented and the crystals filtered under CO and dried briefly (ca. 10 min) in a stream of CO, while the pressure was being reduced at the opposite side of the filtering apparatus. The crystals were mostly twinned; a few, however, were found to be suitable for X-ray work.

Weissenberg photographs taken with Cu-K_α radiation indicated a monoclinic lattice with systematic absences ($h0l$, $h + l \neq 2n$ and $0k0$, $k \neq 2n$) consistent with the space group $P2_1/n$, a non-standard setting of space group $P2_1/c$ which was maintained throughout the structure solution and refinement because of the near orthogonality of the axes.

A single crystal (0.12 × 0.32 × 0.61 mm) suitable for diffraction work was chosen and sealed into a Lindemann-glass capillary to protect it from moisture and air during data collection. The crystal was centred on an on-line Siemens AED diffractometer and the unit-cell parameters were obtained by a least-squares fit to the carefully measured ϑ values of 23 strong reflections lying in the ϑ range 8.5—17.5°. These parameters are listed with other relevant crystallographic data in Table 2.

Niobium-filtered Mo-K_α radiation and a five-points measuring procedure [14], together with a $\omega/2\vartheta$ scanning mode, were used in data collection. The pulse height analyser was adjusted to the K_α energy in such a way that 90% of the diffracted intensity was counted. The takeoff angle of the X-ray tube was 4°. After systematic absences were deleted and equivalent reflections were averaged, the number of unique data ($+h$, $+k$, $+l$), with 2ϑ values in the range 5.0—40.0°, was 3154. Only 1466 reflections were used in subsequent calculations having intensities greater than $2[\sigma^2(I) + 10^{-4} I^2]^{1/2}$ where I is the relative intensity and $\sigma^2(I)$ its variance. Metal foil attenuators were automatically inserted between the detector and the crystal whenever the counting rate exceeded about 9000 counts s^{-1}.

The intensity of a standard reflection ($\bar{3}$ 3 1), recorded every twenty reflec-

TABLE 2

SUMMARY OF CRYSTALLOGRAPHIC DATA FOR FePc(CO)DMF · DMF

Molecular formula	$C_{39}H_{30}FeN_{10}O_3$
Molecular weight (g mol^{-1})	742.58
Crystal size (mm)	0.12 × 0.32 × 0.61
Space group	$P2_1/n$
Unit cell data (Å or deg)	a 9.86(1)
	b 17.35(3)
	c 19.79(4)
	β 87.9(2)
Volume (Å^3)	3383
Z	4
Density (calcd)(g cm^{-3})	1.458
Radiation used in data collection	Mo-K_α (λ 0.71069 Å)
Linear absorption coefficient μ(cm^{-1})	4.98
Number of independent reflections used in the least-squares refinement	1466
$F(000)$	1536

tions to monitor crystal and instrument stability, exhibited an average decline of ~40% during the time required to collect data. This decline was due to decomposition caused by X-rays. Intensities were converted to unscaled F_0 values after corrections for decay and for Lorentz and polarization effects. Since the crystal was sealed in a glass capillary, reliable determination of the indices of the crystal faces was not possible. Thus no absorption correction was applied.

Structure Determination and Refinement. The structure was solved by the heavy-atom technique. The coordinates of the iron atom, which occupies a general position in the space group $P2_1/n$, were determined from a Patterson map calculated from all intensity data. The remainder of the atomic positions for the non-hydrogen atoms, with the exception of those of the solvent molecule, were located in subsequent difference Fourier maps. Full-matrix least-squares refinement of their coordinates, using isotropic temperature factors gave convergence at $R = 14.91\%$. At this stage a full-data difference Fourier map revealed, with some difficulty, five electron density maxima in chemically reasonable positions for a dimethylformamide molecule as well as all the hydrogen atoms belonging to the phthalocyanine molecule. While the solvate molecule was subsequently refined with isotropic temperature factors, attempted refinement of the hydrogen atom did not result in convergence with reasonable parameters. Consequently the coordinates of these atoms were fixed at the values obtained from the difference map (U_{iso} 0.10 Å^2) and their contribution were included in least-squares refinement. Attempts to locate the hydrogen atoms of the two dimethylformamide units were unsuccessful. Two more cycles of refinement in which iron and the four coordinated nitrogen atoms were allowed to vibrate anisotropically reduced R to 9.98%. Due to the increased number of parameters in anisotropic refinement and the limited amount of data, anisotropic refinement of all non-hydrogen atoms was discouraged. The number of observations used in the least-squares procedure was 1466 and the number of variable parameters was 238, yielding a data : parameter ratio of 6.2 : 1. Since a scan of the "observed" reflections revealed that several reflections were at the limit of observability, the 285 reflections for which $6\sigma(F_0)$ is greater then F_0 have been suppressed from the last cycle of refinement together with six $h0l$ reflections which suffered from obvious errors in measurements. The final R's were: $R = 8.25$ and $R_w = 8.50\%$. The $|F_0| - |F_c|$ values for strong, low-order reflections were randomly negative and positive, indicating no secondary extinction effect. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, where the weight, w, applied to each observation was taken as unity at first, and as $1/\sigma^2(F_0) + 0.005\ F_0^2$ at the end of refinement. A final difference map showed a peak of 0.5 e Å^{-3} close to the solvate molecule, thus suggesting some disorder and/or a slight inadequacy of the isotropic treatment. The remaining electron density was all less than 0.27 e Å^{-3}.

Final atomic coordinates and thermal parameters are given in Tables 3 and 4, respectively. A listing of the observed and calculated structure factors is available as Supplementary Material. Neutral-atom scattering factors were taken from ref. 15 for non-hydrogen atoms; those for hydrogen atoms were from ref. 16. The scattering by iron was corrected for the real and imaginary components of anomalous dispersion using data from ref. 15. All the calculations were per-

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) OF THE HEAVY ATOMS OF FePc(CO)DMF · DMF

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Fe	342(4)	976(2)	2376(2)	C(15)	−4940(24)	65(13)	2729(11)
N(1)	2122(18)	1426(10)	2424(9)	C(16)	−3577(23)	135(12)	2490(11)
N(3)	963(18)	399(9)	1602(10)	C(17)	−2445(24)	582(13)	2710(12)
N(5)	−1378(18)	497(9)	2348(8)	C(18)	−1462(27)	1490(13)	3450(12)
N(7)	−211(20)	1500(10)	3140(9)	C(19)	−1603(23)	1982(12)	4048(12)
O(1)	−307(19)	2271(11)	1559(10)	C(20)	−2664(26)	2172(14)	4466(13)
O(2)	993(16)	61(8)	2950(8)	C(21)	−2369(27)	2665(14)	4993(14)
N(2)	3150(17)	946(11)	1475(9)	C(22)	−1108(27)	3009(14)	5069(13)
N(4)	−947(19)	−373(10)	1386(9)	C(23)	−98(25)	2815(13)	4658(12)
N(6)	−2579(19)	1064(12)	3274(9)	C(24)	−320(25)	2291(14)	4088(12)
N(8)	1738(19)	2201(10)	3449(10)	C(25)	478(24)	2004(13)	3568(12)
N(9)	750(22)	−797(12)	3771(11)	C(26)	2444(25)	1949(14)	2967(13)
N(10)	8554(33)	4102(20)	145(19)	C(27)	3740(23)	2215(12)	2807(11)
C(1)	3117(26)	1383(14)	2012(13)	C(28)	4617(23)	2750(13)	3136(11)
C(2)	2146(24)	495(12)	1292(11)	C(29)	5878(25)	2874(13)	2852(12)
C(3)	2262(24)	−13(12)	698(12)	C(30)	6249(29)	2542(15)	2271(15)
C(4)	3170(24)	−115(13)	213(12)	C(31)	5403(26)	2000(14)	1925(12)
C(5)	2998(23)	−656(13)	−322(12)	C(32)	4191(23)	1870(12)	2222(11)
C(6)	1755(25)	−1095(14)	−258(12)	C(33)	−102(26)	1733(15)	1872(13)
C(7)	864(24)	−952(14)	169(12)	C(34)	410(28)	−157(16)	3442(15)
C(8)	1054(22)	−434(12)	711(11)	C(35)	−12(34)	−1023(20)	4396(18)
C(9)	303(23)	−132(13)	1248(11)	C(36)	1821(28)	−1309(15)	3535(14)
C(10)	−1660(24)	−87(12)	1835(12)	O(3)	7701(43)	5312(24)	−104(23)
C(11)	−3107(22)	−295(12)	1981(11)	C(37)	8327(62)	4958(40)	302(35)
C(12)	−3897(24)	−815(13)	1616(12)	C(38)	8232(54)	4022(32)	−464(30)
C(13)	−5197(24)	−885(13)	1858(11)	C(39)	9060(59)	3698(36)	715(32)
C(14)	−5737(24)	−445(14)	2382(12)				

TABLE 4

THERMAL PARAMETERS ($\times 10^4$) OF NON-HYDROGEN ATOMS OF FePc(CO)DMF · DMF WITH THEIR ESTIMATED STANDARD DEVIATIONS [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	385(21)	268(18)	361(20)	14(21)	−144(16)	−29(21)
N(1)	195(128)	458(132)	232(115)	124(102)	47(116)	39(98)
N(3)	206(122)	161(105)	539(138)	12(105)	−40(116)	−1(97)
N(5)	329(133)	264(113)	183(114)	−50(99)	290(110)	136(104)
N(7)	476(150)	372(127)	455(136)	−127(110)	−261(131)	93(112)

Atom	*U*	Atom	*U*	Atom	*U*	Atom	*U*
O(1)	768(58)	C(5)	437(69)	C(17)	309(63)	C(29)	414(67)
O(2)	416(45)	C(6)	469(71)	C(18)	395(70)	C(30)	676(85)
N(2)	365(51)	C(7)	408(63)	C(19)	337(62)	C(31)	510(74)
N(4)	297(49)	C(8)	316(60)	C(20)	529(77)	C(32)	274(59)
N(6)	460(55)	C(9)	288(61)	C(21)	598(78)	C(33)	510(76)
N(8)	318(51)	C(10)	284(60)	C(22)	534(74)	C(34)	578(81)
N(9)	604(62)	C(11)	311(62)	C(23)	473(71)	C(35)	1058(113)
N(10)	1496(111)	C(12)	464(70)	C(24)	464(72)	C(36)	678(86)
C(1)	355(72)	C(13)	461(67)	C(25)	339(64)	O(3)	2822(181)
C(2)	249(58)	C(14)	449(66)	C(26)	391(68)	C(37)	2878(273)
C(3)	329(63)	C(15)	404(69)	C(27)	302(60)	C(38)	2302(215)
C(4)	413(67)	C(16)	320(62)	C(28)	363(67)	C(39)	2814(240)

[a] The form of the thermal ellipsoid is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + \ldots)]$

formed on the Cyber 76 computer using the SHELX-76 computing programme [17].

Results and discussion

A. Synthesis and properties of the complexes

The preparation of the carbonyl adduct of FePc with DMF as axial ligand was carried out starting from $Fe(CO)_5$ with phthalonitrile in DMF as solvent:

$$Fe(CO)_5 + 4o\text{-}C_6H_4(CN)_2 \xrightarrow[(B)R.T.;p_{CO}=1\,atm]{(A)130\text{—}135^\circ C,\,80h} FePc(CO)DMF \cdot DMF + 4\,CO \quad (1)$$

The second stage (B) at room temperature under an atmosphere of CO is necessary since some CO dissociation occurs at 130—135°C as shown by the fact that more than four moles of CO are evolved during stage A of the reaction. Reaction 1 appears to be the first known case of a metal phthalocyaninato carbonyl derivative synthesized from phthalonitrile by this type of template reaction, exemplified by equation 1 for iron. By using a substituted phthalonitrile, reaction 1 should permit the preparation of substituted phthalocyaninato metal derivatives: a preliminary communication has reported [18] that t-butyl phthalocyaninato iron(III) derivatives were obtained by using t-butyl substituted phthalonitrile and $Fe(CO)_5$, possibly by the intervention of adventitious air. A specific role is believed to be played in reaction 1 by the solvent. The reactions of $Fe(CO)_5$ and $Cr(CO)_6$ with phthalonitrile in 1-chloronapthalene as solvent [19] (b.p. 259.3°C) to yield the corresponding metal phthalocyaninato complexes had been reported earlier. We find that in halogenated solvents such as *sym*-tetrachloroethane and in an aromatic hydrocarbon (toluene), FePc shows no significant CO absorption attributable to the formation of a well defined chemical substance at room temperature. Some CO absorption was observed (0.1—0.3 mol per mol of iron), but we regard these observations as originating from chemisorption phenomena, especially since the gasvolumetric measurements were performed with suspensions of FePc. This interpretation is substantiated by the observation that in acetone as medium, the CO absorption by FePc was essentially zero.

While this work was in progress, a paper reporting the preparation of the corresponding ruthenium(II) derivative, RuPc(CO)DMF [20], together with CO-amine adducts of ruthenium was published. The CO-DMF adduct of ruthenium(II) is the product [21] of the thermal reaction of RuPc with DMF, indicative that the coordinated CO must arise from the ruthenium-promoted decarbonylation of DMF, a process which has been previously been observed [22].

Recrystallised FePc(CO)DMF is converted to FePc by moderate heating at 100—120°C. The α- and β-phthalocyaninatoiron(II) obtained by this method was shown to be analytically and magnetically pure. Specifically, the room temperature magnetic moment was, within experimental error, the same as that reported [23] for samples of repeatedly sublimed FePc. In view of this result, reaction 1 can be regarded as an alternative method [24] for the preparation of pure FePc in gram quantities, avoiding the tedious and slow step of sublimation at ca. 400° C in a high vacuum. A further advantage of reaction 1 is that FePc(CO)DMF can be separated from the rest of the iron containing products (unidentified) in view of its much lower solubility. A simple filtration under CO yields the carbonyl adduct sufficiently pure for most chemical purposes. At this stage the yields of the reaction are around 60% and they can be increased up to slightly above 70% by increasing the reaction time.

FePc(CO)DMF tends to retain DMF in variable amounts depending on the drying conditions. This is a fact common to most of the carbonyl adducts of this series. The IR spectrum showed two bands in the 1600—1700 cm^{-1} region, one of them (1650 cm^{-1}) attributable to iron-coordinated DMF [25], while the other (1682 cm^{-1}) is due to lattice DMF. This hypothesis was confirmed by the X-ray diffractometric study (vide infra). That we were dealing with a clathrate phenomenon was further confirmed by the observation that also toluene, if used as washing agent, can enter the analytical composition of the solid.

The availability of the parent compound FePc(CO)DMF and the isolation of this carbonyl derivative containing the hitherto unknown axial *O*-coordination to iron, prompted us to explore the possibility of preparing other complexes of the same family with Group VI donor atoms. The THF derivative FePc(CO)-THF was prepared by one of the following methods:

$$\mathrm{FePc(CO)DMF + THF \xrightarrow{THF} DMF + FePc(CO)THF} \qquad (2)$$

$$\mathrm{FePc + CO + THF \xrightarrow{THF} FePc(CO)THF} \qquad (3)$$

IR and gasvolumetric measurements show that reaction 2 is substantially complete in THF as solvent under an atmosphere of carbon monoxide; for preparative purposes, however, reaction 3 is more suitable. Similarly to FePc(CO)DMF, the CO-THF adduct also tends to retain THF in the crystal lattice and is thermally decomposed to a mixture of α- and β-FePc.

We noted that air caused a shift of the carbonyl band of FePc(CO)L (L = DMF, THF, DMSO) to higher wavenumbers. Having excluded that O_2 or N_2 were involved, we suspected the existence of a carbonyl derivative of FePc with H_2O as axial ligand. Similar spectral changes have been briefly mentioned [26] and attributed to the formation of a CO-H_2O adduct of ruthenium(II) porphyrin, but no product was isolated. Our hypothesis was confirmed by the preparation of the H_2O-carbonyl adduct of phthalocyaninatoiron(II) by one of the following routes: (i) addition of CO and H_2O to FePc in an inert medium, such as acetone or acetonitrile, reaction 4, (ii) ligand displacement by H_2O in acetonitrile as solvent, reaction 5. When operating at low H_2O : Fe molar ratios

$$\mathrm{FePc + CO + H_2O \xrightarrow[H_2O\,:\,Fe=1-2]{Me_2CO\ or\ MeCN} FePc(CO)H_2O \cdot \mathit{x}\ solvent} \qquad (4)$$

$$\mathrm{FePc(CO)L + H_2O \xrightarrow[(L=DMF,\,THF)]{MeCN} FePc(CO)H_2O \cdot \mathit{x}\ H_2O} \qquad (5)$$

(between 1 and 2), the solid isolated contained some of the reaction solvent. The presence of coordinated H_2O was shown by the following observations: (a) the IR spectra show the stretching and bending modes of H_2O at the expected wavenumber values undergoing the correct shift on deuteration; (b) the Mössbauer and IR spectra in the carbonyl stretching region (strong main band at 1997 cm^{-1}) are typical (vide infra) of a six-coordinate carbonyl derivative of FePc; (c) the compound is substantially diamagnetic and the small positive value of χ_M^{corr} found (see Experimental section) must be attributed to small amounts of unreacted FePc and/or to some contribution from TIP.

The 1997 cm^{-1} band always shows at least one additional shoulder at higher wavenumbers, normally at 2006 cm^{-1} (Nujol mull) which is not due to impurities of other carbonyl products having the solvent (Me_2CO or MeCN) as axial ligand. Although acetone and acetonitrile enter the chemical composition of the CO-H_2O adduct, they are believed to occupy lattice sites or some peripheral positions within the molecule, since MeCN or Me_2CO suspensions of FePc do not give any chemically significant absorption of CO, according to gasvolumetric measurements. Furthermore, a low yield preparation of FePc(CO)H_2O was also carried out in the absence of any solvent, simply by exposing sublimed FePc to moist CO at atmospheric pressure. The resulting carbonyl adduct obtained in admixture with unreacted FePc shows the same multiple pattern in the carbonyl stretching region. Plausible explanations for the IR data are the following: (i) a crystal site effect, (ii) the presence of other molecular structures, resulting from intra- or intermolecular interactions, such as c—d in Fig. 1, in addition to the predominant structure a, which is believed to be responsible for the main absorption at 1997 cm^{-1}. It is to be noted that structures 1c and 1d would in fact decrease the basicity of the H_2O ligand and therefore an increase of the CO stretching vibration seems reasonable. The zwitterionic form 1b seems unlikely since CO and H_2O are readily lost from the carbonyl adduct at about 80° C in vacuo, while recombination of H_2O for 1b would presumably occur under more vigorous conditions.

A few aquo-carbonyl complexes of transition elements are known: the examples include compounds of copper(I) [27], ruthenium(II) [28—30], manganese(I) [31—33] and osmium(III) [34]. Hieber and coworkers have also shown [35] that treatment of $Cr(CO)_6$ with alkali leads to the $[Cr(CO)_3(H_2O)OH]^-$ anion. The still limited knowledge of aquo carbonyl complexes is probably attributed to the rare use of water as a reagent or solvent towards metal carbonyls, and also to the sometimes pronounced nucleophilic reactivity of water towards coordinated carbon monoxide. The latter type of reactivity remains a subject of considerable current interest [36] and, moreover, natural systems may easily interact with both CO and H_2O. For example, spectroscopic evidence exists [37] that iron(II)-protoporphyrin IX (M) interacts with CO to give rise to a species of the type OC—M—OH_2, although no such a compound was isolated and, to the best of our knowledge, the FePc(CO)H_2O of this paper is the first well authenticated aquo-carbonyl of a macrocyclic N_4 system to be reported in the literature. A ruthenium(II) mesoporphyrin IX aquo-carbonyl is alluded to in a recent paper [38].

Preliminary gasvolumetric experiments in neat methanol had shown that carbonylation of FePc is substantially quantitative. For preparative purposes, the best approach to FePc(CO)MeOH is the reaction of FePc with methanol in

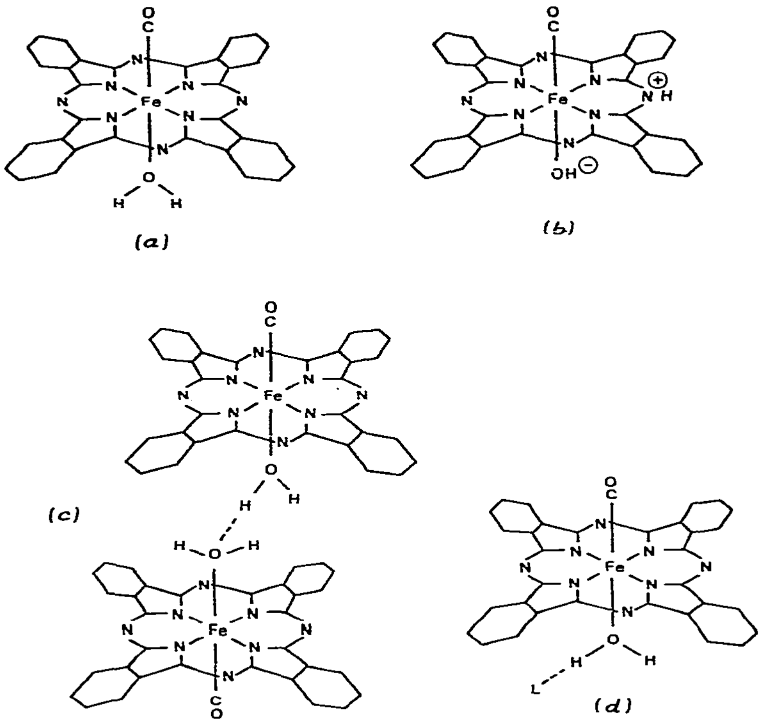


Fig. 1. Possible molecular structures of $FePc(CO)H_2O \cdot L$ ($L = H_2O$, solvent).

dichloromethane:

$$FePc + CO + MeOH \xrightarrow{CH_2Cl_2} FePc(CO)MeOH \qquad (6)$$

The reaction in methanol yields an analytically pure product, IVb in Table 1; however, the magnetic susceptibility is higher than that of the product obtained by reaction 6, thus suggesting the presence of some unreacted FePc. This is plausible in view of the higher solubility of the reaction product in dichloromethane. The solid from reaction 6 is characterised by a carbonyl stretching vibration at 1995 cm^{-1} with at least one shoulder at higher wavenumbers. Considerations similar to those already mentioned for the aquo-carbonyl adduct can be applied to explain the complex IR pattern.

Metal complexes containing both alcohols and CO as ligands are rather rare. Examples are known among metal porphyrins, namely Ru(porphyrin)CO-(EtOH), where porphyrin = tetraphenyl- and tetra-iso-propylporphyrin, [39] mesoporphyrin IX [38], and Os(porphyrin)CO(ROH) [40]. The ruthenium-tetraphenylporphyrin complex was studied crystallographically [39] and contains, as expected, *trans* axial CO and EtOH groups. Hieber and coworkers [41] reported the isolation of methanolo-carbonyl derivatives of tungsten obtained by the attack of alkali on the hexacarbonyl.

As mentioned in the introductory part, work by Gaspard et al. [2] indicated that FePc in DMSO solution interacts with CO, as judged by a bathochromic shift of 8.5 nm relative to the 652.5 nm band. No solid product was isolated and no experimental evidence was presented about the extent of carbonylation. By gasvolumetric measurements of the CO absorbed, we now find that solutions of FePc in DMSO are only partially carbonylated and the K' constant for equilibrium 7 is 0.49 at 27.5°C (in neat DMSO and at 1 atm CO, that is the car-

$$\mathrm{FePc} + \mathrm{CO} \rightleftharpoons \mathrm{FePc(CO)} \tag{7}$$

$$K = \frac{[\mathrm{FePc(CO)}]}{[\mathrm{FePc}][\mathrm{CO}]} \tag{8}$$

$$K' = K[CO] = \frac{[\mathrm{FePc(CO)}]}{[\mathrm{FePc}]} \tag{9}$$

bonylation of FePc does not go to completion. In other words, of the two simultaneous reactions, 10 and 11, the former, i.e.

$$\mathrm{FePc} + 2\ \mathrm{DMSO} \rightleftharpoons \mathrm{FePc(DMSO)_2} \tag{10}$$

$$\mathrm{CO} + \mathrm{FePc(DMSO)_2} \rightleftharpoons \mathrm{FePc(CO)DMSO} + \mathrm{DMSO} \tag{11}$$

the formation of the bis-adduct is competing strongly with the second. In agreement with this, the isolation of solid FePc(CO)DMSO was possible only when the DMSO : Fe molar ratio was kept low and dichloromethane was used as solvent. In neat DMSO and under an inert atmosphere, the bis-adduct, FePc-$(\mathrm{DMSO})_2 \cdot 2$ DMSO was isolated [13].

Some insight into the molecular structure of FePc(CO)DMSO may be gained from its IR spectrum. The 900—1200 $\mathrm{cm^{-1}}$ region of the spectrum is usually informative about the type of bonding between the metal and the DMSO ambidentate ligand [42,43]. For samples of the CO-DMSO adduct treated in such a way as to have the minimum possible amount of lattice DMSO, the IR spectrum does not show any significant absorption around 950 $\mathrm{cm^{-1}}$, which could be attributed to the S—O stretching vibration of *O*-bonded DMSO. On the other hand, the 1100 $\mathrm{cm^{-1}}$ region is covered by vibrations of the phthalocyaninato moiety. Under these circumstances, and in view of the fact that the bis-adduct $\mathrm{FePc(DMSO)_2} \cdot 2$ DMSO was found [13] crystallographically to contain *S*-bonded DMSO, coordination through sulphur could be a likely possibility for the carbonyl derivative also. However, *O*-coordination of DMSO would favour electron density to CO through iron, thus stabilising the Fe—CO bond. This problem can only be solved by a X-ray investigation of the solid. The same ambiguity arises with the recently isolated Ru(Pc(CO)DMSO complex [21].

As noted already [13], to the best of our knowledge, $\mathrm{FePc(DMSO)_2}$ is the only well authenticated example of a *S*-bonded phthalocyaninatoiron(II) system. This contrasts with the well known [44,45] interaction of hemoglobin with H_2S, but it is in agreement with the general paucity of data concerning coordination of S-containing ligands to iron(II) heme systems [46], although the iron(III)—S bond is well established in heme and heme-like systems [47—50]. It was clearly of interest to further investigate the possibility of bonding the FePc—CO moiety to a S-containing ligand. Tetrahydrothiophene was a good candidate because of possible comparisons with the oxygen analogue, II.

The isolation of pure FePc(CO)THT proved impossible since it always separated out in admixture with the corresponding bis adduct [13]. In the solid isolated, of analytical composition $[\mathrm{FePc(CO)THT}]_{0.7}[\mathrm{FePc(THT)_2}]_{0.3}$, the presence of the carbonyl derivative was definitely established by the following observations: (i) the carbonyl absorption (Nujol) at 1995 $\mathrm{cm^{-1}}$; (ii) the Mössbauer spectrum (vide infra) which may be interpreted as the superposition of two resonances, one of them (δ 0.38 mm/s) being typical of the carbonyl derivatives of FePc. The preparation of the CO-THT adduct establishes for the first time that the Fe—CO bond in phthalocyaninatoiron(II) can be stabilised by a sulphur containing ligand. With THT, perhaps even more than with the DMSO derivative, the stability of the bis-adduct is high relative to that of the corresponding carbonyl adduct, thus reducing the range of experimental conditions available for the isolation of the pure carbonyl adduct.

The elevated stability of the bis-adduct is a limiting factor also in the isolation of the carbonyl derivatives FePc(CO)L, with L being a nitrogen-containing axial ligand. This paper reports the isolation of some new carbonyl complexes of this type, obtained by one of the following reactions:

$$\mathrm{FePc + L + CO \rightarrow FePc(CO)L} \tag{12}$$

$$\mathrm{FePcL_2 + CO \rightarrow FePc(CO)L + L} \tag{13}$$

$(\mathrm{L = NH_3,\ n\text{-}C_3H_7NH_2,\ Et_2NH,\ Et_3N})$

The elevated stability of the amine bis-adducts in neat amine is evidenced by the fact that all the carbonyl complexes reported in this paper were found to evolve CO with pyridine quantitatively.

B. Crystal and Molecular Structure of FePc(CO)DMF · DMF

As illustrated in the projections of Fig. 2 (which also gives the atom labelling scheme) and Fig. 3, the structure of the compound consists of discrete monomeric FePc(CO)DMF units and DMF solvent molecules. There are no unusually short contacts and the lattice is stabilized mainly by Van der Waals interactions. Selected bond distances and angles are given in Table 5.

The iron atom is hexacoordinated to the four inner nitrogen atoms of the macrocyclic phthalocyaninato at the equatorial sites and by the carbonyl group and DMF ligand occupying the axial positions. The four nitrogen atoms chelate to metal in a nearly planar fashion with iron displaced only 0.04 Å from the plane towards the carbonyl group.

Crystallographically determined carbonyls of phthalocyaninato metal derivatives are unknown in the literature; the most closely related structures to the present one are the two hexacoordinated iron(II) complexes of the 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato ligand containing CO and pyridine or hydrazine in the axial positions [51], a hexacoordinated bis-α-diimine macrocyclic iron(II) complex having CO and $\mathrm{CH_3}$ as axial ligands [52], and Fe(TPP)CO(pyridine), TPP = tetraphenylporphyrin [53]. In all these compounds are well as in the present one the equatorial Fe—N bond lengths (1.941, 1.944, 1.900, 2.02 and 1.889 Å are the average values for the pyridine, hydrazine, methyl, TPP and dimethylformamido

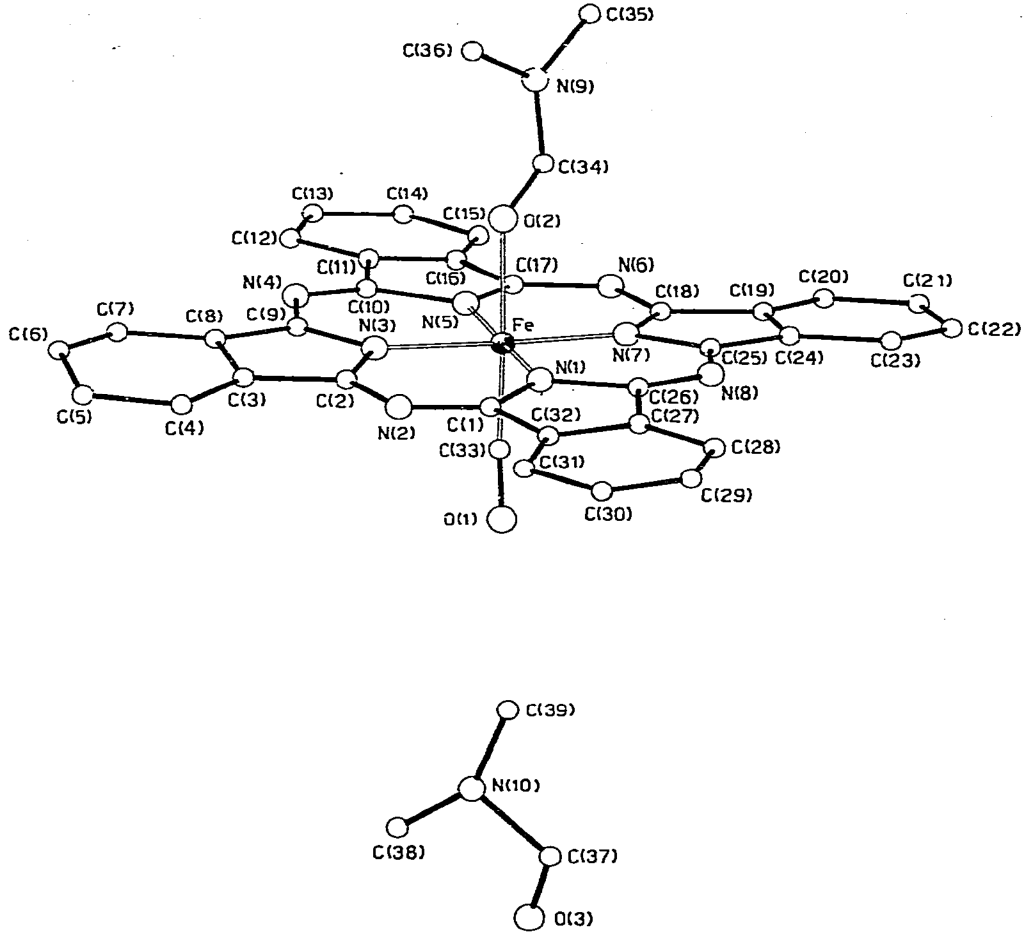


Fig. 2. Molecular structure of FePc(CO)DMF · DMF showing atom labelling.

derivatives, respectively) are very close to or shorter than 2.01 Å, the threshold value indicated by Hoard [54], above which the metal is expected to be displaced from the plane of the four nitrogen atoms of the porphyrin system. On the other hand, the average M—N bond length (1.889 Å) of the present compound is significantly lower than those found (1.937(3), 1.932(3) Å) in FePc-(4-Me-py)$_2$ [56,57] and in FePc itself (1.926(1), 1.927(1) Å) [58]. Moreover, the individual values of the Fe-N bond distances of our compound (see Table 5) are such that the FePc moiety deviates considerably from D_{4h} symmetry. It is tempting to suggest that some shortening of the Fe—N bond distances may result in part from the strong π-back bonding effect of the CO group.

The Fe—C distance is 1.72(2) Å, a value shorter than those found in the afore mentioned hexacoordinated iron(II) compounds (1.730, 1.751, 1.772 and 1.77 Å are the values for the pyridine, hydrazine, methyl and TPP derivatives, respectively), and in good agreement with the value of 1.77 Å reported for Ru(tetraphenylporphinato)CO(EtOH) [39], once the difference of ionic

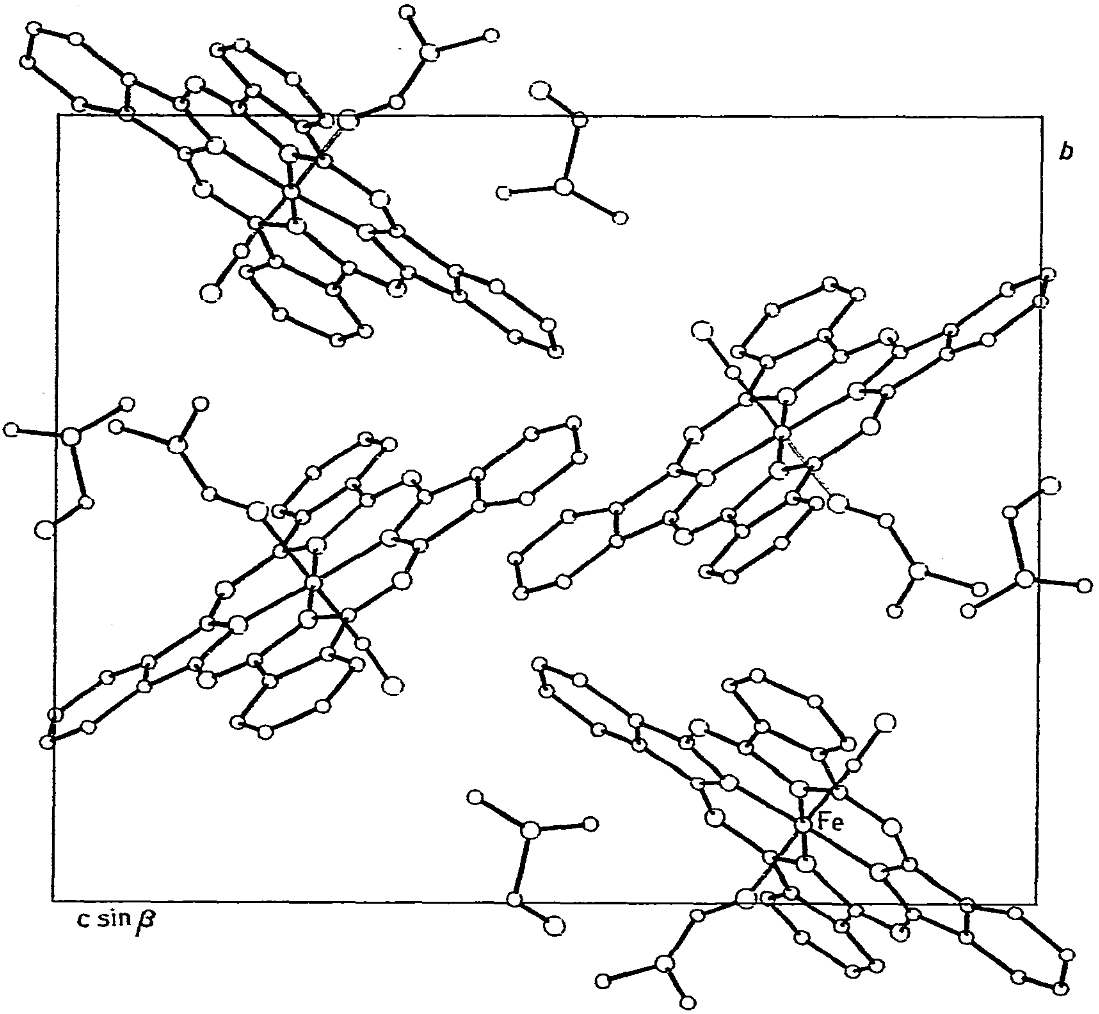


Fig. 3. Packing of FePc(CO)DMF · DMF in the unit cell.

radii between iron(II) and ruthenium(II) is taken into consideration. The deviation from collinearity of the carbon atom from the CO group is small, the Fe—C—O angle being 174(2)°, in agreement with the data reported for the TPP-iron(II) system [53]. The C—O bond is nearly perpendicular to the equatorial plane, the dihedral angle being 81.4°.

The planarity of the macrocyclic system is worthy of some comment. The arrangement of the non-hydrogen atoms can be considered as a whole to be slightly but significantly non planar, the largest displacements of any atom from the mean least-squares plane being 0.19 Å. Moreover the C_8N_8 inner ring cannot be considered as planar since the largest deviations from the least-squares plane, involving the four uncoordinated nitrogen atoms, are 0.10—0.12 Å. On the contrary, each isoindole moiety is practically planar as the dihedral angles between an individual pyrrole ring and its associated benzene

TABLE 5

SELECTED BOND DISTANCES (Å) AND ANGLES (deg)

(a) In the coordination polyhedron

Fe—N(1)	1.93(2)	Fe—N(5)	1.89(2)	Fe—C(33)	1.72(2)
Fe—N(3)	1.91(2)	Fe—N(7)	1.83(2)	Fe—O(2)	2.07(1)

N(1)—Fe—N(3)	89.2(9)	N(3) —Fe—C(33)	90.9(11)
N(1)—Fe—N(5)	177.6(8)	N(3) —Fe—O(2)	86.6(7)
N(1)—Fe—N(7)	90.1(9)	N(5) —Fe—C(33)	94.1(11)
N(3)—Fe—N(5)	90.4(8)	N(5) —Fe—O(2)	88.6(7)
N(3)—Fe—N(7)	177.5(9)	N(7) —Fe—C(33)	91.4(11)
N(5)—Fe—N(7)	90.1(9)	N(7) —Fe—O(2)	90.9(8)
N(1)—Fe—C(33)	88.3(11)	C(33)—Fe—O(2)	176.4(11)
N(1)—Fe—O(2)	89.0(8)		

(b) In the six membered chelation rings

N(1) —C(1)	1.25(3)	N(4) —C(10)	1.22(3)	C(18)—N(7)	1.36(3)
C(1) —N(2)	1.30(3)	C(10)—N(5)	1.47(3)	N(7) —C(25)	1.41(3)
N(2) —C(2)	1.32(3)	N(5) —C(17)	1.26(3)	C(25)—N(8)	1.30(3)
C(2) —N(3)	1.31(3)	C(17)—N(6)	1.40(3)	N(8) —C(26)	1.24(3)
N(3) —C(9)	1.34(3)	N(6) —C(18)	1.38(3)	C(26)—N(1)	1.45(3)
C(9) —N(4)	1.32(3)				

C(26)—N(1) —C(1)	109(2)	C(10)—N(5) —C(17)	107(2)
C(26)—N(1) —Fe	121(1)	C(10)—N(5) —Fe	121(1)
C(1) —N(1) —Fe	129(2)	C(17)—N(5) —Fe	131(2)
N(1) —C(1) —N(2)	124(2)	N(5) —C(17)—N(6)	125(2)
C(1) —N(2) —C(2)	125(2)	C(17)—N(6) —C(18)	118(2)
N(2) —C(2) —N(3)	128(2)	N(6) —C(18)—N(17)	128(2)
C(2) —N(3) —C(9)	107(2)	C(18)—N(7) —C(25)	101(2)
C(2) —N(3) —Fe	124(1)	C(18)—N(7) —Fe	127(2)
C(9) —N(3) —Fe	129(2)	C(25)—N(7) —Fe	132(2)
N(3) —C(9) —N(4)	125(2)	N(7) —C(25)—N(8)	122(2)
C(9) —N(4) —C(10)	122(2)	C(25)—N(8) —C(26)	123(2)
N(4) —C(10)—N(5)	132(2)	N(8) —C(26)—N(1)	131(2)

(c) In the carbonyl group

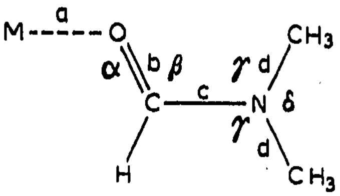
C(33)—O(1)	1.14(3)
Fe—C(33)—O(1)	174(2)

ring are all less than 2° . The four six-membered chelation rings are planar within experimental errors.

The DMF ligand is bonded to iron at a Fe—O distance of 2.07 Å. As far as we are aware, this is the first structurally characterised dimethylformamide iron(II) complex. Furthermore, only a few crystal structures have been reported for coordination compounds containing DMF as ligand, this molecule usually prefers solvate behaviour, and some reports are notes which do not describe the DMF geometry. So, it is of interest to consider the structural parameters available for coordinated DMF (see Table 6), even though a detailed comparison is not useful, since the difference in the nature of the metal and consequently in the M—O distance will have a quantitative effect on the other structural parameters. Nevertheless, the geometry of the DMF ligand in these compounds is generally almost the same. The DMF ligand in the present com-

TABLE 6

A COMPARISON OF STRUCTURAL PARAMETERS FOR COORDINATED *N*,*N*-DIMETHYLFORMAMIDE [a]



M	*a*	*b*	*c*	*d*		α	β	γ		δ	Ref.
Sb(V)	2.048(6)	1.300(10)	1.287(12)	1.504(12)	1.505(14)	124.49(60)	120.15(89)	120.20(92)	122.08(82)	117.67(89)	59
Sn(IV)	2.39(2)	1.31(4)	1.36(3)	1.46(3)	1.49(4)	120(1)	116(2)	124(2)	117(2)	118(2)	60
Th(IV)	2.519(6)	1.233(11)	1.325(11)	1.455(12)	1.461(12)	135.3(6)	123.6(8)	121.1(8)	120.6(8)	18.3(8)	61
Cr(III)	1.91(2)	1.28(2)	1.34(2)	1.46(3)	1.45(3)	128(1)	122(2)	121(2)	122(2)	117(2)	62
Cu(II)	2.293	1.220	1.308	1.460	1.500	131.18 [b]	127.21	120.54	120.06	119.40	63
Co(II)	2.150(7)	1.222(11)	1.310(11)	1.452(16)	1.455(12)	121.5(6)	126.7(10)	121.4(8)	121.8(9)	116.6(8)	64
Fe(III)	1.979(21)	1.25(2)	1.30(2)	1.47(1)	1.47(2)	128.9(5)	123.6(7)	120.7(6)	121.6(7)	117.4(6)	65
	1.993(5)	1.26(1)	1.30(1)	1.47(1)	1.47(2)	124.8(4)	124.0(6)	122.3(6)	119.9(6)	117.7(6)	
	1.997(14)	1.27(1)	1.30(1)	1.47(1)	1.48(1)	127.6(4)	122.5(6)	120.7(6)	120.3(6)	119.0(6)	
Fe(II)	2.07(1)	1.18(3)	1.34(3)	1.48(4)	1.44(3)	123(1)	123(3)	120(2)	123(2)	117(2)	This work

[a] Distances in Å, angles in deg. [b] This value has been recalculated on the basis of the coordinates given by the authors [63].

pound is planar within 0.02 Å; it is not exactly perpendicular to the plane of the four coordinated nitrogens, the dihedral angle being 81.4°. No comparison can be made with the structural parameters of the uncoordinated DMF, due to its abnormally high thermal parameters.

C. Infrared spectra

All the compounds reported in this paper are characterised by a strong absorption in the carbonyl stretching region around 2000 cm^{-1}. The lowest value observed was that of FePc(CO)DMF (ν(CO) = 1972 cm^{-1}, Nujol), close to that measured for the THF adduct (1975 cm^{-1}, Nujol; 1995 cm^{-1}, THF solution). In terms of π-back bonding theory, this would correspond to a particularly elevated strength of the Fe—CO bond within this class of compounds. It is interesting to note that the corresponding ruthenium complex, RuPc(CO)DMF has ν(CO) at 1943 cm^{-1} [20].

The Fe—CO bond order may be inferred from the ν(CO) value which is in turn affected by the nature of the *trans* axial ligand. By comparing the THF- and the THT-carbonyl adducts, one can observe a significant increase of the ν(CO) from 1975 cm^{-1} (THF) to 1997 cm^{-1} (THT). This probably indicates that the degree of π-back bonding, $Fe \rightarrow CO$, is lower for the S-containing adduct. This seems reasonable considering the π-acidity of sulphur (through its *d* orbitals) and the subsequent competition by CO and THT for the same orbital electrons of iron.

D. Magnetic measurements

All the carbonyl derivatives reported in this paper are low spin and substantially diamagnetic. The samples show, however, small residual paramagnetic susceptibilities in the range 200—850 × 10^{-6} cgsu, which can be attributed, at least in part, to small amounts of unreacted FePc. The presence of small residual paramagnetism in supposedly low spin d^6 complexes of the type $FePcL_2$ was noted earlier [6] by Taube. The magnetic susceptibilities reported in this paper were not corrected for the temperature independent paramagnetism from which a contribution to the observed magnetic susceptibility could possibly come. On the other hand, the presence of unreacted FePc is evidenced by the fact that the χ_M^{corr} depends on the method of preparation of the compound. This is particularly true for the CO-H_2O and for the CO-MeOH adducts; preparations from FePc in H_2O-acetone at low H_2O : Fe molar ratios and in methanol rather than in dichloromethane, respectively, lead to products which, although analytical pure, show unsatisfactory magnetic data.

E. Mössbauer spectra

The literature reports Mössbauer data for only one carbonyl derivative of FePc, namely FePc(CO)piperidine [66]. The Mössbauer data obtained for our complexes containing O and S axial donor atoms are presented in Table 7, together with the data of some bis-adducts obtained either by us or in some other laboratories.

An important consideration is that the isomer shift represents a powerful analytical tool within the class of phthalocyaninatoiron(II) complexes, since it permits a classification of the complexes in three categories: (a) FePc; (b) bis-

TABLE 7

ROOM TEMPERATURE MÖSSBAUER DATA OF PHTHALOCYANINATOIRON(II) COMPLEXES

Compound	δ [a] (mm/s)	ΔE_q (mm/s)	χ^2	Γ_1/Γ_2	Ref.
FePc	0.63	2.62	1.02	1.01	This work
	0.66	2.62	—	—	67
Bis-adducts					
FePc(piperidine)$_2$	0.52	2.22	—	—	68
	0.54	2.34	—	0.93	66
FePc(pyridine)$_2$	0.53	2.01	—	—	68
	0.52	2.02	—	—	69
FePc(n-C$_3$H$_7$NH$_2$)$_2$	0.50	1.97	—	—	6
FePc(Et$_2$NH$_2$)	0.51	2.22	—	—	6
FePc(THT)$_2$	0.53	2.20	1.09	1.01	This work
FePc(DMSO)$_2$	0.50	2.08	1.15	0.95	This work
Carbonyl Derivatives					
FePc(CO)(piperidine)	0.37	1.57	—	1.08	66
FePc(CO)DMF	0.35	1.56	0.90	1.01	This work
FePc(CO)THF	0.36	1.82	1.80	1.11	This work
FePc(CO)H$_2$O	0.37	1.75	1.12	1.02	This work
FePc(CO)MeOH	0.37	1.55	1.61	0.94	This work
FePc(CO)DMSO	0.36	1.56	1.11	1.03	This work
FePc(CO)THT [b]	0.38 (0.53)	1.55 (2.35)	—	—	This work

[a] From sodium nitroprusside. [b] In admixture with FePc(THT)$_2$. Values in parenthesis are those relative to the less intense resonance, attributed to FePc(THT)$_2$.

adducts FePcL$_2$, and (c) carbonyl complexes FePc(CO)L. More important is that within each of the last two categories the value of δ (mm/s) is substantially independent of the nature of the ligand L. All the bis-adducts have values of δ around 0.5 mm/s (relative to nitroprusside ion), whereas the carbonyl derivatives are all characterised by a corresponding value ranging from 0.35 to 0.38 mm/s. The Mössbauer spectrum of the FePc(THT)$_2$-FePc(CO)THT mixture, showing the two resonances indicated in Table 7 (0.38, 0.53 mm/s), definitely establishes the existence of the carbonyl adduct. The substantially constant value of the isomer shift for the bis-adducts with nitrogen containing axial ligands had been noted earlier by Taube [6]. The results of the present investigation show that even when changing the nature of the axial ligand considerably (from nitrogen to oxygen and sulphur as donor atom), no substantial effect on the isomer shift parameter is observed for either series of compounds. This must be related to the buffering electronic effect of the conjugated π-system of the phthalocyaninato macrocyclic ring.

The decrease of the isomer shift parameter from the bis-adducts to the carbonyl adducts and the decrease of the ΔE_q parameter from the bis-adduct to the corresponding carbonyl derivative are well established phenomena also in other structurally related families of iron(II) complexes [69,70]. The decrease of the δ parameter from the bis-adducts to the corresponding carbonyl derivatives should be related to the sinergic effect of the σ and π components of the Fe—CO bond, both leading to an increase of the *s* electron density at the iron nucleus.

As for the ΔE_q parameter, it depends on the component of the electric field gradient (efg, which is positive for phthalocyaninatoiron(II) complexes [67] and phthalocyaninato(carbonyl)piperidineiron(II) [66] and is assumed to be positive in all of the carbonyl adducts of Table 7) along the z axis. According to the usual theoretical treatment [66,71] and neglecting the lattice contribution, the variation of the efg depends on the d electron distribution (see equation 14). The generally observed decrease of ΔE_q on going from the bis-adduct to its corresponding carbonyl adduct is difficult to interpret since both a decrease of the d_{xz} and d_{yz} electron population by π-bonding and an increase of the $d_{x^2-y^2}$ electron population by Pc → Fe σ-bonding should lead to an increase of the ΔE_q parameter. Pertinent to this discussion is the observation that, as noted above, the Fe—N (equatorial) bond distances of the FePc(CO)-DMF complex are quite similar or perhaps somewhat lower than in the corresponding ones in FePc(4-Me-py)$_2$ and FePc. This suggests that no crystallographically detectable reduction of the σ component to the Fe—N (equatorial) bond has occurred in the carbonyl adduct relative to the bis-adduct and that the d_{xz} and d_{yz} orbital contribution to π bonding on the equatorial plane has not greatly changed. A possible interpretation of the reduced ΔE_q values for the carbonyl adducts comes then from the assumption that the likely reduction of d_{xz} and d_{yz} electron population by π bonding to CO is more than compensated by the strong σ component to the bonding along the z axis, thus increasing the d_{z^2}

$$V_{zz} = k\ [n_{x^2-y^2} - n_{z^2} + n_{xy} - \tfrac{1}{2}(n_{xz} + n_{yz})] \tag{14}$$

electron population. If our interpretation of the data is correct, strong σ donors should tend to decrease ΔE_q and the opposite should be true for weak σ donors.

A bis-adduct and its corresponding carbonyl adduct represent two completely different systems and the comparison of their ΔE_q parameters may be somewhat unrewarding. A better chance of solving this problem may come from comparing the data within the same family of carbonyl adducts, as indicated in Table 7.

If attention is confined for the time being to O- and S-containing ligands, ΔE_q of FePc(CO)L decreases in the following sequence of L:

THF > H_2O > DMF ≃ MeOH, DMSO, THT

More data are of course necessary for complexes with N-containing ligands and several concomitant factors play their role in determining the value of ΔE_q. It is not, however, without significance in our opinion that tetrahydrofuran has a low value of donicity (20.0), [72], as compared with DMF (26.6) and DMSO (29.8). It is also chemically significant that solvents of even lower donicity than THF such as organic nitriles, acetone (17.0) and ethyl acetate (17.1), failed to form the carbonyl adducts of FePc.

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