Bis Adducts of Phthalocyaninatoiron(II) with Group 6 Axial Donor Atoms. Crystal and Molecular Structure of Sulphur-bonded Bis(dimethyl sulphoxide)phthalocyaninatoiron(II)–Dimethyl Sulphoxide (1/2)

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The bis adducts of tetrahydrothiophen (tht) and dimethyl sulphoxide (dmso) with phthalocyaninatoiron(II), [Fe(pc)L_2], have been obtained by direct combination of the components. The crystal and molecular structure of the dmso adduct, [Fe(pc)$(\text{dmso})_2$]·2dmso, has been solved by Patterson and Fourier methods. The crystals are monoclinic, space group $P2_1/c$, with a = 7.993(2), b = 16.175(7), c = 16.086(7) Å, β = 104.53(3)°, U = 2 013 Å^3, D_m (flotation) = 1.45 ± 0.01 g cm^{-3}, Z = 2, D_c = 1.454 g cm^{-3}, R = 0.067 for 1 062 independent reflections. The iron is six-co-ordinated to the four inner nitrogens of the macrocycle and to the sulphur atom of the dmso ligands, with Fe–S 2.308(4), S–O 1.474(14), and Fe–N(average) 1.94 Å. The bonding parameters of the lattice dmso present in the bis adduct have also been determined, S–O 1.443(18) Å. Unsuccessful attempts to prepare some bis adducts with oxygen donors are reported.

It has been known for many years that phthalocyaninatoiron(II), [Fe(pc)], forms bis adducts with ligands occupying axial positions around the central metal atom, *i.e.* above and below the plane of the macrocycle.[1] Among carbon donors, the isocyanide [2] and cyanide [3] bis adducts have been reported. Contrary to a report [4] describing bis(carbonyl) derivatives of iron porphyrins, no evidence has ever been found of bis(carbonyl) adducts of [Fe(pc)].[5] The bis adducts of [Fe(pc)] with nitrogen donors are well established;[6] their Mössbauer spectra have been studied extensively [7-9] and the substitution reactions by dimethyl sulphoxide [10] and by carbon monoxide [11] have been reported. The electrochemical behaviour of bis(amine) adducts of [Fe(pc)] has also been studied.[12] The addition of phosphorus ligands has been reported [13] to yield products of formula [Fe(pc)L_2] [L = PBu_3 or $P(OR)_3$]. In contrast to the large number of data available for bis adducts of ligands containing Group 4 and 5 donor atoms, little is known of the bis adducts of [Fe(pc)] with Group 6 ligands, *i.e.* oxygen and sulphur. Dimethyl sulphoxide (dmso) solutions of [Fe(pc)] are diamagnetic [10,14] and they were assumed to contain the bis adduct but no product was isolated. Also, equilibria [15] and kinetic [16] studies of substitution by dmso on [Fe(pc)L_2] (L = nitrogen donor) have appeared, and, finally, the isolation of a bis adduct of [Fe(pc)] with tetrahydrofuran (thf) was reported.[17]

We have succeeded in isolating the bis adducts of [Fe(pc)] with dmso and tetrahydrothiophen (tht), and we report the crystal and molecular structure of the former of the two compounds, thus showing that it contains *S*-bonded dmso.

EXPERIMENTAL

Unless otherwise stated, all of the operations described in this paper were carried out under an atmosphere of pre-purified argon or nitrogen, in order to prevent attack by oxygen and/or moisture. Solvents were carefully purified by conventional methods prior to use. Phthalocyaninatoiron(II), [Fe(pc)], used in the preparation of the complexes was either sublimed or obtained by thermal decomposition (at *ca.* 120 °C) of recrystallized [Fe(pc)(CO)(dmf)]·dmf (dmf = dimethylformamide).[5]

The i.r. spectra were measured with a Perkin-Elmer model 283 instrument on Nujol mulls of the complexes and the magnetic susceptibilities with a magnetic balance equipped for the Faraday method and calibrated with $Cu[SO_4]\cdot 5H_2O$.

Preparation of [Fe(pc)$(\text{dmso})_2$]·2 dmso, (1).—[Fe(pc)] (1.697 g, 2.98 mmol) was treated with dmso (30 cm^3) for 7 h at 110 °C. After cooling to room temperature, the suspension was filtered and the resulting solid dried *in vacuo* (77% yield). The bis adduct is a violet microcrystalline solid (Found: C, 54.95; H, 4.50; N, 12.95; S, 15.05. Calc. for $C_{40}H_{40}FeN_8O_4S_4$: C, 54.55; H, 4.55; N, 12.75; S, 14.55%). $\chi_{m\text{corr.}}$ = 3.02 × 10^{-9} m^3 mol^{-1} (diamagnetic correction = −7.3 × 10^{-9} m^3 mol^{-1}), corresponding to an apparent $\mu_{\text{eff.}}$ = 0.74 B.M.†

Infrared spectrum: 1 610vw, 1 590vw, 1 512m–s, 1 423m–s, 1 409m–w, 1 328m, 1 310vw, 1 288m, 1 160s, 1 120vs, 1 115(sh), 1 095s, 1 068m–w, 1 055s, 1 049(sh), 1 010m–w, 985w, 955w, 949m, 910w, 778m, 750m–s, 735s, 695vw, 570w, 515vw, 434w, and 420vw cm^{-1}.

Preparation of [Fe(pc)$(\text{tht})_2$]·2tht, (2).—[Fe(pc)] (0.47 g, 0.83 mmol) was treated at 110—115 °C with tht (50 cm^3) for 5 h. After filtration, the resulting solution was slowly cooled to room temperature. The bis adduct separated out as violet crystals, which were collected by filtration and dried *in vacuo* (34% yield) (Found: C, 62.15; H, 4.95; N, 12.35; S, 14.35. Calc. for $C_{48}H_{48}FeN_8S_4$: C, 62.6; H, 5.25; N, 12.15; S, 13.9%). χ_m corr. = 1.63 × 10^{-9} m^3 mol^{-1} (diamagnetic correction = −8.54 × 10^{-9} m^3 mol^{-1}), corresponding to an apparent $\mu_{\text{eff.}}$ = 0.55 B.M.

Infrared spectrum: 1 605vw, 1 590vw, 1 505m–s, 1 440w, 1 422m–w, 1 330m, 1 305vw, 1 290m–s, 1 255vw, 1 165s, 1 120s, 1 097s, 1 070m–w, 1 005w, 956w, 910w, 885vw, 780m, 750m–s, 739s, 575w, 520vw, and 445vw cm^{-1}.

X-*Ray Diffractometric Study of* [Fe(pc)$(\text{dmso})_2$]·2 dmso.—

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† Throughout this paper: 1 B.M. = 9.274 × 10^{-24} A m^2.

The single crystals for this study were obtained by slowly cooling a saturated solution of [Fe(pc)] in dmso under an inert atmosphere.

Crystal data. $C_{40}H_{40}FeN_8O_4S_4$, $M = 880.90$, Monoclinic, $a = 7.993(2)$, $b = 16.175(7)$, $c = 16.086(7)$ Å, $\beta = 104.53(3)°$, $U = 2\,013$ Å^3, $D_m = 1.45 \pm 0.01$ (by flotation), $Z = 2$, $D_c = 1.454$ g cm^{-3}, $F(000) = 917.76$, Mo-K_α radiation, $\lambda = 0.710\,73$ Å, graphite monochromator, μ(Mo-K_α) = 6.40 cm^{-1}, space group $P2_1/c$ (C^5_{2h}, no. 14) from systematic absences.

Structure determination and refinement. Unit-cell dimensions were determined by least-squares refinement of the setting angles of 15 reflections on a Syntex $P2_1$ automated diffractometer. A total of 3 456 intensities were collected by the θ—2θ scan technique within the limit $3 \leqslant 2\theta \leqslant 45°$, of which 1 062 independent reflections, with $F_o \geqslant 6\sigma(F_o)$, were used for structure determination *via* Patterson and Fourier methods, and for the refinement. The data were corrected for background and for Lorentz and polarization effects. A semi-empirical absorption correction, based on a 360° ψ scan around the scattering vector of the $0\ 1\ \bar{1}$ reflection, was also applied. The structure was refined by block-diagonal least squares using anisotropic temperature factors for non-hydrogen atoms. The weighting scheme was $w = (\sin\theta)/\lambda$. The final refinement, with the hydrogen atoms of the phthalocyanine molecule included at calculated positions, gave $R = 0.067$.

TABLE 1

Atomic positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Fe	0	0	0
S(1)	−2 357(5)	−773(3)	116(2)
S(2)	2 202(7)	3 660(4)	1 433(3)
O(1)	−3 203(14)	−472(8)	774(7)
O(2)	3 506(20)	3 112(11)	1 266(9)
N(1)	387(13)	237(7)	1 210(6)
N(2)	1 488(13)	−969(7)	284(6)
N(3)	2 191(13)	−922(7)	1 835(6)
N(4)	−1 286(14)	1 502(7)	1 168(7)
C(1)	−293(16)	889(9)	1 565(8)
C(2)	176(17)	823(9)	2 500(8)
C(3)	−248(18)	1 308(8)	3 130(8)
C(4)	401(21)	1 046(9)	3 973(9)
C(5)	1 432(23)	349(10)	4 163(8)
C(6)	1 904(17)	−118(9)	3 547(7)
C(7)	1 224(14)	145(8)	2 690(7)
C(8)	1 336(14)	−230(7)	1 884(7)
C(9)	2 238(16)	−1 259(8)	1 105(8)
C(10)	3 134(15)	−2 020(8)	1 026(7)
C(11)	4 090(19)	−2 560(9)	1 635(9)
C(12)	4 782(20)	−3 271(10)	1 350(10)
C(13)	4 498(20)	−3 424(10)	486(11)
C(14)	3 572(20)	−2 897(10)	−127(9)
C(15)	2 863(16)	−2 196(8)	156(9)
C(16)	1 819(15)	−1 533(8)	−312(9)
C(17)	−4 029(20)	−914(12)	−909(10)
C(18)	−1 964(27)	−1 878(10)	355(11)
C(19)	1 331(27)	3 187(11)	2 233(13)
C(20)	3 391(26)	4 474(14)	2 062(16)
H[C(3)]	−977	1 816	2 986
H[C(4)]	117	1 368	4 451
H[C(5)]	1 853	179	4 778
H[C(6)]	2 677	−611	3 693
H[C(11)]	4 281	−2 443	2 262
H[C(12)]	5 481	−3 667	1 775
H[C(13)]	4 987	−3 939	296
H[C(14)]	3 411	−3 012	−754

Data reduction, Patterson and Fourier syntheses, and structure factor calculations were made on the HP-21MX computer of the Area della Ricerca di Montelibretti del C.N.R.; least-squares refinements were carried out on the UNIVAC 1108 computer of the University of Rome, using the set of programs of Laboratorio di Strutturistica Chimica, National Research Council (C.N.R.), Rome.[18] Neutral atomic scattering factors were taken from ref. 19. Final atomic co-ordinates are in Table 1. Temperature parameters and structure factors have been deposited as Supplementary Publication No. SUP 22800 (10 pp.).*

Attempts to Prepare Other Bis Adducts of [Fe(pc)].—(*a*) NN-*Dimethylformamide.* [Fe(pc)] (2.303 g) was treated with dmf (10 cm^3) for 6 h at *ca.* 100 °C. After cooling, the suspension was filtered and the solid dried *in vacuo* at room temperature (2.00 g). The solid was found to be identical with the starting [Fe(pc)] (i.r.) and no significantly intense bands around 1 650 cm^{-1} were observed, associated with co-ordinated or lattice dmf.[5] Similar results were obtained in an experiment carried out near the boiling point of dmf.

(*b*) *Tetrahydrofuran* (thf). [Fe(pc)] (0.298 g) was treated with thf (5 cm^3) at room temperature for 12 h. After evaporation of thf at reduced pressure, no weight increase was found for the solid left behind. In another experiment [Fe(pc)] (0.841 g) was heated at the reflux temperature of thf (50 cm^3) for 1.5 h. After cooling to room temperature and filtration, 0.754 g of solid was recovered which had an i.r. spectrum almost identical to that of the starting [Fe(pc)] {Found: C, 66.5; H, 2.90; N, 19.15. Calc. for [Fe(pc)]: C, 67.6; H, 2.85; N, 19.7%}. Similar results were obtained with the following substances: acetone, acetone + D_2O, methyl alcohol, and ethyl acetate.

RESULTS AND DISCUSSION

Phthalocyaninatoiron(II) readily adds dimethyl sulphoxide and tetrahydrothiophen to give the corresponding bis adducts (equation). As was also found

$$[\mathrm{Fe(pc)}] + 2\,\mathrm{L} \longrightarrow [\mathrm{Fe(pc)L_2}]$$

to be the case with the carbonyl derivatives of [Fe(pc)], the complexes tend to retain lattice solvent, the analytical formula being [Fe(pc)L_2]·2L. This is completely substantiated by the *X*-ray investigation of the bis(dmso) derivative (see below) and of the derivative [Fe(pc)(CO)(dmf)]·dmf.[5,20]

The geometrical details of the molecular and crystal structure of compound (1) are shown in Figures 1 and 2. The iron lies on an inversion centre in a tetragonally elongated octahedral geometry: it is co-ordinated to the four inner nitrogen atoms of the phthalocyaninato-macrocycle and to two equivalent dmso units *through their sulphur atom.* The Fe–N distances [1.931(10) and 1.951(11) Å] (Table 2) are not significantly different from the corresponding values found in [Fe(pc)(4Me-py)$_2$] [21] [1.937(3) and 1.932(3) Å] and in [Fe(pc)] itself [22] [1.926(1) and 1.927(1) Å]. Within the macrocycle, the C–N and C–C distances are close to those found [21] for the bis(4-methylpyridine) adduct. The Fe–S distance of 2.308(4) Å suggests little, if any, iron-to-sulphur π back donation in view of the fact that the sum of the iron(II) and

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

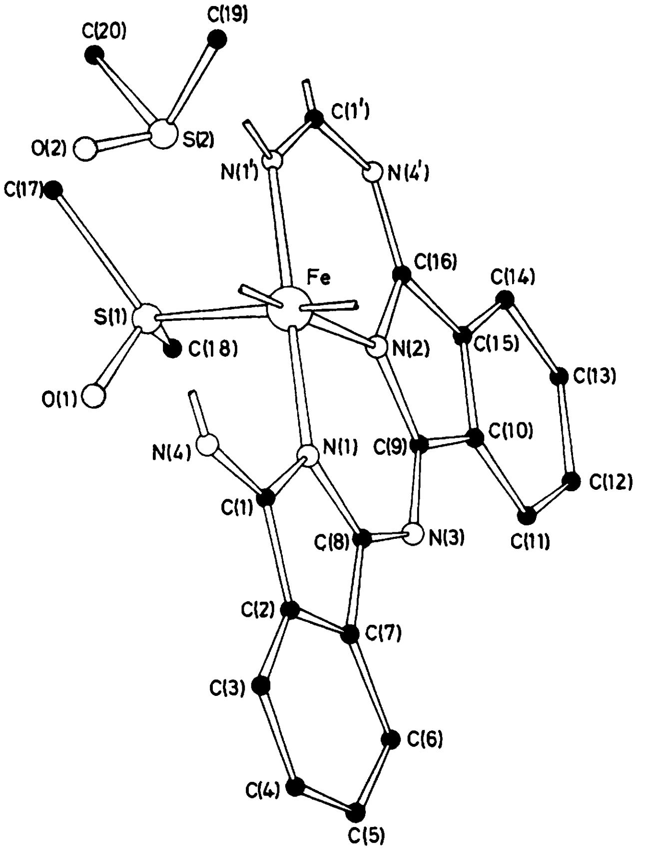

FIGURE 1 A view of the molecular structure of [Fe(pc)(dmso)$_2$]·2 dmso showing the asymmetric unit and the atom labelling. The centrosymmetric counterparts are not shown

sulphur covalent radii[23] (1.17 and 1.04 Å, respectively) is lower than the observed value.

The presence of unco-ordinated dmso units in the compound has its counterpart in the crystallographically observed unco-ordinated dmf in [Fe(pc)(CO)(dmf)]·dmf.[5] In this case, a comparison can be made of the molecular parameters of co-ordinated and unco-ordinated dmso units. Some relevant structural parameters of co-ordinated and unco-ordinated dmso are listed in Table 3. The S–O distance [1.474(14) Å] of the co-ordinated dmso in [Fe(pc)(dmso)$_2$]·2 dmso is somewhat longer than that [1.443(18) Å] for the lattice dmso unit. On the other hand, by reference to the data of Table 3, it can be seen that the observed S–O distance in our compound is well within the range of values observed for most of the *S*-bonded metal complexes, whereas *O*-bonding to a metal increases the S–O distance by *ca.* 1.54 Å. This is in agreement with the generally accepted view of increased S–O bond order in *S*-bonded complexes. Although the so called $\Delta\nu$(SO) rule[24] [based on the difference between the ν(SO) values in cm^{-1} for the unco-ordinated and the co-ordinated dmso] fails in certain cases,[25] the change in S–O bond distances (see Table 3) is of the right magnitude for O $\longrightarrow$ S p_π–d_π bonding in *S*-bonded dmso metal complexes, which is the basis of the above rule.

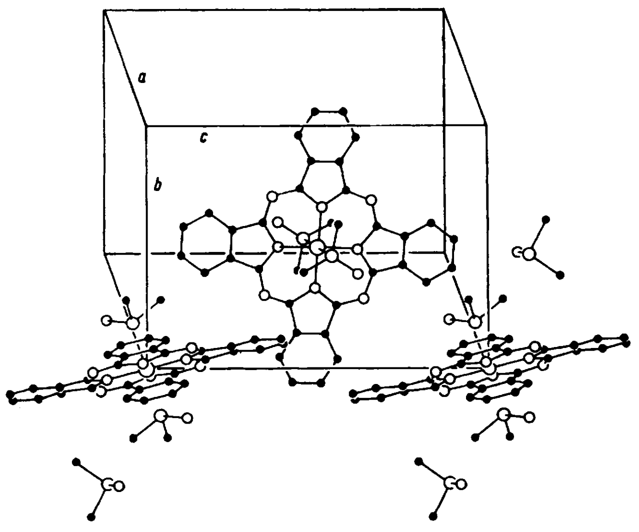

FIGURE 2 The unit-cell contents of [Fe(pc)(dmso)$_2$]·2 dmso. For the sake of clarity some of the unco-ordinated dmso groups have been omitted

TABLE 2

Bond lengths and angles, with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

Fe–S(1)	2.308(4)	C(1)–C(2)	1.459(18)
Fe–N(1)	1.931(10)	C(2)–C(3)	1.389(20)
Fe–N(2)	1.951(11)	C(2)–C(7)	1.367(18)
S(1)–O(1)	1.474(14)	C(3)–C(4)	1.390(18)
S(1)–C(17)	1.858(14)	C(4)–C(5)	1.385(23)
S(1)–C(18)	1.838(16)	C(5)–C(6)	1.373(21)
S(1)–O(2)	1.443(18)	C(6)–C(7)	1.413(16)
S(2)–C(19)	1.783(23)	C(7)–C(8)	1.455(16)
S(2)–C(20)	1.782(22)	C(9)–C(10)	1.446(18)
N(1)–C(1)	1.375(18)	C(10)–C(11)	1.389(18)
N(1)–C(8)	1.381(14)	C(10)–C(15)	1.390(18)
N(2)–C(9)	1.387(15)	C(11)–C(12)	1.403(23)
N(2)–C(16)	1.395(18)	C(12)–C(13)	1.373(24)
N(3)–C(8)	1.324(16)	C(13)–C(14)	1.370(21)
N(3)–C(9)	1.304(16)	C(14)–C(15)	1.395(22)
N(4)–C(1)	1.329(17)	C(15)–C(16)	1.449(18)
N(4′)–C(16)	1.337(17)		

(*b*) Angles (°)

S(1)–Fe–N(1)	87.3(3)	C(1)–C(2)–C(7)	105.9(12)
S(1)–Fe–N(2)	90.4(3)	C(3)–C(2)–C(7)	122.5(11)
N(1)–Fe–N(2)	89.4(4)	C(3)–C(2)–C(4)	116.1(12)
Fe–S(1)–O(1)	114.2(5)	C(3)–C(4)–C(5)	121.3(14)
Fe–S(1)–C(17)	114.5(6)	C(4)–C(5)–C(6)	123.0(12)
Fe–S(1)–C(18)	116.3(7)	C(5)–C(6)–C(7)	115.5(13)
O(1)–S(1)–C(17)	108.8(7)	C(2)–C(7)–C(6)	121.6(12)
O(1)–S(1)–C(18)	104.4(8)	C(2)–C(7)–C(8)	107.8(10)
C(17)–S(1)–C(18)	96.6(8)	N(1)–C(8)–N(3)	127.3(10)
O(2)–S(2)–C(19)	107.5(10)	N(1)–C(8)–C(7)	109.1(10)
O(2)–S(2)–C(20)	104.6(10)	N(2)–C(9)–N(3)	127.7(11)
C(19)–S(2)–C(20)	99.0(11)	N(2)–C(9)–C(10)	108.0(10)
Fe–N(1)–C(1)	126.2(8)	C(9)–C(10)–C(15)	107.9(10)
Fe–N(1)–C(8)	126.9(8)	C(11)–C(10)–C(15)	120.1(12)
C(1)–N(1)–C(8)	106.8(10)	C(10)–C(11)–C(12)	108.5(13)
Fe–N(2)–C(9)	126.0(9)	C(11)–C(12)–C(13)	120.0(14)
Fe–N(2)–C(16)	125.0(8)	C(12)–C(13)–C(14)	122.6(16)
C(9)–N(2)–C(16)	108.7(10)	C(13)–C(14)–C(15)	117.4(14)
C(8)–N(3)–C(9)	122.6(10)	C(10)–C(15)–C(14)	121.4(12)
C(1)–N(4)–C(16′)	123.0(10)	C(10)–C(15)–C(16)	107.2(12)
N(1)–C(1)–N(4)	128.5(12)	N(2)–C(16)–C(15)	108.1(11)
N(1)–C(1)–C(2)	110.2(11)	N(2)–C(16)–N(4′)	127.8(12)

Co-ordination of dmso through sulphur in [Fe(pc)-(dmso)$_2$] is not a surprising result in view of the fact that iron has a similar affinity for oxygen as for sulphur,

Table 3

Structural parameters of unco-ordinated dmso and of some dmso metal complexes

Compound	M–S	M–O	S–O	C–S	Ref.
	Å				
dmso			1.471	1.812 1.801	*a*
dmso			1.531	1.798	*b*
dmso [c]			1.44	1.78	This work
$[CuCl_2(dmso)_2]$		1.955	1.53	1.77	*d*
$[Fe(pc)(dmso)_2]$	2.308		1.47	1.85	This work
$[FeCl_2(dmso)_4]^+$		2.006	1.541	1.804	*e*
$[Ru(dmso)(NH_3)_5]^{2+}$	2.188		1.527	1.821 1.810	*f*
$[RuCl_3(dmso)_3]^-$	2.261		1.48	1.78	*g*
$[RuCl_2(dmso)_4]$	2.252 2.277 2.276		1.483 1.485 1.485	1.808, 1.779 1.795, 1.783 1.787, 1.794	*h*
		2.142	1.557	1.783, 1.793	
$[IrCl_2(baph)(dmso)_2]$ [i]	2.229 2.243		1.46 1.44	1.80, 1.82 1.80, 1.85	*j*
cis-$[Pd(NO_3)_2(dmso)_2]$	2.231 2.253		1.463	1.789	*k*
cis-$[PdCl_2(dmso)_2]$	2.244 2.229		1.469 1.454	1.77—1.79	*l*
trans-$[PdCl_2(dmso)_2]$	2.298		1.475	1.778	*m*

[a] Temperature = −60 °C; M. A. Vismamitra and K. K. Kannan, *Nature*, 1966, 209, 1016. [b] R. Thomas, C. B. Shoemaker, and K. Eriks, *Acta Cryst.*, 1966, **21**, 12. [c] For the lattice dmso of $[Fe(pc)(dmso)_2]\cdot 2$ dmso. [d] R. D. Willet and K. Chang, *Inorg. Chim. Acta*, 1970, **4**, 447. [e] M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Acta Cryst.*, 1967, **23**, 581. [f] F. C. March and G. Ferguson, *Canad. J. Chem.*, 1971, **49**, 3590. [g] R. S. McMillan, A. Mercer, B. R. James, and J. Trotter, *J.C.S. Dalton*, 1975, 1006. [h] A. Mercer and J. Trotter, *J.C.S. Dalton*, 1975, 2480. [i] baph = Benzylacetophenone. [j] M. McPartlin and R. Mason, *J. Chem. Soc.* (*A*), 1970, 2206. [k] D. A. Langs, C. R. Hare, and R. G. Little, *Chem. Comm.*, 1967, 1080. [l] R. Melanson and F. D. Rochon, *Canad. J. Chem.*, 1975, **53**, 2371. [m] M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams, and W. H. Watson, *Acta Cryst.*, 1967, **23**, 788.

i.e. is a borderline element in the A and B classification of metals.[26] Moreover, the highly delocalized π system of the phthalocyaninato-macrocycle will certainly tend to make the metal centre more soft [27] than other iron(II) complexes. This is substantiated by the isolation of several carbonyl adducts of [Fe(pc)], recently obtained in these laboratories [5] with Group 6 axial donor atoms, of the type [Fe(pc)(CO)L]. However, the $[Fe(pc)(dmso)_2]$ and $[Fe(pc)(tht)_2]$ complexes reported in this paper are the first well established derivatives of [Fe(pc)] containing axial sulphur ligands.

Attempts have been made to prepare adducts of [Fe(pc)] with potential oxygen donors such as dimethylformamide, tetrahydrofuran, acetone, water, methyl alcohol, and ethyl acetate. In all these cases, unreacted [Fe(pc)] was recovered. Some special comment is required concerning the failure to observe co-ordinative addition of thf to [Fe(pc)], since a bis(thf) adduct has been reported by Taube and Drevs.[17] The latter was, however, prepared by a different route, namely by the reaction of $Li_2Fe(pc)$ with CCl_4 in thf. The compound $[Fe(pc)]\cdot 2$thf should therefore be regarded [28] as a metastable compound, accessible only by the route indicated by Taube and Drevs.

Although [Fe(pc)] is somewhat soluble in dmf and thf, no stable solid-state bis adducts appear to be accessible from a combination of the components.

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REFERENCES

[1] A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 27.

[2] D. V. Stynes, *J. Amer. Chem. Soc.*, 1974, **96**, 5942; D. V. Stynes, *Inorg. Chem.*, 1977, **16**, 1170.

[3] Results by J. A. Elvidge, A. B. P. Lever, and M. P. Sammes, quoted in ref. 1.

[4] B. B. Wayland, L. F. Mehne, and J. Swartz, *J. Amer. Chem. Soc.*, 1978, **100**, 2379.

[5] F. Calderazzo, G. Pampaloni, D. Vitali, G. Pelizzi, I. Collamati, S. Frediani, and A. Serra, *J. Organometallic Chem.*, 1980, **191**, 217; F. Calderazzo, D. Vitali, G. Pampaloni, and I. Collamati, *J.C.S. Chem. Comm.*, 1979, 221.

[6] P. A. Barrett, D. A. Frye, and R. P. Linstead, *J. Chem. Soc.*, 1938, 1157.

[7] A. Hudson and H. J. Whitfield, *Inorg. Chem.*, 1967, **6**, 1120; B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, *Trans. Faraday Soc.*, 1968, **64**, 620.

[8] D. C. Grenoble and H. G. Drickamer, *J. Chem. Phys.*, 1971, **55**, 1624.

[9] R. Taube, *Pure Appl. Chem.*, 1974, **38**, 427.

[10] J. G. Jones and M. V. Twigg, *Inorg. Chem.*, 1969, **8**, 2120.

[11] D. V. Stynes and B. R. James, *J. Amer. Chem. Soc.*, 1974, **96**, 2733.

[12] K. M. Kadish, L. A. Bottomley, and J. S. Cheng, *J. Amer. Chem. Soc.*, 1978, **100**, 2731.

[13] D. A. Sweigart, *J.C.S. Dalton*, 1976, 1476; J. J. Watkins and A. L. Balch, *Inorg. Chem.*, 1975, **14**, 2720.

[14] J. G. Jones and M. V. Twigg, *J. Chem. Soc.* (*A*), 1970, 1546.

[15] J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta*, 1974, **10**, 103; *ibid.*, 1975, **12**, L15.

[16] J. G. Jones and M. V. Twigg, *J.C.S. Dalton*, 1978, 1709.

[17] R. Taube and H. Drevs, *Z. anorg. Chem.*, 1977, **429**, 5.

[18] R. Spagna, unpublished work.

[19] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[20] F. Calderazzo, D. Vitali, G. Pampaloni, I. Collamati, G. Pelizzi, S. Frediani, and A. Serra, 'Proceedings of the XIIth National Meeting of Inorganic Chemistry,' Trieste, September 1979, Paper A4.

[21] F. Cariati, F. Morazzoni, and M. Zocchi, *J.C.S. Dalton*, 1978, 1018.

[22] J. F. Kirner, W. Dow, and W. R. Scheidt, *Inorg. Chem.*, 1976, **15**, 1685.

[23] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 224.

[24] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986; F. A. Cotton, R. Francis, and W. D. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534.

[25] C. V. Senoff, E. Maslowky, and R. G. Goel, *Canad. J. Chem.*, 1971, **49**, 3585.

[26] H. M. N. H. Irving, 'The Stability of Metal Complexes,' *Special Publ.*, The Chemical Society, London, 1959, no. 13.

[27] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

[28] R. Taube, personal communication.