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Synthesis and Molecular Structure of Kryptofix 222 Potassium Phthalocyaninato Ferrate, $[\mathrm{K} \subset 222]$-[FePc], and (18-crown-6) lithium (18-crown-6)-(tetrahydrofuran) lithium phthalocyaninato ferrate, $[\mathrm{Li} \subset 18\mathrm{c}.6][\mathrm{Li(THF)} \subset 18\mathrm{c}.6][\mathrm{FePc}]$

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Electrochemical and spectral studies of iron phthalocyanine complexes have led to the conclusion that the first reduction of iron(II) phthalocyanine, [Fe(II)Pc] (Pc = phthalocyanine), occurs at the metal to form $[\mathrm{Fe(I)Pc}(2-)]^-$ whereas the second reduction takes place at the ring to yield $[\mathrm{Fe(I)Pc}(3^{\cdot -})]^{2-}$ [1–3]. Several papers have indicated that the doubly reduced species reacts with a number of small molecules such as N_2, CO, NO and several organic substrates [4–5]. In order to study the reactivity of the 1 and 2 electron reduced species of [Fe(II)Pc], we have synthesized and isolated in the solid state derivatives containing the $[\mathrm{FePc}]^-$ and $[\mathrm{FePc}]^{2-}$ anions. We report here the synthesis and structural characterization of $[\mathrm{K} \subset 222][\mathrm{FePc}]$ and $[\mathrm{Li_2(THF)}(18\mathrm{c}.6)_2][\mathrm{FePc}]$.

Experimental

Fe(II)Pc was prepared according to standard procedures [6] and purified by repeated sublimation at 400 °C under reduced pressure (10^{-4} Torr). Potassium t-butylthiolate, used as reducing agent for the synthesis of $[\mathrm{FePc}]^-$, was prepared by the reaction of KOH with t-butylthiol in ethanol. The reducing agent used for the preparation of $[\mathrm{FePc}]^{2-}$ was $\mathrm{LiAlH_4}$. This reagent was obtained from Aldrich as were Krytofix 222(4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) and the polyether 18-crown-6(1,4,7,10,13,16-hexaoxacyclooctadecane). All experiments were done under an inert atmosphere either by Schenk techniques or in a Vacuum Atmospheres drybox. Solvents were rigorously purified and dried under argon. Electronic spectra were recorded either on a Cary 210 or 219 spectrometer.

$[\mathrm{K} \subset 222][\mathrm{FePc}]$ (**1**) was synthesized by reaction of $[\mathrm{K} \subset 222]$[t-butyl S] (40 mg, 0.08 mmol) in chlorobenzene (15 ml) with a suspension of iron(II) phthalocyanine (15 mg, 26×10^{-3} mmol) in chlorobenzene (10 ml). After stirring for 15–20 min, the pink solution was filtered, pentane was added (40 ml) and the solution was set aside for crystallization. The green crystals were collected and washed with pentane.

UV–Vis THF or chlorobenzene solutions: $\lambda_{\max}$ (log ϵ) 682 (4.91), 624sh, 546 (4.85), 523 (4.83), 475 (4.75), 438 (4.63) nm; solid state: $\lambda_{\max}$ 681, 632, 553, 522, 470, 439sh nm.

$[\mathrm{Li_2(THF)}(18\mathrm{c}.6)_2][\mathrm{FePc}]$ (**2**) was prepared by adding to a THF solution (10 ml) containing $\mathrm{LiAlH_4}$ (1.4 mg, 37×10^{-3} mmol) and 18-crown-6 (10 mg, 38×10^{-3} mmol) to a suspension of Fe(II)Pc (10 mg, 17×10^{-3} mmol) in THF (10 ml). The purple solution obtained was set aside for crystallization after filtration and addition of pentane (30 ml). The green crystals were collected and washed with pentane. UV–Vis (THF solutions) $\lambda_{\max}$ (log ϵ) 699 (4.62), 642 (4.90), 689sh, 524 (5.53), 346 (5.89).

Single crystals suitable for X-ray studies were obtained in sealed tubes by slow diffusion of pentane into chlorobenzene solutions containing $[\mathrm{FePc}]^-$ and THF solutions of $[\mathrm{FePc}]^{2-}$.

1, $\mathrm{C_{50}H_{52}N_{10}O_6KFe}$, $M_r = 983.48$, $a = 22.748(8)$, $b = 17.312(8)$, $c = 12.037(5)$ Å, $\beta = 92.48(1)°$, $V = 4736$ Å^3, space group $P2_1/n$, $Z = 4$, $D_{\mathrm{calc}} = 1.38$ g cm^{-3}.

2, $\mathrm{C_{60}H_{72}N_8O_{13}Li_2Fe}$, $M_r = 1182.31$, $a = 12.841(3)$, $b = 18.107(5)$, $c = 12.325(3)$ Å, $\alpha = 97.24(1)$, $\beta = 91.19(1)$, $\gamma = 94.53(1)°$, $V = 2833$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_{\mathrm{calc}} = 1.37$ g cm^{-3}.

Diffraction intensities were collected on a Philips PW-1100 diffractometer with graphite monochromated Cu Kα radiation ($\lambda = 1.5405$ Å) at room temperature for **1** and −100 °C for **2**. The structure solutions were based on 2765 and 4196 reflections having $I > 3\sigma(I)$ respectively for **1** and **2**. Final R values were for **1** and **2** respectively: $R_1 = 0.045$, $R_2 = 0.055$ and $R_1 = 0.053$, $R_2 = 0.071$. The asymmetric units of both crystals contain two halves of the phthalocyanine anions located on crystallographic inversion centers. The $[\mathrm{FePc}]^-$ and $[\mathrm{FePc}]^{2-}$ present in **1** and **2** present thus at least C_i symmetry.

Results and Discussion

The electronic spectra of $[\mathrm{FePc}]^-$ and $[\mathrm{FePc}]^{2-}$ in THF or chlorobenzene are given in Fig. 1. For $[\mathrm{FePc}]^-$, the spectrum is notably different from those given in the literature [2–7]. We controlled that the solution spectrum matched the solid state spectrum which was obtained by crushing crystals of **1** on the walls of a cell under inert atmosphere.

Figure 2 displays a perspective view of the monoanion $[\mathrm{FePc}]^-$. The structure of $[\mathrm{FePc}]^{2-}$ is very

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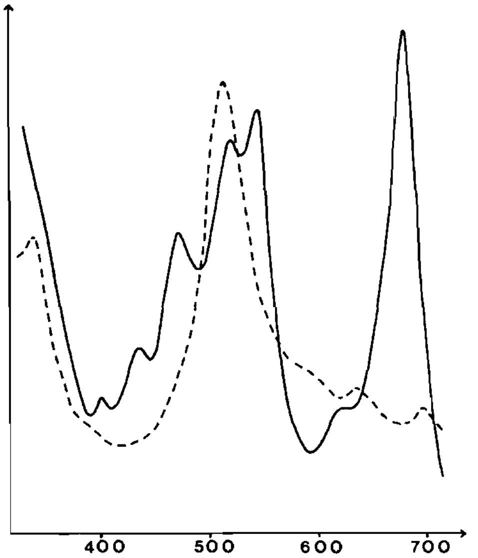

Fig. 1. Electronic spectra of [K ⊂ 222][FePc] (chlorobenzene solution, full line) and of $[Li_2(THF)(18c.6)_2]$-[FePc] (THF solution, dashed line).

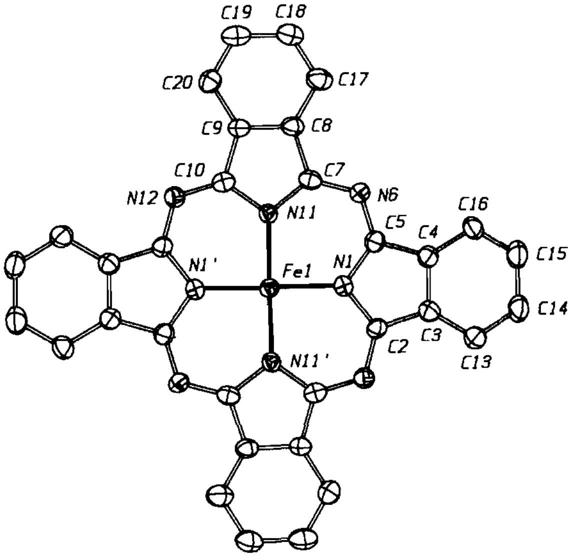

Fig. 2. ORTEP plot of the $[FePc]^-$ anion present in [K ⊂ 222][FePc] with part of the atom numbering scheme. Ellipsoids are scaled to enclose 30% of the electron density. Hydrogen atoms are omitted.

TABLE I. Comparison of Bond Lengths Found in Isoindole Moieties of $[Fe(II)(4MePy)_2Pc]$[a], $[FePc]^-$, $[FePc]^{2-}$ and [Co(II)Pc][b]

	$[Fe(II)(4MePy)_2Pc]$	$[FePc]^-$	$[FePc]^{2-}$	[Co(II)Pc]
$Fe-N_{iso}$	1.934(3)	1.910(2)	1.910(2)	1.908(2)
$N_{iso}-C\alpha$	1.374(4)	1.386(2)	1.395(2)	1.375(3)
$C\alpha-C\beta$	1.453(4)	1.436(2)	1.446(2)	1.450(3)
$C\beta-C\beta$	1.400(4)	1.378(3)	1.393(2)	1.384(3)
$C\alpha-N_m$	1.327(4)	1.326(3)	1.327(2)	1.318(3)

[a] Ref. 8. [b] Ref. 9.

similar to that of the monoanion, thus no figure is given for the dianion.

Selected bond distances are given in Table I for $[FePc]^-$ and $[FePc]^{2-}$. Iron is four-coordinate in both compounds and linked only to the four isoindole nitrogens of the Pc rings. The mean values of the $Fe-N_{iso}$ bonds are identical in both compounds and equal to 1.910(2) Å. The conformation of both phthalocyanine rings are unremarkable. The inner cores are planar within ±0.06 Å in **1** and ±0.03 Å in **2**. The bond parameters within the Pc rings of **1** and **2** are not significantly different. Table I compares in order the average Fe–Np distances and average phthalocyaninato core dimensions in four species: low-spin six-coordinate, $[Fe(II)(4MePy)_2Pc]$ [8], $[FePc]^-$, $[FePc]^{2-}$ and [Co(II)Pc] [9].

A decrease in the formal oxidation state of iron enclosed in a phthalocyanine ring would be expected to lead to small increases in the $Fe-N_{iso}$ bond lengths relative to the distances present in the complexes having iron in a formally higher oxidation state. The observed trend is in fact opposite to that expected. Indeed, $Fe-N_{iso}$ in $[Fe(II)(4MePy)_2Pc]$ is 1.934(3) and only 1.910(2) in $[FePc]^-$ and $[FePc]^{2-}$.

Expected $Fe-N_{iso}$ bond distance values could be based on the $Co-N_{iso}$ bond lengths observed in the isoelectronic d^7 Co(II) species with an appropriate allowance for the decreased effective nuclear charge in the iron complexes. For [Co(II)Pc], the $Co-N_{iso}$ distance is 1.907(2) Å. Thus, the expected $Fe-N_{iso}$ distance would be slightly longer than the observed length of 1.910(2) Å. It appears thus, that the $Fe-N_{iso}$ distances in $[FePc]^-$ and $[FePc]^{2-}$ are shorter than predicted for iron(I) and iron(0) formulations.

In addition, the bond distances in the phthalocyanine cores show some trends which are not present in most metallophthalocyanines of known structures [10]. Table I shows that the $N_{iso}-C\alpha$

bond lengths are somewhat longer whereas the Cα–Cβ bond distances are slightly shorter. Unfortunately, a too close comparison of the bond distances present in $[FePc]^-$ and $[FePc]^{2-}$ is not possible, the structure of the former has been studied at normal temperature whereas the latter compound has been studied at −100 °C.

In conclusion, our X-ray studies show that the structural parameters are very similar for both anions: $[FePc]^-$ and $[FePc]^{2-}$. Thus, although not identical their electronic structures must be similar. This conclusion can be rationalized by assuming, as it was proposed for the reduced iron(II) porphyrinates [11], that $[FePc]^-$ and $[FePc]^{2-}$ correspond respectively to resonance hybrids of the type:

$$[Fe(I)Pc(-2)]^- \rightleftharpoons [Fe(II)Pc(-3\cdot)]^-$$

and

$$[Fe(I)Pc(-3\cdot)]^{2-} \rightleftharpoons [Fe(II)Pc(-4:)]^{2-}$$

EPR and Mössbauer studies of both derivatives are presently underway.

References

1 A. B. P. Lever and J. P. Wilshire, *Can. J. Chem., 54,* 2514 (1976).
2 A. B. P. Lever and J. P. Wilshire, *Inorg. Chem., 17,* 1145 (1978).
3 P. C. Minor, M. Gouterman and A. B. P. Lever, *Inorg. Chem., 24,* 1894 (1985).
4 M. Sudo, M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *J. Phys. Chem., 72,* 1174 (1968).
5 K. Tamaru, *Catal. Rev., 4,* 161 (1971).
6 H. Tomoda, S. Saito and S. Shiraishi, *Chem. Lett.,* 313 (1983).
7 D. W. Clack and J. R. Yandle, *Inorg. Chem., 11,* 1738 (1972).
8 F. Cariati, F. Morazzoni and M. Zocchi, *J. Chem. Soc., Dalton Trans.,* 1018 (1978).
9 R. Mason, G. A. Williams and P. E. Fielding, *J. Chem. Soc., Dalton Trans.,* 676 (1979).
10 A. De Cian, M. Moussavi, J. Fischer and R. Weiss, *Inorg. Chem., 24,* 3162 (1985) and refs. therein.
11 T. Mashiko, C. A. Reed, R. J. Haller and R. W. Scheidt, *Inorg. Chem., 23,* 3192 (1984).