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The Electronic Structure and Mössbauer Spectra of Iron(II)–Phthalocyanine Complexes as Studied by Semiempirical MO–LCAO Calculations

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Abstract

The electronic structure of complexes FePc(L_1)(L_2) (L_1, L_2 = H_2O, CO, formamide and pyridine) have been investigated by means of MO–LCAO–INDO calculations with the aim of obtaining a consistent description of the principal electronic and geometrical factors influencing the Mössbauer quadrupole splitting. The obtained general agreement with the available experimental data proves the reliability of the adopted simple theoretical model. The results show that the ΔE_Q quantity is very sensitive to the geometry of the first coordination shell, and to all the ligand effects which can modify the individual metal d orbital occupancies. The Mössbauer spectrum of the FePc(py) complex recorded using ^{57}CoPc(py) as γ emitter is theoretically analyzed and a $^5A_1$ ground state is proposed.

1. Introduction

The impact of the ferrous–phthalocyanine complex FePc and its adducts FePcL_1L_2 (L_1 and L_2 are pyridine (py) or methyl substituted pyridine molecules) as homogeneous catalysts or as models of biologically important iron enzymes [1] challenged the interest of several authors who reported on theoretical [2] and experimental [3] investigations of the electronic structure of this class of compounds. In particular, the optical spectra have been interpreted according to the crystal field theory [4], while the Mössbauer spectra have been the subject of numerous investigations [5] based on simplified ligand field theories or Extended Huckel (EH) type calculations. In addition, Mössbauer spectra of complexes FePc(CO)L (L = H_2O or dimethylformamide) have been recorded and qualitatively discussed [6] with the aim of settling possible relationships between experimental findings and σ-donor and π-acceptor capabilities of the axial ligands.

However, due to the difference in the level of sophistication of the above theoretical approaches, a consistent and unified picture of the electronic structure of the series FePcL_1L_2 is still lacking. The aim of the present report is to contribute to a better understanding of the most important electronic factors governing the Mössbauer spectral behaviour of this class of complexes. To this end, the study of the electronic structure of the complexes FePc(CO)(H_2O) (**I**), FePc(CO)(H_2NCHO) (**II**), FePc(H_2O)$_2$ (**III**), FePc (**IV**), FePC(py) (**V**) and FePc(py)$_2$ (**VI**), has been carried out employing an approximate MO–LCAO method.

The carbonyl–formamide adduct (**II**) has never been isolated but it can be assumed as representative of the corresponding dimethylformamide adduct. The bis-aquo complex (**III**), experimentally unknown, has been considered here because the comparison of its electronic structure with that of complex **I** may give useful information about the influence of the π-acceptor CO axial ligand. Finally, **IV** and **VI** are the most widely investigated species of which also the molecular structure is known from X-ray diffraction studies [7].

The synthesis of FePc(py) (**V**) has never been reported and the complex cannot be isolated probably because of the high tendency of FePc to form the

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TABLE I. Experimental Values for Quadrupole Splitting (ΔE_Q) and Isomer Shift (*IS*) for some $FePcL_1L_2$ Complexes

Complex	*IS* (mm s^{-1})	ΔE_Q (mm s^{-1})	Reference
FePc(CO)(DMF)[a]	0.35	1.56	6
FePc(CO)(H_2O)[a]	0.37	1.75	6
$FePc(py)_2$[a]	0.53	1.96	6
$FePc(py)_2$[b]	0.31	2.04	
FePc[c]	0.63	2.62	5g
FePc[b]	0.45	2.62	
FePc(py)[b]	0.46	2.22	

[a] At room temperature. [b] Present work, at liquid nitrogen temperature. [c] At 4 K.

bis-pyridine adduct. On the contrary, in the case of the corresponding CoPc complex, both mono- and bis-pyridine adducts can be easily obtained [8]. As described in the next section, we were able to obtain the Mössbauer spectrum of the monopyridine adduct FePc(py) using a sample of ^{57}CoPc(py) as a γ emitter, supposing that the iron compound remains intact when the high energy iron atom is formed during the cobalt decay process, as it happens for the ^{57}CoPc complex [5h].

2. Experimental

2.1. Preparative Method

The compound ^{57}CoPc was synthesized according to the method reported for CoPc [9], except that a few drops of 0.1 M HCl solution of $^{57}CoCl_2$ containing 1 mc of activity were added to the required amount of $CoCl_2 \cdot 6H_2O$. Practically, 2.37 g of $CoCl_2 \cdot 6H_2O$ with the little amount of $^{57}CoCl_2$ were added to 150 ml of a chinoline solution containing 5.12 g of phthalonitrile. The reaction mixture was maintained at boiling temperature for 1 h and then left to cool to room temperature.

The compound CoPc, containing a little amount of ^{57}CoPc, precipitated. It was filtered, washed with water, ethyl alcohol and then dried under vacuum. CoPc has been classified as β-form by its infrared spectrum [9].

The ^{57}CoPc(py) and $^{57}CoPc(py)_2$ adducts were prepared from ^{57}CoPc according to the literature method [8].

2.2. Measuring the Mössbauer Spectra

The Mössbauer spectra were recorded in the constant acceleration mode with a single-line stainless steel absorber and using the ^{57}Co-containing samples as Mössbauer sources, held at 80 K under a nitrogen atmosphere inside a cryostatic equipment. The velocity scale was calibrated using a thin metallic iron foil and all isomer shifts are referred to the centre of the spectrum of an α-Fe adsorber. Lorentzian lineshapes were used for the least-square fitting of the experimental data. The two lines of each doublet were constrained to have the same width and intensity, and possible effects of preferential orientation were not taken into account.

The Mössbauer parameters derived from the present set of measurements are reported in Table 1, where comparison is made with other data available from the literature. Source Mössbauer experiments with ^{57}CoPc derivatives have shown complete equivalence of the generated ^{57}Fe atoms.

3. Computational Method

The theoretical investigation of the electronic structure of the complexes $FePcL_1L_2$ has been performed with a MO–LCAO–INDO type [10] method, with the aim of obtaining a consistent rationalization of the quadrupole splitting ΔE_Q observed in the Mössbauer spectra. The basic approximations adopted in evaluating the INDO–Hamiltonian matrix elements have been previously reported [11]. Few comments are needed in order to settle the validity and limitations of the present computational approach. As well known, the predicting capability of approximate MO theories may strongly depend upon the basic approximations and the chosen set of empirical parameters. In particular, the β_{ij} quantities entering the definition of the two-center one-electron matrix elements are largely undefined in their physical meaning and are usually treated as adjustable parameters. In the present computations, standard values of β_{ij} [12] have been adopted for H, C, N and O atoms, while in the case of orbitals centered on the iron atom and 'ad hoc' optimization of the β_{ij} parameters has been carried out in order to reproduce as close as possible the ΔE_Q quantity experimentally observed for the FePc(CO)(H_2O) complex [6]. The aim of this procedure is to obtain a set of parameters well adapted for the evaluation of a specific physical quantity and transferable within a series of related complexes.

Worthy of mention are some difficulties met during the optimization of the INDO wavefunction.

For molecular systems of large dimensions such as the phthalocyanine iron complexes, several electronic states exist within an energy range even smaller than 1 eV. These states, all characterized by the same spin and spatial symmetry, differ just in the occupancy of the MOs belonging to the different irreducible representations, and, as a consequence, in the occupancy of the orbitals centered on the iron atom which are primarily responsible for the ΔE_Q value. This means that the search for the true ground state wavefunction is not an easy task even in the case when the computations are carried out according to an approximate scheme. In particular, the use of the 'aufbau' principle in selecting the occupied MOs can lead to a wavefunction with energy higher than the true ground state energy. In order to overcome these difficulties the final SCF wavefunction is obtained with a multi-step procedure: starting from the 'aufbau' solution, different electronic states are optimized in order to identify the lowest energy configuration.

The theoretical evaluation of the quadrupole splitting relevant for the interpretation of the Mössbauer spectra has been carried out according to the method outlined by Trautwein and Harris [13], with the obvious modifications required by the INDO approximation. The quadrupole splitting defined as

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

depends upon the principal values V_{ii} of the Electric Field Gradient (EFG) tensor and on the asymmetry parameter

$$\eta = |V_{xx} - V_{yy}|/|V_{zz}|\ (V_{zz} > V_{xx} > V_{yy})$$

The matrix elements of the V_{pq} ($p, q = x, y, z$) operators over the iron atomic basis functions are evaluated using the corresponding block of the INDO one-particle density matrix (that is neglecting effects connected with configuration mixing or spin–orbit coupling perturbation) while the contributions from the electron densities associated with the ligand atoms are estimated by means of a simple point-charge approximation. Numerical values of γ and Q quantities needed for evaluating the ΔE_Q observable are taken from ref. 14.

In order to reduce the computational effort, a ligand simplified with respect to the true phthalocyanine macrocycle has been considered (see Fig. 1). The ligand of Fig. 1 has a structure identical to that of the phthalocyanine ligand in the first and second coordination shell; it includes also a largely delocalized π-electron system without, however, any aromatic character. This reduction of the complexity of the macrocycle can be justified considering that the actual electronic densities in molecular regions far from the coordination site cannot influence to a large extent the trend of the electronic distribution on the iron atom upon which the values of ΔE_Q quantity mainly depend. This view has been criticized by Quedrago *et al.* [5f]. However, test calculations performed on complex **I** using both a complete and a simplified macrocycle have shown that this is an acceptable approximation (see Section 4).

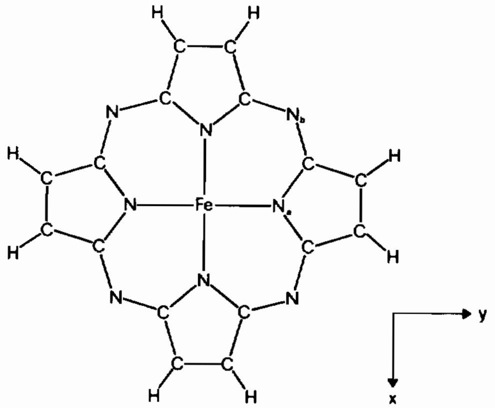

Fig. 1. Schematic molecular structure of the FePc complex with a simplified ligand.

The molecular structure of the basic FePc complex is derived from the experimental X-ray data quoted in ref. 7. Standard molecular geometries [15] have been considered for the other ligand groups such as water and formamide, in the case of the complexes for which no experimental molecular geometry is available.

4. Results and Discussion

FePc(CO)(H$_2$O)

The geometry of the Fe–CO moiety has been taken from ref. 6, while a value of 2.07 Å is assumed for the Fe–OH$_2$ distance. Two different orientations have been considered for the coordinated water molecule: in the first case (A) H_2O belongs to the xz plane (see Fig. 1), while in the second (B) the water molecule is rotated by 45° around the z axis. Both the forms A and B belong to the C_{2v} point group. The case A is found to be the most stable conformation, and its singlet ground state wavefunction corresponds to the following MO occupancy: $22(a_1)^2$ $13(a_2)^2$ $17(b_1)^2$ $17(b_2)^2$, while the corresponding occupancies for the case B are $22(a_1)^2$ $12(a_2)^2$ $18(b_1)^2$ $17(b_2)^2$. Therefore, the wavefunction of case B can be approximately obtained from that of case A by a pair excitation from the MO set a_2 to the MO set b_1. This corresponds to a charge transfer from the in plane 3d orbitals of the iron atom partially to the d_{xz}, d_{yz} out of plane orbitals and partially to orbitals centered on ligand atoms. This observation can explain why in going from case A to case B the net charge on the iron center increases from 0.806 to 1.164, while the

TABLE II. Electronic Charge Distribution and Mössbauer Parameters for the FePc(CO)H_2O Complex[a]

Atom	Electronic configuration	Net charge
Fe^b	s(0.240) p(0.542) d(6.412) 0.708 1.967 0.713 1.515 1.509	0.806
N_a	s(1.278) p(3.801)	−0.079
N_b	s(1.404) p(3.560)	0.036
$H(H_2O)$	s(0.850)	0.150
$O(H_2O)$	s(1.630) p(4.531)	−0.160
C(CO)	s(1.447) p(2.607)	−0.144
O(CO)	s(1.725) p(4.397)	−0.123
$\Delta E_Q = 1.75$ mm s^{-1} $\eta = 0.0074$		
Fe^b	s(0.250) p(0.590) d(5.997) 0.867 0.980 0.506 1.834 1.821	1.164
N_a	s(1.252) p(3.957)	−0.209
N_a'	s(1.269) p(3.848)	−0.117
N_b	s(1.408) p(3.604)	−0.013
$H(H_2O)$	s(0.831)	0.169
$O(H_2O)$	s(1.621) p(4.552)	−0.173
C(CO)	s(1.499) p(2.500)	0.000
O(CO)	s(1.729) p(4.220)	0.051
$\Delta E_Q = -4.72$ mm s^{-1} $\eta = 0.0649$		

[a] The first group of data refers to the complex in which the water molecule lies in the xz plane, the second group of data are relative to the case in which the water molecule is rotated by 45° around the z axis (see Fig. 1). [b] The 3d orbital populations of the Fe atom are reported in second entry in the order d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz} and d_{yz}.

four nitrogen atoms of the first coordination shell undergo a charge accumulation (see Table II). The two different electronic distributions have a very evident effect on the Mössbauer parameters ΔE_Q which have been computed equal to 1.75 and −4.72 mm/s, for case A and B, respectively.

The theoretical result for case A perfectly reproduces the observed value reported in ref. 6, proving that our β parameter optimization has been performed successfully.

Considerations based both on the relative stability and computed Mössbauer data suggest that the conformation B for the coordinated water molecule is very unfavorable. The fact that this result is independent of the particular assumptions of our computational scheme was checked by several additional calculations carried out with different sets of INDO parameters. Evidence has been obtained that the conformation B cannot be characterized by a positive value of the ΔE_Q quantity.

As mentioned in the previous section, in the case of the FePc(CO)(H_2O) complex, a calculation was carried out using the complete set of atoms of the Pc ligand. The ground state wavefunction, expanded in a basis of 199 atomic orbitals, may be represented by the following valence electron distribution: $33(a_1)^2$ $20(a_2)^2$ $26(b_1)^2$ $26(b_2)^2$.

The iron atom can be described by the electronic configuration $4s^{0.24}$ $4p^{0.54}$ $3d^{6.44}$ and the individual d orbital populations have been found equal to 0.694, 1.965, 0.691, 1.516, 1.498, respectively. (See Tables for the ordering of the d orbitals). The latter values are very close to those obtained from a calculation carried out with the simplified Pc ligand (see Table II), and, as expected, the small differences cannot influence to a large extent the computed quadrupole splitting which, in fact, has been found equal to 1.72 mm/s. The results clearly show that our assumption about the structure of the macrocycle ligand is quite acceptable.

FePc(CO)(H_2NCHO)

Complex **II** is here considered as a model of the *N,N'*-dimethylformamide derivative of which the molecular structure and Mössbauer spectrum have been experimentally determined by Calderazzo *et al.* [6]. Our theoretical calculations performed with an assumed C_s symmetry led to a lowest energy state with a $43(a')^2$ $31(a'')^2$ orbital occupancy. The electron populations associated with the atomic orbitals, reported in Table III, indicate that the non-axially symmetric formamide ligand has little effect on the near-degeneracy of the d_{xz}, d_{yz} iron orbitals found in the case of complex **I**. The computed ΔE_Q value of 1.54 mm/s is in very good agreement with the experimental one (1.56 mm/s [6]), and only slightly smaller than the corresponding value found for complex **I**. Our calculations show that the decrease in ΔE_Q is mainly due to a smaller occupancy of the d_{xy} iron orbital.

To point out that the prediction of the quadrupole splitting based on simplified ligand field theories may be in error in the case of low symmetry complexes, we call attention to the fact that in the case of FePc(CO)(H_2NCHO) the one particle density matrix for the iron d orbitals (and consequently the EFG tensor) has non-negligible off diagonal elements. When the latter are completely neglected (as would be the case in crystal field calculations) the resulting ΔE_Q value is 1.43 mm/s, smaller than the experimental and the theoretical values reported above.

A characteristic which differentiates complex **II** from complex **I** is that the asymmetry parameter of the former (0.21) is much larger than that of the latter (0), a fact that must be ascribed to the non-axial symmetry of the formamide ligand. The importance of the local geometry of the axially coordinated ligand is further demonstrated by a calculation performed with the H_2N group twisted by 90° with respect to the HCO one. Despite the fact that this geometry distortion is not expected to alter significantly the donor–acceptor capability of the formamide ligand, the ΔE_Q value is computed equal

TABLE III. Electronic Charge Distribution and Mössbauer Parameters for the FePc(CO)(H_2NCHO) Complex[a]

Atom	Electronic configuration	Net charge
Fe[b]	s(0.242) p(0.494) d(6.362) 0.730 1.969 0.638 1.527 1.498	0.902
N_a	s(1.206) p(3.980)	−0.186
N_a'	s(1.264) p(3.817)	−0.081
N_b	s(1.413) p(3.555)	0.032
N_b'	s(1.401) p(3.549)	0.049
O(H_2NCHO)	s(1.698) p(4.444)	−0.142
C(CO)	s(1.447) p(2.686)	−0.133
O(CO)	s(1.725) p(4.385)	−0.110

ΔE_Q = 1.54 mm s^{-1} η = 0.2101

[a] Due to the low symmetry, the four N atoms of the first and second coordination shell are equivalent in pairs and have been denoted as N_a, N_a', N_b and N_b', respectively. [b] The 3d orbital populations of the Fe atom are reported in second entry in the order d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz} and d_{yz}.

to 1.47 mm/s with an η value of 0.5. These changes in computed Mössbauer parameters are mainly caused by the complete removal of the degeneracy of the d_{xz}, d_{yz} orbitals and by a further reduction in d_{xy} orbital occupancy.

FePc(H_2O)$_2$

For this experimentally unknown complex an Fe–OH_2 distance equal to 2.16 Å has been assumed, with the water molecules lying in the *xz* plane. Some relevant orbital populations derived from the singlet ground state C_{2v} wavefunction with occupancies equal to $21(a_1)^2$ $13(a_2)^2$ $17(b_1)^2$ $17(b_2)^2$ are reported in Table IV. A ΔE_Q value of 1.90 mm/s and an asymmetry parameter nearly equal to zero have been computed. A comparison between the bisaquo complex **III** and complex **I** may be interesting in order to estimate the importance of the σ-donor and π-acceptor properties of the axial ligands. Comparing the data of Tables IV and II, it is apparent that the positive charge on a single water molecule in complex **I** (0.139) is very similar to that of the two water molecules in complex **III** (0.137). This implies that the water-to-metal charge transfer in complex **III** is nearly exactly twice as large as in complex **I**. This produces the raising of the mean energy of the d_{z^2} iron orbital and a corresponding lowering of its occupancy. Moreover, the d_{xz}, d_{yz} orbitals are less populated in **I** than in **III** due to the possibility of back-donation to the CO group. All these variations in charge distribution account for the fact that the computed ΔE_Q value of complex **III** is higher (1.90 mm/s) than that of complex **I** (1.75 mm/s). Our theoretical findings qualitatively agree with the predictions based on the additive contributions to ΔE_Q proposed for different axial ligands [16]. However, as was pointed out in ref. 17, the additive rules may be of little reliability in the case of π ligands.

TABLE IV. Electronic Charge Distribution and Mössbauer Parameters for the FePc(H_2O)$_2$ Complex[a]

Atom	Electronic configuration	Net charge
Fe[b]	s(0.217) p(0.519) d(6.575) 0.409 1.961 0.668 1.779 1.758	0.690
N_a	s(1.286) p(3.792)	−0.078
N_b	s(1.404) p(3.563)	0.033
H(H_2O)	s(0.854)	0.146
O(H_2O)	s(1.628) p(4.528)	−0.155

ΔE_Q = 1.90 mm s^{-1} η = 0.0111

[a] The nitrogen atoms of the macrocycles are nearly equivalent. Only average charge density data are reported. [b] The 3d orbital populations of the Fe atom are reported in second entry in the order d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz} and d_{yz}.

In order to investigate the effect of the perturbation produced by the water ligand, other calculations have been carried out with different Fe–OH_2 distances ranging from 2.16 to 1.90 Å. The variations caused by the approaching of the water ligand to the iron center in the computed quadrupole splitting are found to be relatively small (1.90–1.85 mm/s) as are the variations in the d orbital populations. Moreoever, the shortening of the Fe–OH_2 distance by about 0.3 Å does not significantly alter the asymmetry parameter which is computed nearly equal to zero for all the considered geometries.

FePc(py)$_2$

In our investigation, two different sets of calculations have been carried out for a Fe–N(py) distance equal to 2.04 and 2.33 Å, respectively. The two values correspond to the distances experimentally observed for FePc(py)$_2$ and CoPc(py)$_2$ [7], respectively.

The ΔE_Q quantity has been computed equal to 1.90 and 1.98 mm/s for short and large Fe–N(py)

TABLE V. Electronic Charge Distribution and Mössbauer Parameters for the FePc(py)$_2$ Complex[a]

Atom	Electronic configuration	Net charge
Fe[b]	s(0.245) p(0.553) d(6.582) 0.548 1.961 0.674 1.770 1.629	0.621
N$_a$	s(1.287) p(3.796)	−0.083
N$_b$	s(1.404) p(3.567)	0.029
N(py)	s(1.290) p(3.642)	0.068

$\Delta E_Q = 1.90$ mm s^{-1} $\eta = 0.4229$

[a] The nitrogen atoms of the macrocycles are nearly equivalent. Only average charge density data are reported. The results are relative to the Fe–N(py) distance equal to 2.04 Å (see text). [b] The 3d orbital populations of the Fe atom are reported in second entry in the order d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz} and d_{yz}.

TABLE VI. Electronic Charge Distribution and Mössbauer Parameters for the FePc Complex[a]

Atom	Electronic configuration	Net charge
Fe[b]	s(0.298) p(0.371) d(6.252) 1.152 1.989 0.931 1.090 1.090	1.080
N$_a$	s(1.289) p(3.729)	−0.017
N$_b$	s(1.369) p(3.515)	0.116

$\Delta E_Q = 2.89$ mm s^{-1} $\eta = 0.0000$

[a] The data reported refer to the electronic state ^{3}EA (see text). [b] The 3d orbital populations of the Fe atom are reported in second entry in the order d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz} and d_{yz}.

distances, respectively (see Table V). Our theoretical results are in fairly good agreement with the experimental ones obtained for FePc(py)$_2$ (1.96 mm/s at 4.2 K [5b], 2.02 mm/s at room temperature [5a] and 2.044 mm/s at 77 K (see Section 2) for ^{57}CoPc(py)$_2$ as γ emitter). Moreover, the positive sign of the computed EFG agrees with the experimental observations of Dale *et al.* [5b]. The EFG z principal axis is found to be coincident with the C_2 symmetry axis.

We obtained less satisfactorily results for the asymmetry parameter at a Fe–N(py) distance equal to 2.04 Å. The computed value (0.4) seems to be overestimated with respect to that suggested on the basis of the analysis of the experimental Mössbauer spectrum [5b]. However, it must be noted that on increasing the Fe–N(py) distance to 2.33 Å the η value drops to 0.04.

The variation in ΔE_Q caused by a change in the Fe–N(py) distance of about 0.3 Å is very similar to that found for an equivalent elongation of the Fe–OH$_2$ distance in FePc(H$_2$O)$_2$, but the ability of the pyridine ligand to perturb also the d_π iron orbitals produces a dependence of the asymmetry parameter upon the Fe–N(py) distance much stronger than that we found in the case of the water adduct.

FePc

The molecular structure of this complex has been known for several years [7] and has been recently reinvestigated in a low temperature X-ray diffraction study [18]. From the analysis of the deformation electron density maps, Coppens and Li [18] were able to indicate that the ground state of FePc is ^{3}E, assuming an idealized D_{4h} symmetry and neglecting possible Jahn–Teller distortions or spin–orbit coupling effects which can be operative in removing the degeneracy of the electronic ground state [19].

In the present study, the complex FePc, as well as the complex FePc(py), has been considered to show that our computational procedure can be satisfactorily applied also in the case of low coordination species. Since our calculations have been carried out without including spin–orbit coupling perturbation and without configuration interaction (both effects are expected to be important in the case of a manifold of low lying excited states) we decided to investigate the ^{3}E state, assumed as ground state, in agreement with the Coppens suggestion [18]. Two electron configurations for the iron center assumed in a d^6 valence state are compatible with an ^{3}E state. In the first (^{3}EA) the iron ion should have an electron occupancy of type $(d_{x^2-y^2})^2(d_{z^2})^1(d_{xz}, d_{yz})^3$, but of type $(d_{z^2})^2(d_{x^2-y^2})^1(d_{xz}, d_{yz})^3$ in the second state (^{3}EB). Calculations carried out on the ^{3}EB state have shown that the corresponding ΔE_Q cannot be positive, in contrast with the experimental evidence which gave $\Delta E_Q = 2.62$ mm/s [5h] or 2.615 mm/s as obtained at liquid nitrogen temperature using a sample of ^{57}CoPc as γ emitter (present work). On the contrary, our theoretical results concerning the quadrupole splitting (2.89 mm/s) confirmed that ^{3}EA should be the ground state. The EFG gradient computed for this state is characterized by a principal z axis coincident with the C_4 symmetry axis. It is worth noting that when the wavefunction is allowed to assume a symmetry lower than that of the nuclear frame (C_{2v}) which corresponds to a ^{3}B$_1$ state, the computed E_Q value decreases to 2.46 mm/s. Both our theoretical values can be considered acceptable when compared with the experimental data, showing, moreover, that the E_Q quantity is in some cases extremely sensitive to small distortions of the molecular geometry or intrinsic symmetry of the wavefunction. On the basis of the analysis of the electron densities in terms of multipoles, Coppens and Li [18] proposed for the ^{3}EA state the following values for the 'experimental' d orbital occupancies: 0.88, 1.65, 0.75 and 2.13 electron for d_{z^2}, $d_{x^2-y^2}$, d_{xy} and (d_{xz}, d_{yz}) orbitals, respectively. From Table VI, it can be derived that our computed values are 1.15, 1.99, 0.93 and 2.18, respectively. The comparison is fairly good

TABLE VII. Electronic Charge Distribution and Mössbauer Parameters for the FePc(py) Complex[a]

Atom	Electronic configuration	Net charge
Fe^b	s(0.236) p(0.470) d(6.140) 1.233 1.979 0.805 1.061 1.062	1.155
N_a	s(1.288) p(3.835)	−0.122
N_b	s(1.406) p(3.523)	0.070
N(py)	s(1.351) p(3.671)	−0.021
$\Delta E_Q = 2.17$ mm s^{-1} $\eta = 0.0039$		

[a] The data reported refer to the electronic state $^5A_1$ computed for a Fe–N(py) distance equal to 2.33 Å (see text). [b] The 3d orbital populations of the Fe atom are reported in second entry in the order d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz} and d_{yz}.

especially if one considers the relative orbital occupation, that is the ratio between the individual orbital population and the total number of d electrons.

FePc(py)

The Mössbauer spectrum of this complex has been recorded as discussed in Section 2. Due to obvious experimental difficulties which inhibit the possibility of obtaining EPR spectra or magnetic measurements, no experimental indications are available for the spin multiplicity of the ground state. Several calculations have been carried out on $S = 0$, $S = 1$ and $S = 2$ spin states of C_2 symmetry and assuming Fe–N(py) distances ranging from 2.32 to 2.57 Å (Table VII). All the low spin ($S = 0$ or $S = 1$) states were found to be characterized by ΔE_Q values far from the observed one (2.22 m/s), while ΔE_Q values in the range 2.17–2.35 mm/s have been computed for the quintuplet state, for small and large Fe–N(py) distances, respectively. This seems to suggest that the ground state of FePc(py) may be $^5A_1$. However, it must be pointed out that our proposal concerning the ground state is based only on the agreement we obtained from the ΔE_Q quantity. We do not believe that our present theoretical method is accurate enough to give a direct, energy based, assignment of the ground state, since, as is well known, the state energy ordering (or splitting) of low and high spin states primarily depends on the exchange energy terms which are only partially and approximately accounted for by an INDO type scheme.

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