$(dtp)_3]$ becomes pale brown with pyridine” (dpt = $(C_2H_5O)_2PS_2^-$), although no further details were given, and very recently de Vries, *et al.*,[16] have reported that $[Fe(Et_2dtc)_2Cl]$ ($Et_2dtc = (C_2H_5)_2NCS_2^-$) in frozen pyridine solution at 78°K shows two sets of peaks: one set at $\delta = 0.70$ mm/sec, $\Delta = 0.71$ mm/sec [certainly due to the iron(III) complex], and the second set at $\delta = 1.41$ mm/sec, $\Delta = 3.71$ mm/sec. It is most likely that in both of these cases bis(pyridine)iron(II) complexes have formed.

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Registry No. Pyridine, 110-86-1; $[Fe(Me(xn))_3]$, 24555-78-0; $[Fe(Et(xn))_3]$, 19543-92-1; $[Fe(Ph_2dtp)_3]$, 37733-75-8; $[Fe(c\text{-}Hx_2dtp)_3]$, 51329-38-5; $[Fe(Me(xn))_2(py)_2]$, 51329-39-6; $[Fe(Et(xn))_2(py)_2]$, 51364-34-2; $[Fe(Ph_2dtp)_2(py)_2]$, 51381-67-0; $[Fe(c\text{-}Hx_2dtp)_2(py)_2]$, 51329-40-9.

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Contribution from the Department of Chemistry,
Drexel University, Philadelphia, Pennsylvania 19104

Mossbauer Study of the Intermolecular Interactions in the α and β Polymorphs of Iron and Cobalt Phthalocyanines

T. S. SRIVASTAVA, J. L. PRZYBYLINSKI, and AMAR NATH*

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In the β polymorphs of phthalocyanines, the nitrogen atoms of the neighboring molecules are situated axially above and below the central metal atom at about 3.38 Å. In the α form, the nitrogens of the nearest molecules are not in axial positions. The observed differences in the Mossbauer parameters of the two crystal polymorphs permit us an insight into the nature of the interaction between the central metal atom and the axially situated nitrogens of the neighboring molecules. Both the chemical shifts and quadrupole splittings of the β polymorphs are larger than the ones observed for the α form. The larger chemical shift for the β form can be understood if we consider the delocalization of the π electrons of the aromatic rings of the neighboring molecules, through the axially situated nitrogens, onto the $3d_{xz,yz}$ orbitals of the central iron atom. The larger quadrupole splitting of the β form can be interpreted by assuming that the two axial nitrogens are not situated exactly on the octahedral positions. The slightly asymmetrical disposition of the nitrogens can result in the splitting of the $3d_{xy,yz}$ orbitals, which in turn would lead to a nonzero value of the asymmetry parameter, η.

Introduction

Phthalocyanines exist in several polymorphic forms of which α and β polymorphs are fairly well characterized.[1-8] The β form is the most stable form. The different polymorphs of phthalocyanines are identified by their characteristic infrared spectra. They have also been characterized by their X-ray powder diffraction and by high-resolution electron diffraction.[6-11]

The crystal structure of the β polymorph was extensively studied by Robertson[12-14] and more recently by Ercolani[6] and Brown.[15] Detailed X-ray analysis of the α form is not available, because it has not been possible to grow sufficiently large single crystals of this polymorph.

From the differences in lattice constants and electron microscopy observation,[10] it has been inferred by several workers[7,16] that the difference in the α and β polymorph lies essentially in the orientation of the molecules with respect to the crystallographic axes, whereas the perpendicular distance between the planes of the molecules remains, to a first approximation, the same, *viz.*, 3.38 Å (Figure 1). In a metal phthalocyanine molecule, the metal atom is at the center of a square of ligating nitrogens at approximately 1.83 Å. In the β polymorph, there are in addition nitrogen atoms of the neighboring molecules present in the octahedral positions, *i.e.*, above and below the central metal atom, at 3.38 Å (Figures 1 and 2). In the α form, the nitrogens from the nearest molecules are not in axial positions and therefore do not form the nitrogen octahedron about the central metal atom.

Heilmeier and Harrison[17] invoked an out-of-plane interaction of copper 3d orbitals with orbitals of axially situated nitrogens, to explain the much greater mobility of charge carriers in β-CuPc crystals as compared to $\beta\text{-}H_2Pc$. They suggested that a π electron, delocalized from the nitrogen of the neighboring molecules, spends part of its time on the copper atom and that the copper atom acts as a bridge to the transfer of π electrons between nitrogens above and

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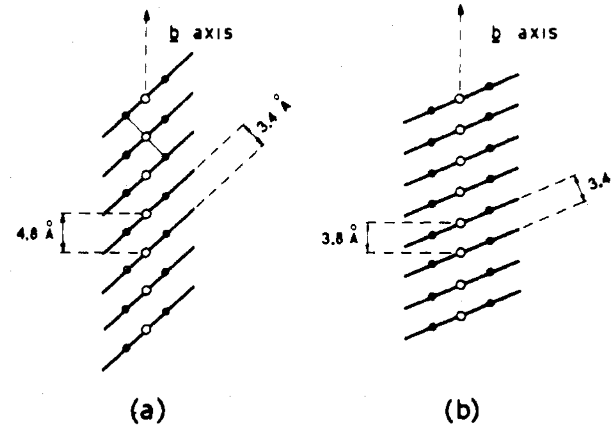

Figure 1. Schematical representation of the arrangement of the molecules in the *β* (a) and *α* (b) polymorphs of the metal phthalocyanines (reproduced from reference 7).

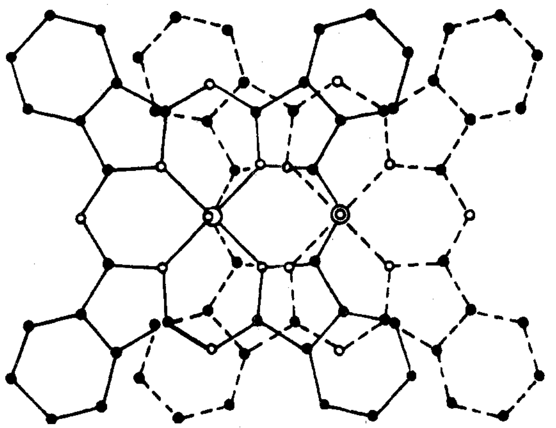

Figure 2. Normal projection of two parallel molecules, ● carbon atoms, ∘ nitrogen atoms, ○ central metal atom. Solid lines outline the upper molecules and the dotted lines the underlying molecule. (reproduced from reference 18).

below the copper atom. An analysis of the esr data of *β*-CuPc in terms of molecular orbitals also suggests a strong out-of-plane *π* interaction.[18] A comparative esr study of *α*- and *β*-CoPc revealed that the *β* polymorph exhibits a lower value for $g_{\parallel}$, a faster spin-lattice relaxation, and a higher value for the magnetic moment.[19] These observations suggest a greater orbital contribution due to interaction of cobalt atom with the axial nitrogens.

We felt that Mossbauer studies would give an insight into the nature of the interaction between the central metal atom and the axially situated nitrogens of the neighboring molecules.

Experimental Section

Synthesis of *α*-^{57}CoPc. A method reported earlier[14] using phthalic anhydride and urea for synthesis of CuPc was adapted for the synthesis of *α*-^{57}CoPc. A few drops of 0.1 *M* HCl solution of carrier-free ^{57}CoCl$_2$ containing 2 mCi of activity were added to a mass of 3.1 mg of $CoCl_2 \cdot 6H_2O$ in a 15-ml centrifuge tube. The substance was heated at ~125° for 30 min and cooled to room temperature. To the active $CoCl_2$ were added 7.5 mg of phthalic anhydride, 12.2 mg of urea, a speck of ammonium molybdate, and three drops of chloronaphthalene. After mixing and heating at 180° for 1 hr, the mixture was washed several times with petroleum ether at room temperature. The solid was dried in an oven at 125° for 15 min, ground in a mortar, and washed with water. Then it was stirred with 6 *M* NaOH solution, centrifuged, decanted, washed with water, washed with 6 *M* HCl, and finally washed repeatedly with water. The solid was dissolved in a minimum quantity of concentrated H_2SO_4, and the solution was added to crushed ice. The precipitate was filtered and washed several times with water and dried in air (I).

A sample of I was sublimed under vacuum at about 500°. The sublimate was deposited on a "finger" which was cooled with circulating water (II).

Preparation of *β*-^{57}CoPc. Two different methods were employed to prepare the *β* form: (a) a sample of I was heated in a thoroughly evacuated and sealed tube at about 325° for 16 hr (III); (b) the *β* polymorph was also obtained by sublimation, the sublimate being collected on a "finger" which was maintained above 250° (IV).

α and *β* polymorphs of FePc were obtained from the commerically available phthalocyanine by sublimation being carried out as in the cases of II and IV, respectively.

The polymorphs were characterized by their ir spectra.

Mossbauer measurements were carried out on Elscint AME-30 in a constant-acceleration mode. A potassium ferrocyanide (0.25 mg of ^{57}Fe/cm^2) obsorber was used. The velocity scale was calibrated with the help of the NBS standard iron foil. The data were computer fitted with two lorentzian lines of equal width.

Results and Discussion

The emission and absorption Mossbauer parameters of *α*- and *β*-phthalocyanines are given in Tables I and II. The emission line widths are about 30% wider than the absorption line widths. A fraction of this broadening can be attributed to the less favorable geometry used in the emission spectroscopy. The source was mounted closer to the detector because of the fact that the labeled emission sources used are much weaker than the standard ^{57}Co (in copper) source used for absorption spectroscopy.

It is apparent from the data that the isomer shift (δ) and quadrupole splitting (Δ) observed for *β*-FePc are greater than that of the *α* form by about 0.02 and 0.19 mm/sec, respectively. Similar differences are observed for the *α* and *β* polymorphs of CoPc as probed by ^{57}FePc, *viz.*, 0.02 and 0.17 mm/sec, respectively. The cobalt and iron forms are polymorphic.[6,11] Since these molecules are coplanar, the differences in parameters for *α* and *β* polymorphs can be attributed to intermolecular interactions.

It may be mentioned that differences in δ and Δ have also been reported[20] for the two different forms of cesium hexachloroferrate(III), Cs_3FeCl_6. Since a detailed X-ray diffraction study of the two forms has not been made, it is not possible to understand the nature of these differences.

The electronic configuration of FePc as given by the MO calculations of Zerner, *et al.*,[21] can be approximated by $(d_{xy})^2(d_{xz,yz})^3(d_{z^2})^1(d_{x^2-y^2})^1$. This electronic configuration would result in a positive V_{zz}, the principal component of the gradient at the iron nucleus, which has been verified experimentally.[22] Dezsi, *et al.*,[23] calculated Δ for FePc using the above electronic configuration and the expression

$$\Delta = {}^1/_2(e^2Q)(1 - R)\langle r^{-3}\rangle[(\Sigma\alpha f)^2 + {}^1/_3(\Sigma\beta f)^2]^{1/2}$$

where $\alpha = -\langle 3\cos^2\theta - 1\rangle$, $\beta = -\langle 3\cos^2\theta\cos 2\phi\rangle$, and f is the orbital occupation number. The asymmetry parameter η is given by $\Sigma\beta f$. The values of α for the hydrogenic d orbitals $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{yz}$, $3d_{xz}$, and $3d_{z^2}$ are $^4/_7$, $^4/_7$, $-^2/_7$, $-^2/_7$, and $-^4/_7$, respectively. Similarly, the values for β are 0, 0, $^6/_7$, $-^6/_7$, and 0, respectively.

The larger chemical shifts of the *β* polymorphs can be

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Table I.[a] Emission Mossbauer Parameters of α- and β-$^{57}Co^{II}Pc$ at 80°K

Polymorph and its source	δ,[b] mm/sec	Δ, mm/sec
(I) α-^{57}CoPc (sulfuric acid precipitation	0.45 ± 0.01	2.50 ± 0.01
(II) α-^{57}CoPc (sublimation)	0.45 ± 0.01	2.54 ± 0.01
(III) β-^{57}CoPc (heating of I)	0.47 ± 0.01	2.70 ± 0.01
(IV) β-^{57}CoPc (sublimation)	0.47 ± 0.01	2.67 ± 0.01

[a] The observed emission line widths are about 0.43 mm/sec as compared to absorber line widths of 0.33 mm/sec. The average values of δ and Δ resulting from several independent experiments are reported here. [b] Isomer shifts are reported with respect to iron.

Table II. Absorption Mossbauer Parameters of α- and β-$Fe^{II}Pc$ at 80°K and Parameters Reported in the Literature without Characterizing the Form

	δ,[a] mm/sec	Δ, mm/sec
α form	0.46 ± 0.01	2.49 ± 0.01
β form	0.48 ± 0.01	2.68 ± 0.01
Hudson and Whitfield[b]	0.51 ± 0.02	2.62 ± 0.02
Taube, *et al.*[c]	0.48 ± 0.01	2.60 ± 0.01
Moss and Robinson[d]	0.53 ± 0.02	2.62 ± 0.02
Dezsi, *et al.*[e]	0.64	2.64
Thompson, *et al.*[f]	0.48	2.63

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understood if we visualize the π electrons of the aromatic rings of the neighboring molecules as being delocalized through the two axially situated nitrogens onto the $3d_{xz}$ and $3d_{yz}$ orbitals of the central iron atom as originally suggested by Heilmeier and Harrison.[17] This would enhance the shielding of the s electrons by the d electrons and thereby decrease the s-electron density on the iron nucleus. Therefore, this can account for the larger chemical shifts observed. The degree of delocalization of electrons in d orbitals required to produce the observed increase can be roughly estimated as 0.02 electron. This estimate is based on the observation that a complete removal of a d electron, as in going from Fe^{2+} to Fe^{3+}, results in a change of about 1 mm/sec in the isomer shift.

Regarding the differences in Δ, the contributions of $3d_{xz,yz}$ orbitals toward the V_{zz} are negative and therefore a slight increase in the electronic density in these orbitals could only lead to a small diminution in the quadrupole splittings of the β forms. However, we observe an enhancement of Δ. It seems that the two axial nitrogens are not situated exactly on the octahedral positions but form a very slightly distorted octahedron. The slightly asymmetrical situation of the nitrogens presumably results in a stronger interaction with one of the $3d_{xy,yz}$ orbitals and thereby lifts the degeneracy of the orbitals. This would lead to a nonzero value for the asymmetry parameter of the field gradient, η. The decrease in quadrupole splitting due to flow of about 0.02 electron in the $3d_{xz,yz}$ can be more than compensated by the increase in Δ arising from the asymmetry parameter η, *i.e.*, $^1/_3(\Sigma\beta f)^2$ in the expression. An orbital occupation of approximately $(3d_{xz})^{1.6}(3d_{yz})^{1.4}$ or *vice versa* for the β forms can account for the experimentally observed increase in quadrupole splitting.

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Registry No. $^{57}Co^{II}Pc$, 51271-00-2; $Fe^{II}Pc$, 132-16-1; $^{57}CoCl_2$, 16413-89-1; phthalic anhydride, 85-44-9; urea, 57-13-6.

Contribution from the Department of Chemistry,
The Johns Hopkins University, Baltimore, Maryland 21218

Cis and Trans Effects on the Proton Magnetic Resonance Spectra of Cobaloximes

WILLIAM C. TROGLER, ROBERT CHARLES STEWART, LEON A. EPPS, and LUIGI G. MARZILLI*

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The pmr spectra of cobaloximes $LCo(DH)_2X$, with X = NO_3, SeCN, Cl, Br, NCS, N_3, SCN, *i*-PrXan, CN, NO_2, and CH_3, L = 4-*tert*-butylpyridine (*t*-Bu(py)) and tri-*n*-butylphosphine (Bu_3P), and DH = monoanion of dimethylglyoxime, are reported. Except for the linear triatomics, which form a bent bond to cobalt (N_3, SCN, SeCN), the chemical shifts of the cis dioxime methyl resonance and the trans α H resonance of $(t\text{-Bu(py)})Co(DH)_2X$ are linearly related. The slope of the line is approximately in agreement with the screening formula of an axially anisotropic group with the cobalt at the center. Analysis of the dependence of the chemical shifts on X in $(t\text{-Bu(py)})Co(DH)_2X$ and of the variation of coupling constants in $Bu_3PCo(DH)_2X$ is consistent with rehybridization of the Co–X bond. Specifically, it is suggested that the degree of 4s character in the Co–X bond increases along the series. According to Ramsey's equation, the paramagnetic contribution perpendicular to the axial direction should decrease. This interpretation differs from a previous study of cobaloximes.[1] It is shown that previous work utilized incorrectly formulated compounds. More specific synthetic procedures are reported, as is the fractional separation of the N- and S-bonded thiocyanate complexes when L = *t*-Bu(py). Evidence is presented for the formation of the transient species $(1\text{-MeImd})Co(DH)_2(ONO)$, during the ligand-exchange reaction of $(Ph_3P)Co(DH)_2NO_2$ with 1-MeImd (1-methylimidazole).

Introduction

A detailed study of the effect of the variation of one ligand on the pmr spectra of other ligands in cobaloxime complexes has been reported.[1] Cobaloximes[2] are complexes containing the moiety $Co(DH)_2$, where DH = monoanion of dimethylglyoxime. The specific cobaloximes studied were reported as being the neutral species $LCo(DH)_2X$, where L = triphenylphosphine (Ph_3P) and pyridine (py) and X = NO_2, CN, Cl, Br, I, ONO, and alkyls.[1] We felt that this series was worthy of extension and reinvestigation for several reasons, which are outlined below.

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