

Furthermore, (II-6) plus (II-10) gives the total rate by k_1 or

$$d[\text{total Fe(phen)}_2(\text{CN})_2]/dt = k_1[\Lambda\text{-Fe(phen)}_3^{2+}][\text{CN}^-] \quad (\text{II-11})$$

The product distribution will be in proportion to the rates of the species. That is, the total by k_1 will be (II-11) divided by the sum of the k_0 and k_1 rates. The observable per cent inverted will be the difference in the Δ and Λ isomer production through the k_1 path [(II-6)-(II-10)] divided by the sum of the k_0 and k_1 rates. Therefore, the (% by k_1)/(% inverted) ratio eliminates the rate sums (through cancelation) and is equal to

$$\frac{d[\text{total Fe(phen)}_2(\text{CN})_2]/dt}{k_1[\Lambda\text{-Fe(phen)}_3^{2+}][\text{CN}^-]} = \frac{\left(\frac{d[\Delta\text{-Fe(phen)}_2(\text{CN})_2]}{dt} - \frac{d[\Lambda\text{-Fe(phen)}_2(\text{CN})_2]}{dt} \right)}{k_1[\Lambda\text{-Fe(phen)}_3^{2+}][\text{CN}^-]} = \frac{\left(\frac{k_{\text{di}}k_{1r}[\Lambda\text{-Fe(phen)}_3^{2+}][\text{CN}^-]^2}{k_{\text{ar}} + k_{\text{di}}[\text{CN}^-]} \right)}{k_1[\Lambda\text{-Fe(phen)}_3^{2+}][\text{CN}^-]} \quad (\text{II-12})$$

Canceling and rearranging give

$$\frac{\% \text{ by } k_1}{\% \text{ inverted}} = \frac{k_1(k_{\text{ar}} + k_{\text{di}}[\text{CN}^-])}{k_{\text{di}}k_{1r}[\text{CN}^-]} \quad (\text{II-13})$$

which is equivalent to eq 18 of ref 2, keeping in mind that $k_1 = k_{1i} + k_{1r}$. Further rearrangement gives

$$\frac{\% \text{ by } k_1}{\% \text{ inverted}} = \frac{k_1}{k_{1i}} + \frac{k_1 k_{\text{ar}}}{k_{1i} k_{\text{di}} [\text{CN}^-]} \quad (\text{II-14})$$

so that a plot of (% by k_1)/(% inverted) vs. $1/[\text{CN}^-]$ has an intercept of k_1/k_{1i} (or as given in ref 2: $1 + k_{1r}/k_{1i}$) and a slope of $k_1 k_{\text{ar}}/k_{1i} k_{\text{di}}$.

Registry No. $\Lambda\text{-[Fe(phen)}_3](\text{ClO}_4)_2$, 51174-98-2; CN^- , 57-12-5.

Supplementary Material Available. Appendix III, showing the data used for determining specific rate constants for the reaction of aqueous Fe(o-phen)_3^{2+} with cyanide, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1551.

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Reaction of Iron(III) Tris(xanthates) and Tris(dithiophosphinates) with Pyridine

RAMZI Y. SALEH and DAREL K. STRAUB*

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The reaction of pyridine with tris(*O*-methyl xanthato)iron(III), tris(*O*-ethyl xanthato)iron(III), tris(diphenyl dithiophosphinato)iron(III), and tris(dicyclohexyl dithiophosphinato)iron(III) leads to bright yellow complexes which have magnetic moments of 4.9–5.0 BM, isomer shifts of 1.2 mm/sec, and large quadrupole splittings of ~3 mm/sec at room temperature. Such values are strongly indicative of iron(II) complexes. From conductivity and infrared data, these adducts are most likely dipyridinobis(xanthato or dithiophosphinato)iron(II) complexes.

Introduction

Almost 60 years ago, Dubsy, *et al.*, reported that tris(*O*-ethyl xanthato)iron(III)¹ and tris(*O*-methyl xanthato)iron(III)² form golden yellow, crystalline 1:3 adducts, of limited stability, with pyridine. Various structures have been proposed for these adducts, including those with pyridine coordinated to the iron(III)³ and monodentate xanthate and with pyridine forming a kind of semipolar bond with the carbon atom in bidentate xanthate.³ None of the proposed structures is really satisfactory. Because of our interest in iron complexes with bidentate sulfur ligands⁴⁻⁶ we have investigated these adducts and similar ones of iron(III) tris(dithiophosphinates), using Mossbauer spectroscopy, magnetic sus-

ceptibility measurements, conductivity measurements, and infrared spectroscopy, and have found that they are most likely complexes of iron(II).

Experimental Section⁷

Unless otherwise indicated all starting materials and solvents were reagent grade. Ferric methyl and ethyl xanthates, $[\text{Fe}(\text{Me}(\text{xn}))_3]$ and $[\text{Fe}(\text{Et}(\text{xn}))_3]$, were prepared from aqueous solutions of ferric nitrate and the potassium xanthate and were recrystallized several times from benzene-cyclohexane mixtures. These complexes were used within 3 days after preparation. Ferric tris(dithiophosphinates), $[\text{Fe}(\text{R}_2\text{PS}_2)_3]$, $\text{R} = \text{C}_6\text{H}_5$ and C_6H_{11} , were prepared by mixing solutions of anhydrous ferric chloride and diphenyldithiophosphinic acid (Practical grade, Aldrich Chemical Co. and K and K Chemical Co.) or ammonium dicyclohexyl dithiophosphinate (Aldrich Chemical Co.) and recrystallizing the precipitates from methylene chloride-ethanol mixtures.

Anal. Calcd for $[\text{Fe}(\text{Ph}_2\text{dtp})_3]$: C, 53.79; H, 3.76; S, 23.93. Found: C, 54.02; H, 3.77; S, 23.74 (Galbraith Laboratories, Knoxville, Tenn.). Calcd for $[\text{Fe}(\text{c-Hx}_2\text{dtp})_3]$: C, 51.47; H, 7.92; P, 10.95. Found: C, 51.82; H, 8.02; P, 9.33 (Chemalytics Inc., Tempe, Ariz.).

(7) Abbreviations used: Me, CH_3 ; Et, C_2H_5 ; Ph, C_6H_5 ; c-Hx, C_6H_{11} ; R_{xn}, ROCS_2^- ; R₂dtp, R_2PS_2^- .

(1) J. V. Dubsy and A. Vretos, *J. Prakt Chem.*, [2] 90, 116 (1914).

(2) J. V. Dubsy, Th. Beer, and H. Frank, *J. Prakt Chem.*, [2] 93, 151 (1916).

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(6) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, 11, 259 (1972).

The disulfides $(ROCS_2)_2$, where $R = CH_3, C_2H_5,$ and $(R_2PS_2)_2$, where $R = C_6H_5, C_6H_{11}$, were prepared from potassium xanthate, diphenyldithiophosphinic acid, and ammonium dicyclohexyl dithiophosphinate by oxidation in aqueous solution with triiodide ion or with iodine in acetone solution. The dixanthogens were obtained as oils⁸ and were not further purified. The phosphine disulfides were recrystallized from methylene chloride-ethanol; mp 145–146° for $(Ph_2PS_2)_2$ (lit.⁹ mp 146–147°) and 166–167° for $(c-Hx_2PS_2)_2$.

Reaction of Pyridine with $[Fe(Me(xn))_3]$ and $[Fe(Et(xn))_3]$.

Two grams of the xanthate was dissolved in 20 ml of pyridine at room temperature. Cyclohexane was then slowly added with stirring to the pyridine solutions, causing bright yellow crystals to form. These were collected, washed with a cyclohexane-pyridine mixture, and sealed, while still moist with pyridine, in a plastic container for the Mossbauer experiments. The crystals are sensitive to air oxidation, especially when dry.

Reaction of Pyridine with $[Fe(Ph_2 dtp)_3]$. Pyridine was added dropwise with continuous stirring to a filtered solution of 1 g of the diphenyl dithiophosphinate in 25 ml of methylene chloride until the initial greenish black color had changed completely to yellow. Addition of cyclohexane caused the precipitation of yellow crystals. These were collected, dissolved in methylene chloride containing a few drops of pyridine, and reprecipitated by the addition of cyclohexane or absolute ethanol. The product was finally washed with cyclohexane-pyridine, dried a short while in air, and then sealed in a plastic Mossbauer sample holder.

Reaction of Pyridine with $[Fe(c-Hx_2 dtp)_3]$. Because of the slight solubility of this dicyclohexyl dithiophosphinate complex in methylene chloride, it was dissolved directly in pure pyridine at 90°. About 0.06 g of complex was used per ml of pyridine. Yellow crystals precipitated from solution upon addition of cyclohexane or absolute ethanol. These were treated in the same way as the diphenyl dithiophosphinate adduct.

An Industrial Instruments Model RC 16B2 conductivity bridge was used for the conductivity measurements. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer and visible and ultraviolet spectra on a Cary 14 spectrophotometer. Magnetic moments in pyridine solutions were measured by the Evans nuclear magnetic resonance method¹⁰ using a Varian A-60 spectrometer. Mossbauer spectra were obtained with a scanned velocity spectrometer operating in the time mode. Calibration with sodium nitroprusside (quadrupole splitting 1.712 mm/sec) was carried out before and after spectra were measured. Frequent checks with ⁵⁷Fe foil were also made. Spectra were fitted with a least-squares approximation assuming two Lorentzian line shapes of equal width. Estimated error limits on the isomer shift, δ , and the quadrupole splitting, Δ , are ± 0.03 mm/sec. A Calcomp plotter was used to plot data.

Results

Equivalent Conductance. The conductivities at 25° of $\sim 10^{-3}$ M solutions of $[Fe(Me(xn))_3]$, $[Fe(Et(xn))_3]$, $[Fe(Ph_2 dtp)_3]$, and $[Fe(c-Hx_2 dtp)_3]$ in pyridine were measured. All were essentially nonelectrolytes, the equivalent conductivity ranging from about 2 to 8 mhos $cm^2/equiv$.

Visible Spectra. Spectra were measured over a 650–300-nm range on solutions of $[Fe(Me(xn))_3]$, $[Fe(Et_2 dtp)_2]$, $[Fe(Ph_2 dtp)_3]$, and $[Fe(c-Hx_2 dtp)_3]$ in methylene chloride and pyridine solutions and in methylene chloride-pyridine mixtures. The two xanthate complexes showed very similar spectra, as did the two dithiophosphinate complexes. Addition of 2 vol % of pyridine to methylene chloride solutions of the xanthate complexes significantly reduced the intensities but did not appreciably change the positions of the three visible peaks. For $[Fe(Me(xn))_3]$ these occurred at 556 ($\epsilon \sim 660$), 456 ($\epsilon \sim 130$), and 363 nm ($\epsilon \sim 6300 M^{-1} cm^{-1}$). Two peaks were found for $[Fe(Me(xn))_3]$ in pure pyridine solution at 453 ($\epsilon \sim 540$) and 407 nm ($\epsilon \sim 810 M^{-1} cm^{-1}$). Figure 1 shows the changes in the visible spectrum of $[Fe(Me(xn))_3]$ upon reaction with pyridine.

The dithiophosphinate complexes in methylene chloride had four peaks in the visible region, e.g., $[Fe(Ph_2 dtp)_3]$ at

(8) S. R. Rao, "Xanthates and Related Compounds," Marcel Dekker, New York, N. Y., 1971, Chapter 5, p 133.

(9) G. Peters, *J. Org. Chem.*, **27**, 2198 (1962).

(10) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

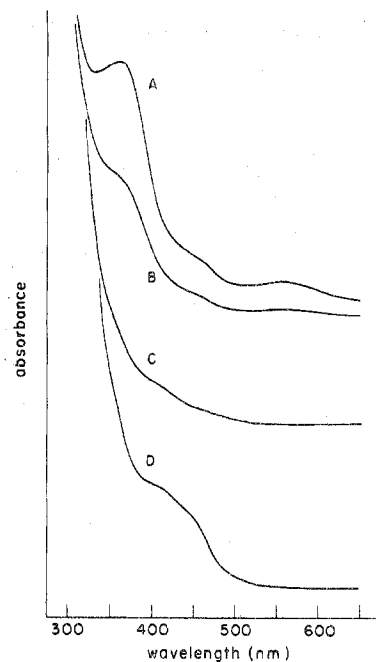


Figure 1. Visible spectra of (A) 1.27×10^{-4} M $[Fe(Me(xn))_3]$ in CH_2Cl_2 , (B) 1.17×10^{-4} M $[Fe(Me(xn))_3]$ in 2 vol % py- CH_2Cl_2 , (C) 1.70×10^{-4} M $[Fe(Me(xn))_3]$ in 10 vol % py- CH_2Cl_2 , and (D) 4.21×10^{-4} M $[Fe(Me(xn))_3]$ in py.

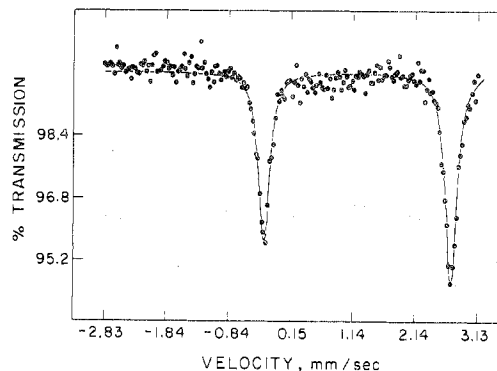


Figure 2. Mossbauer spectrum at 298° K of a pyridine paste of tris-(O-methyl xanthato)iron(III).

Table I. Mossbauer Data at 298° K^c

| Complex in pyridine | δ , ^a mm/sec | Δ , ^b mm/sec |
|----------------------|--------------------------------|--------------------------------|
| $[Fe(Me(xn))_3]$ | +1.20 | 2.98 |
| $[Fe(Et(xn))_3]$ | +1.19 | 2.97 |
| $[Fe(Ph_2 dtp)_3]$ | +1.20 | 2.89 |
| $[Fe(c-Hx_2 dtp)_3]$ | +1.20 | 3.14 |

^a Isomer shift relative to sodium nitroprusside. ^b Quadrupole splitting; sign not determined. ^c Error limits; ± 0.03 mm/sec on both δ and Δ .

Table II. Magnetic Moments at 36°

| Complex | $10^6 \chi_D$, ^a cgsu | $10^6 \chi_M$, ^b cgsu | μ_{eff} , ^c BM |
|----------------------------|-----------------------------------|-----------------------------------|-------------------------------|
| $[Fe(Me(xn))_2(py)_2]$ | -211 | 9,740 | 4.92 |
| $[Fe(Et(xn))_2(py)_2]$ | -223 | 9,650 | 4.90 |
| $[Fe(Ph_2 dtp)_2(py)_2]$ | -413 | 10,230 | 5.05 |
| $[Fe(c-Hx_2 dtp)_2(py)_2]$ | -483 | 10,130 | 5.05 |

^a Diamagnetic correction from Pascal's constants. ^b Corrected value. ^c Estimated error limits: ± 0.10 BM.

613 ($\epsilon \sim 4400$), 525 ($\epsilon \sim 4000$), 419 ($\epsilon \sim 7300$), and 355 nm ($\epsilon \sim 9100 M^{-1} cm^{-1}$) and only two in pyridine solution, e.g., $[Fe(Ph_2 dtp)_3]$ at 431 ($\epsilon \sim 500$) and 375 nm ($\epsilon \sim 1500 M^{-1} cm^{-1}$).

Infrared Spectra. Infrared spectra were measured from

Table III. Room-Temperature Mossbauer and Magnetic Data on High-Spin Iron(II) Complexes^a

| Complex | $\delta,^b$ mm/sec | $\Delta,^c$ mm/sec | $\mu_{\text{eff}},^d$ BM | Comments |
|--|--------------------|--------------------|--------------------------|---|
| [Fe(<i>i</i> -C ₃ H ₇ O) ₂ PS ₂] ₃ ^e | 1.23 | 3.11 | | |
| [Fe(opda) ₂ Cl ₂] | 1.02 | 2.89 | | Likely trans; opda = <i>o</i> -phenylenediamine |
| [Fe(bipy) ₂ (NCS) ₂] | 1.32 | 2.13-2.31 | | bipy = 2,2'-bipyridine |
| [Fe(phen) ₂ Br ₂] | 1.33 | 3.26 | 5.15 | phen = 1,10-phenanthroline |
| [Fe(phen) ₂ (NCS) ₂] | 1.30 | 3.09 | 5.22 | |
| [Fe(py) ₄ (NCO) ₂] | 1.39 | 2.52 | 5.13 | Likely trans |
| [Fe(py) ₄ (NCS) ₂] | 1.34 | 1.56 | | Trans |

^a Values taken from ref 12, pp 142-144, except for the first complex listed. ^b Isomer shift relative to sodium nitroprusside; all values are positive. ^c Quadrupole splitting; sign undetermined. ^d Magnetic moment at room temperature. ^e L. Korecz, K. Burger, and C. K. Jorgensen, *Helv. Chim. Acta*, 51, 211 (1968).

4000 to 625 cm⁻¹ on both Nujol mulls and pyridine pastes of K(Me(xn)), K(Et(xn)), [Fe(Me(xn))₃], [Fe(Et(xn))₃], dimethyl and diethyl dixanthogens, NH₄(*c*-Hx₂dtf), H(Ph₂-dtf), and bis(diphenyl and dicyclohexylthiophosphinyl) disulfides.

A characteristic peak (S-S stretch?) occurred at 840-845 cm⁻¹ (medium intensity) in diethyl dixanthogen and at ~837 cm⁻¹ (rather broad) in the [Fe(Et(xn))₃]-py paste. This peak did not occur in pure [Fe(Et(xn))₃] nor in K(Et(xn)). These same observations were made for the methyl xanthates where the unique disulfide peak occurred at 875-890 cm⁻¹.

Similarly, a characteristic peak occurred at 750 ± 2 cm⁻¹ in (Ph₂PS₂)₂ and (*c*-Hx₂PS₂)₂ and at ~748 cm⁻¹ (rather broad, overlapped somewhat with the pyridine peak at 745 cm⁻¹), and 754 cm⁻¹ for pyridine pastes of [Fe(Ph₂dtf)₃] and [Fe(*c*-Hx₂dtf)₃], respectively. These peaks did not occur in the free ligands nor in Nujol mulls of the pure iron(III) complexes.

Mossbauer Spectra. Mossbauer spectra obtained on pyridine pastes of the xanthate and dithiophosphinate complexes consisted of highly split doublets with narrow peaks of equal intensity and width. A representative spectrum is shown in Figure 2 and the Mossbauer data at 298°K are given in Table I. The spectra of the pyridine pastes are very different from spectra of the pure tris complexes, all of which have isomer shifts of 0.6-0.7 mm/sec (relative to nitroprusside) and quadrupole splittings of less than 0.6 mm/sec.¹¹

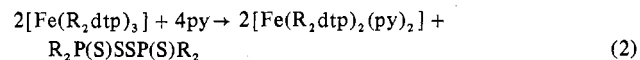
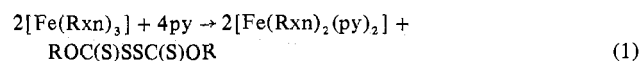
Exposure of the pyridine pastes of the xanthates to the atmosphere resulted in the formation of a brownish substance, insoluble in all common solvents, which gave a Mossbauer spectrum of a symmetrical, rather broad doublet with shift of 0.63 ± 0.02 mm/sec and splitting of 0.8-0.9 mm/sec. This material, probably some iron(III) compound, was not further investigated.

Magnetic Moments. Magnetic moments, measured at 36° in pyridine solutions of the tris complexes, are given in Table II. Each value represents the average of at least three separate determinations and is calculated on the assumption of complete reaction between the tris complex and pyridine, forming a dipyridinobis(xanthato or dithiophosphinato)iron(II) complex. Support for such a reaction is given in the Discussion.

Discussion

The Mossbauer isomer shifts of the pyridine complexes are conclusive evidence against iron(III): complexes with high-spin iron(III) have shifts of 0.6-0.8 mm/sec (relative to nitroprusside) and complexes with low-spin iron(III) have shifts of less than 0.7 mm/sec, at 298°K.¹² Values of about

1.2 mm/sec strongly support high-spin iron(II). Two xanthate or dithiophosphinate ligands must be coordinated to the iron(II) because these complexes are essentially nonelectrolytes in pyridine solution. The formation of disulfides when the tris complexes react with pyridine is shown by the presence of characteristic disulfide peaks at 840-880 cm⁻¹ [for (ROCS₂)₂] and ~750 cm⁻¹ [for (R₂PS₂)₂] in the infrared spectra of pyridine pastes of tris complexes. These observations support the reactions



Alternate formulations, such as four-coordinate species, *e.g.*, [Fe(Rxn)₂] with bidentate ligands or [Fe(Rxn)₂(py)₂] with monodentate ligands or octahedral species such as [Fe(Rxn)₂(py)₄] with monodentate ligands are untenable: it is improbable that a four-coordinate iron(II) species should be formed in the presence of a large excess of pyridine, and Fischer-Hirschfelder-Taylor models show severe steric hindrance in forming [Fe(Rxn)₂(py)₄] or [Fe(R₂dtf)₂(py)₄]. Also the elemental analyses reported by Dubsy, *et al.*, for the [Fe(Et(xn))₃]-py product (6.33% N, 29.15% S; used by Dubsy to support the formula [Fe(Et(xn))₃]-3py, with calculated values of 6.40% N, 29.27% S) are reasonably close to the calculated values of 6.13% N, 28.10% S for [Fe(Et(xn))₂(py)₂].

The measured magnetic moments are in accord with the expected moments of these pyridine complexes. Values of about 5.4 BM (at room temperature) are found for octahedral high-spin iron(II) complexes; distortion from octahedral symmetry and electron delocalization onto ligands reduce the moments.¹³ For example, Holah and Murphy¹⁴ have reported moments of 4.8 and 5.1 BM for α -[Fe(Et(xn))₂(bipy)] and [Fe(Et(xn))₂(1,10-phen)], respectively.

The properties of some high-spin iron(II) complexes are given in Table III in order to show the similarities between these complexes of established stoichiometries (and in some cases, structure) and the [Fe(Rxn)₂(py)₂] and [Fe(R₂dtf)₂(py)₂] complexes.

It is not known yet whether [Fe(Rxn)₂(py)₂] and [Fe(R₂dtf)₂] have a cis or a trans configuration. They are readily oxidized in air to insoluble brown powders.

Scattered reports on the reactions of iron(III) complexes of bidentate sulfur ligands with pyridine have appeared in the literature. Jorgensen¹⁵ has stated, "Unexpectedly, [Fe-

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(15) C. K. Jorgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, p 134

(11) P. M. Valov, S. V. Larionov, D. K. Kaplin, and Yu. E. Razmakhnin, *Sib. Chem. J.*, 3, 285 (1967).

(12) N.N. Greenwood and T. C. Gibb, "Mossbauer Spectroscopy," Chapman and Hall, London, 1971.

(dtp)₃] becomes pale brown with pyridine" (dpt = (C₂H₅O)₂-PS₂), although no further details were given, and very recently de Vries, *et al.*,¹⁶ have reported that [Fe(Et₂dte)₂Cl] (Et₂dte = (C₂H₅)₂NCS₂⁻) in frozen pyridine solution at 78°K shows two sets of peaks: one set at δ = 0.70 mm/sec, Δ = 0.71 mm/sec [certainly due to the iron(III) complex], and the second set at δ = 1.41 mm/sec, Δ = 3.71 mm/sec. It is

(16) J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, *Inorg. Chem.*, 10, 81 (1971).

most likely that in both of these cases bis(pyridine)iron(II) complexes have formed.

Acknowledgment. We wish to thank the National Science Foundation University Science Development Program, Grant No. GU-3184, for support of this research.

Registry No. Pyridine, 110-86-1; [Fe(Me(xn))₃], 24555-78-0; [Fe(Et(xn))₃], 19543-92-1; [Fe(Ph₂dtp)₃], 37733-75-8; [Fe(c-Hx₂-dtp)₃], 51329-38-5; [Fe(Me(xn))₂(py)₂], 51329-39-6; [Fe(Et(xn))₂(py)₂], 51364-34-2; [Fe(Ph₂dtp)₂(py)₂], 51381-67-0; [Fe(c-Hx₂-dtp)₂(py)₂], 51329-40-9.

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 Robertson¹²⁻¹⁴ and more recently by Ercolani⁶ 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.

Heilmeyer and Harrison¹⁷ 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 β-H₂Pc. 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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