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Bonding Character in Tetracoordinate (Phthalocyaninato)iron(II) Complexes with Electron-Releasing Substituents As Studied by Mössbauer Spectroscopy

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Mössbauer spectra of tetracoordinate (phthalocyaninato)iron(II) complexes with electron-releasing substituents were measured. Two kinds of bonding parameters, Σ and Π, that had been introduced by the authors were calculated for substituted phthalocyanines to interpret Mössbauer parameters in connection with the bonding characteristics of the macrocyclic ligands. The bonding parameters, Σ and Π, represent σ- and π-bonding properties, respectively, and are defined to be larger when more electron density is placed on the iron. Calculated orders of Σ and Π are again in good correlations with the sum of the Hammett σ constants, $\Sigma\sigma$, of the substituents: the correlations previously found for electron-withdrawing substituents are revealed to be extended to electron-releasing substituents. The correlations account with reasonable success for a set of Mössbauer data that are difficult to interpret in the usual way.
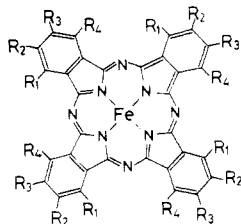
Introduction

Owing to the conjugated nature of the porphyrin ring system, electron-releasing or -withdrawing substituents on the periphery of the molecule have been shown to affect the chemical and physical properties of metalloporphyrins. In hexacoordinate (porphyrinato)- and structurally similar (phthalocyaninato)iron complexes, there is a substantial cis effect between the macrocyclic ligands and the axial ligands: the macrocyclic ligands modify their σ- and π-bonding characteristics in order to accommodate the requirements of the axial ligands[1,2] and vice versa.[3] Thus, the bonding characteristics of the macrocyclic ligands themselves are difficult to elucidate separately by studies of hexacoordinate (porphyrinato)- or (phthalocyaninato)iron complexes. Tetracoordinate planar complexes without any axial ligands are well suited for such studies.

We have reported[4] Mössbauer data for tetracoordinate (phthalocyaninato)iron(II) complexes with electron-withdrawing substituents and a new method for calculating the bonding parameters of macrocyclic ligands from the isomer shift, δ, and the quadrupole splitting, ΔE_Q. We have introduced two kinds of bonding parameters, Σ and Π, which reprsent σ- and π-bonding properties, respectively, and are defined to be larger when more electron density is placed on the iron. Calculated orders of Σ and Π have been shown to be in good correlations with the sum of the Hammett σ constants, $\Sigma\sigma$, of the substituents. We tried to include electron-releasing substituents previously,[4] but the sample preparations of (phthalocyaninato)iron(II) complexes with electron-releasing substituents were rather difficult; this fact itself might reflect the electronic nature of the substituents. Recently, several complexes with electron-releasing substituents were synthesized carefully with success by "nitrile" method.[5] In the present paper, the bonding parameters of (phthalocyaninato)iron(II) complexes with electron-releasing substituents are described, and the correlations previously found for electron-withdrawing substituents are revealed to be extended to electron-releasing substituents.

Experimental Section

A. Synthesis. Substituted (phthalocyaninato)iron(II) complex **2–8** (Table I) were prepared by the "nitrile" method.[5] Complexes **2–6** have electron-releasing substituents, and two complexes with electron-withdrawing substituents, **7** and **8**, were investigated additionally.

Table I. Substituents of (Phthalocyaninato)iron(II) Complexes

abbreviations	substituents
Fe(Pc) (1)	R_1–R_4 = H
Fe(OMePc) (2)	$R_2 = R_3 = CH_3$, $R_1 = R_4 = H$
Fe(TMDPc) (3)	$(R_2, R_3) = OCH_2O$, $R_1 = R_4 = H$
Fe(OMxP) (4)	$R_2 = R_3 = OCH_3$, $R_1 = R_4 = H$
Fe(TBuPc) (5)	$R_2 = C(CH_3)_3$, $R_1 = R_3 = R_4 = H$
Fe(TPPc) (6)	$R_2 = OCH_2C(CH_3)_3$, $R_1 = R_3 = R_4 = H$
Fe(TTPc) (7)	$R_2 = SC_6H_5$, $R_1 = R_3 = R_4 = H$
Fe(Nc) (8)	$(R_2, R_3) = C_4H_4$-fused ring, $R_1 = R_4 = H$
Fe(TDPc) (9)	$R_2 = COOC_{10}H_{21}$, $R_1 = R_3 = R_4 = H$
Fe(ODPc) (10)	$R_2 = R_3 = COOC_{10}H_{21}$, $R_1 = R_4 = H$
Fe(TIPc) (11)	$(R_2, R_3) = CON(C_{10}H_{21})CO$, $R_1 = R_4 = H$
Fe(TNPc) (12)	$R_2 = NO_2$, $R_1 = R_3 = R_4 = H$
Fe(Cl$_{16}$Pc) (13)	R_1–R_4 = Cl
Fe(OCyPc) (14)	$R_2 = R_3 = CN$, $R_1 = R_4 = H$

(2,3,9,10,16,17,23,24-Octamethylphthalocyaninato)iron(II) (2), (2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)iron(II) (4), and (2,9,16,23-Tetra-*tert*-butylphthalocyaninato)iron(II) (5) were prepared from corresponding phthalonitriles by the method of Hanack and co-workers.[5]

(2,3,9,10,16,17,23,24-Tetrakis(methylenedioxy)phthalocyaninato)-iron(II) (3). 1,2-Dibromo-4,5-(methylenedioxy)benzene. Bromine (65 g, 0.4 mol) in carbon tetrachloride (20 mL) was added dropwise to a solution of 1,2-(methylenedioxy)benzene (25 mL, 0.2 mol) in carbon tetrachloride (100 mL) at 0–5 °C in an ice-water bath. After being stirred for 2 h, the solution was washed with 10% NaOH and water. The organic layer was dried over sodium sulfate and evaporated; the oily residue was slowly solidified. Recrystallization from methanol gave colorless needles (38.4 g, yield 67%).

1,2-Dicyano-4,5-(methylenedioxy)benzene. 1,2-Dibromo-4,5-(methylenedioxy)benzene (25 g, 89 mmol) and CuCN (24 g) were suspended in DMF (350 mL) and heated under reflux for 5 h. After the mixture was cooled to room temperature, concentrated ammonium hydroxide (1 L) was added and the mixture was stirred for 12 h under an oxygen atmosphere. The precipitate was filtered out and washed with dilute ammonium hydroxide and then water. After being dried, the green residue was recrystallized from methanol to give colorless plates of the desired compound (8.2 g, yield 53%).

(2,3,9,10,16,17,23,24-Tetrakis(methylenedioxy)phthalocyaninato)-iron(II). Fe(CO)$_5$ (1.8 g, 8.8 mmol) in 1-chloronaphthalene (10 mL) was added to a solution of 1,2-dicyano-4,5-(methylenedioxy)benzene (6 g, 35 mmol) in 1-chloronaphthalene (30 mL) under reflux. The reaction mixture was stirred for 1 h at 270–280 °C under a nitrogen atmosphere and then cooled to room temperature. The black precipitate was collected by filtration, washed with chloroform, ethanol, and acetone, and dried. The residual black solid was boiled in 0.1 N HCl and then in 0.1 N

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NaOH to remove inorganic iron impurities. After being dried in vacuo, 2.96 g of the desired compound was obtained (yield 43%). Anal. Calcd for $C_{36}H_{16}N_8O_8Fe$: C, 58.09; H, 2.17; N, 15.05. Found: C, 58.05; H, 2.31; N, 14.61.

(**2,9,16,23-Tetraneopentoxyphthalocyaninato)iron(II) (6).** Nonmetalated 2,9,16,23-tetraneopentoxyphthalocyanine[6] (342 mg, 0.396 mmol) and $FeCl_2$ (340 mg, 0.268 mmol) were refluxed in DMF (20 mL) for 3 h, and the solvent was removed by using an evaporator and then by drying in vacuo at 100 °C. Silica gel chromatography of the residue with CH_2Cl_2 as eluent gave upon evaporation of the solvent 255 mg of a dark blue, shining solid in 70.2% yield. Anal. Calcd for $C_{52}H_{56}N_8O_4Fe$: C, 68.41; H, 6.18; N, 12.27. Found: C, 68.39; H, 6.58; N, 11.64.

(**2,9,16,23-Tetrakis(phenylthio)phthalocyaninato)iron(II) (7).** 4-**(Phenylthio)phthalonitrile.** In a minor modification of Snow's procedure,[7] 4-nitrophthalonitrile (6.92 g, 0.04 mol), thiophenol (4.40 g, 4.10 mL, 0.04 mol), and potassium carbonate (8.28 g, 0.06 mol, dried at 100 °C under vacuum for 15 h prior to use) were stirred at room temperature under a nitrogen atmosphere for 2 days. The reaction mixture was poured into water (300 mL). The resulting precipitate was collected by filtration, washed thoroughly with water, and dried. The residue was washed with CCl_4-benzene (1:1 v/v) mixture (40 mL × 2) and recrystallized from 1,2-dichloroethane. The first crop weighed 5.27 g, and the second 2.99 g. The filtrate from the second crop was imposed on a silica gel column (10 × 23 cm) with CCl_4-benzene (1:1 v/v) as eluent to give a third crop of 0.59 g. The total yield was 93.7% (mp 164.5–165 °C).

(**2,9,16,23-Tetrakis(phenylthio)phthalocyaninato)iron(II).** To 4-(Phenylthio)phthalonitrile (2.37 g, 10 mmol) in ethylene glycol (25 mL), refluxing under nitrogen, was added $Fe(CO)_5$ (0.49 g, 0.33 mL, 2.5 mmol) dropwise with a syringe. After about 2 min, the reaction mixture had turned green and was further refluxed for 2 h and then cooled and diluted with ethanol (50 mL). The precipitate was collected by filtration and washed with ethanol, water, dilute HCl, water, and ethanol. The residue was dissolved in CH_2Cl_2, which was washed with 5% HCl and then water, and the CH_2Cl_2 layer was dried by $MgSO_4$. After removal of $MgSO_4$, the CH_2Cl_2 solution was condensed to ca. 25 mL and methanol (280 mL) was added. After 2 days, the precipitate was collected by filtration and dried in vacuo (429 mg, yield 18.2%). Anal. Calcd for $C_{56}H_{32}N_8S_4Fe$: C, 71.16; H, 3.41; N, 11.86; S, 13.57. Found: C, 70.67; H, 3.54; N, 11.97; S, 12.28.

(**Naphthalocyaninato)iron(II) (8).** A mixture of 2,3-dicyanonaphthalene prepared by the literature method[8] (1.78 g, 10 mmol) and ethylene glycol (25 mL, stored over 4-Å molecular sieves) was refluxed under nitrogen. $Fe(CO)_5$ (0.49 g, 0.33 mL, 2.5 mmol) was then added portionwise directly into the mixture. The reaction mixture immediately turned green and was kept refluxing for 50 min and then cooled and diluted with water (25 mL). The precipitate formed was filtered off and washed with water, 10% HCl, water, ethanol, benzene, DMF, and ethanol. The crude product was dissolved in the least amount of DMSO and precipitated from the solution by the addition of acetone (containing a small amount of ether). This procedure was repeated three times. The precipitate was collected, dried, and kept at 390–410 °C under high vacuum (<10^{-3} Pa) for 2 days. A sublimed unidentified product was discarded. The remaining residue was dissolved in DMSO, and the mixture was filtered through a fine-pored glass filter. To the filtrate was added acetone (containing a small amount of ether), and the resulting precipitate was collected, washed with water and then methanol, and dried (370 mg, yield 19.3%). Anal. Calcd for $C_{48}H_{24}N_8Fe$: C, 75.01; H, 3.15; N, 14.58. Found: C, 75.03; H, 3.73; N, 13.81.

B. Measurements. Mössbauer spectra were measured with an Elscint AME-30A spectrometer with a $^{57}Co(Rh)$ source and calibrated with ^{57}Fe foil. Spectra were fitted to Lorentzian components by least-squares techniques. Estimated error limits on δ and ΔE_Q are ±0.01 mm s^{-1}. An Air Products LT-3-110 Heli-Tran liquid-transfer refrigeration system was employed for measurements at temperatures in the liquid-helium region, and a precalibrated thermocouple of Au(0.07% Fe) vs Chromel was used as the temperature sensor.

UV/vis spectra were recorded in pyridine with a Hitachi 200-10 spectrophotometer.

Results

UV/vis measurements were carried out on solutions of complexes 1–5 in pyridine; the compounds exist as the bis(pyridine)
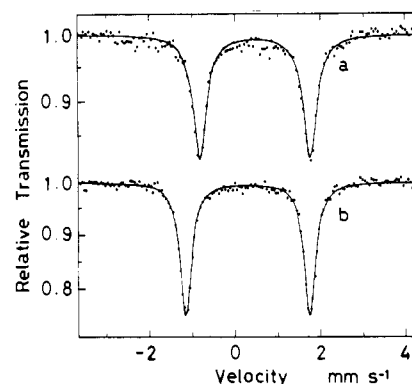

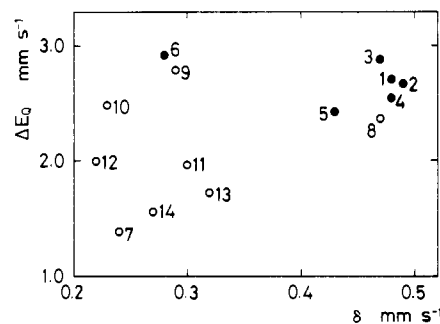**Figure 1.** Mössbauer spectra at 4.2 K of (a) Fe(OMxPc) (**4**) and (b) Fe(TPPc) (**6**).

Figure 2. Mössbauer parameters for tetracoordinate (phthalocyaninato)iron(II) complexes at liquid-helium temperatures with the exception of **5** for which the values at 79 K are indicated. The numbers refer to the complexes in Table I. Solid circles are for the complexes with electron-releasing substituents; open circles for those with electron-withdrawing substituents.

adducts.[5] Hanack and co-workers[5] have reported on the influence of the peripheral groups of the phthalocyaninato ring on the electronic spectra of the bis(pyridine) adducts of several substituted (phthalocyaninato)iron and -cobalt complexes. They found, by comparison of the UV/vis spectra with those of the unsubstituted Fe(Pc) (**1**) or Co(Pc) compounds, that the pyridine adducts of the compounds with electron-releasing substituents exhibit no great spectral change, while the Q-band at 655 nm in the spectrum of **1** is displaced ~20 nm toward longer wavelengths in electron-withdrawing chloro- and nitro-substituted derivatives, and the absorption at 415 nm in **1** ascribed to an Fe → L CT transition is displaced by 24 nm toward longer wavelengths in the chloro derivative **13**.

We observed the same results with respect to the electronic spectra of **1**, **2**, **4**, and **5** in pyridine as compared to those of ref 5. The pyridine adduct of **3**, however, shows absorption maxima at 648, 587, 404, and 346 nm with the relative optical densities 1.0, 0.25, 0.21, and 0.82. The Q and CT bands are displaced by 7 and 11 nm, respectively, toward shorter wavelengths compared to those in **1**; the displacements are in a direction opposite to those exhibited by the compounds described above with electron-withdrawing substituents.

Mössbauer spectra of polycrystalline solids of the (phthalocyaninato)iron(II) complexes with electron-releasing substituents are similar to those of the complexes with electron-withdrawing substituents.[4] They consist of mainly one symmetric quadrupole doublet with line widths of 0.33 ± 0.04 mm s^{-1} down to liquid-helium temperatures. The values of the quadrupole splitting, ΔE_Q, are nearly temperature-independent, and the values of isomer shift, δ, and ΔE_Q are in the range typical of $S = 1$ ferrous porphyrins.[9] Typical spectra are shown in Figure 1. The Mössbauer data are given in Figure 2 and Table II. The latter contains also the sum of the Hammett σ constants[10] for substituents, $\Sigma\sigma$, and bonding

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Table II. Mössbauer Data for Tetracoordinate (Phthalocyaninato)iron(II) Complexes and Bonding Parameters for the Ligands

| complex | Mössbauer data | | | | bonding params | |
	T, K	δ,[a] mm s^{-1}	ΔE_Q, mm s^{-1}	$\Sigma\sigma$[b]	Σ	Π
Fe(Pc)[c] (**1**)	4.2	0.48	2.70	0	10.00	10.48
Fe(OMePc) (**2**)	5.1	0.49	2.66	−0.96	9.88	10.37
	79	0.48	2.67			
	297	0.38	2.58			
Fe(TMDPc) (**3**)	4.6	0.47	2.88	−0.64	10.83	11.30
	79	0.47	2.80			
	292	0.37	2.61			
Fe(OMxPc) (**4**)	4.2	0.48	2.54	−0.61	9.20	9.68
	79	0.46	2.53			
	297	0.33	2.49			
Fe(TBuPc) (**5**)	79	0.43	2.42	−0.59	8.23	8.66
Fe(TPPc) (**6**)	4.2	0.28	2.91	−0.48	9.56	9.85
	79	0.28	2.91			
	299	0.20	2.53			
Fe(TTPc) (**7**)	4.4	0.24	1.38	1.07	1.63	1.88
	79	0.23	1.37			
	296	0.14	1.36			
Fe(Nc) (**8**)	4.3	0.47	2.36		8.23	8.70
	79	0.46	2.31			
	299	0.37	2.28			
Fe(TDPc)[d] (**9**)	4.3	0.29	2.78	1.28	8.99	9.28
Fe(ODPc)[d] (**10**)	4.2	0.23	2.48	2.56	7.02	7.24
Fe(TlPc)[d] (**11**)	4.3	0.30	1.96	2.64	4.97	5.27
Fe(TNPc)[d] (**12**)	4.3	0.22	1.99	2.97	4.52	4.74
Fe(Cl$_{16}$Pc)[d] (**13**)	4.5	0.32	1.72	3.89	3.94	4.27
Fe(OCyPc)[d] (**14**)	4.3	0.27	1.56	4.88	2.69	2.96

[a] Relative to metallic iron. [b] The sum of the Hammett σ constants for the substituents. Reference 10. [c] Mössbauer data taken from ref 12. [d] Reference 4.

parameters, Σ and Π, for ligands that will be discussed in the next section.

Discussion

The data points in Figure 2 are distributed in a rather random fashion, and the set of δ–ΔE_Q data are difficult to interpret in the usual way. The majority of the compounds with electron-releasing substituents have larger δ values than those with electron-withdrawing ones. This fact appears to reflect larger iron 3d occupancies in the covalent bonding in the former compounds. However, the separation of the two regions in the δ–ΔE_Q diagram is not distinct, and the distribution of the data points in each region is quite random. For example, electron-releasing neopentoxy-substituted **6** has an anomalously small δ and electron-withdrawing fused-ring-substituted **8** has a large δ.

In order to obtain more detailed information from the Mössbauer data, the method[4] for calculating the bonding parameters, Σ and Π, of macrocyclic ligands from δ and ΔE_Q is applied to the present complexes. The two parameters are defined so that Σ is larger for a stronger σ donor, while Π is larger for a stronger π donor and for a weak π acceptor. Both Σ and Π are relative values: the value of a parameter for a particular ligand is not significant, but the order of parameter values for different ligands is of significance. The following discussion assumes that
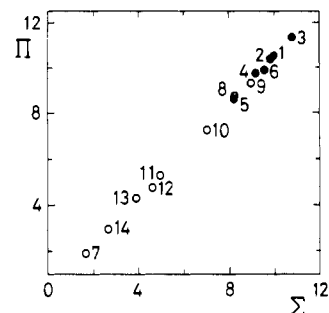
(10) Dean, J. A., Ed. *Lange's Handbook of Chemistry*; McGraw-Hill: New York, 1973; p 3-128. Phthalocyanine is an azaporphyrin to which four benzene rings are fused. The substituent R_2 or R_3 is at the meta position to one exo carbon of a pyrrole ring or at the para position to another exo carbon. Hence, σ_m and σ_p are averaged for R_2 and R_3. R_1 or R_4 is at the ortho or meta positions to the two exo carbons. Although the Hammett relationships fail[11] for ortho substituents, $\sigma_m/2$ is adopted for R_1 and R_4 in **13**. σ values of SC_6H_5 are estimated from those of OCH_3, OC_6H_5, and SCH_3.

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Figure 3. Bonding parameters of substituted phthalocyaninato ligands in tetracoordinate iron(II) complexes. The numbers refer to the complexes in Table I. Solid circles are for the ligands with electron-releasing substituents; open circles for those with electron-withdrawing substituents.
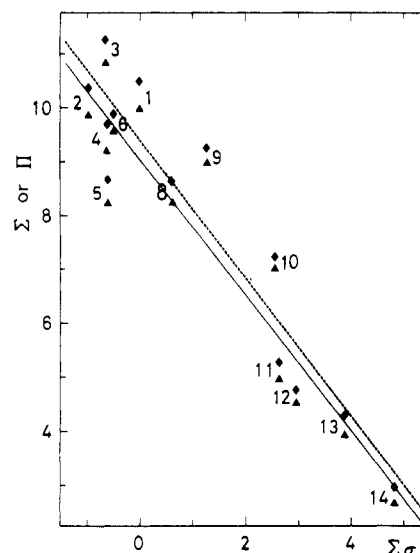

Figure 4. Bonding parameters versus the sum of the Hammett σ constants for the substituents. Triangles are for Σ; diamonds for Π. The numbers refer to the complexes in Table I. The solid and dashed lines are least-squares fitted to Σ and Π, respectively. The points for **8** are not included in the fits because the Hammett σ constants are not defined for the fused ring. They are located at the positions of corresponding Σ and Π on the fitted lines.

$V_{zz} > 0$ and $\eta \simeq 0$, where V_{zz} is the principal component of the electric field gradient (EFG) at the nucleus and η is the asymmetry parameter of EFG; this is confirmed in all the cases studied by applied-field Mössbauer measurements.

The Mössbauer parameters are related to the bonding parameters by

$$\delta = -\Sigma + \Pi \tag{1}$$

$$\Delta E_Q = a\Sigma - b\Pi + c \tag{2}$$

where a, b, and c are constants and $a > b > 0$. The derivation of eqs 1 and 2 is given in ref 4. With the same values of $a = 1.7$, $b = 1.5$, and $c = 1.42$ as in the previous paper, eqs 1 and 2 give the values of Σ and Π for the ligands in the present complexes as shown in Table II and Figure 3. The Mössbauer parameters at temperatures in the liquid-helium region were adopted for the calculation with the exception of **5** for which those at a liquid-nitrogen temperature were adopted. Table II contains the sum of the Hammett σ constants, $\Sigma\sigma$, and Figure 4 shows correlations of both Σ and Π with $\Sigma\sigma$. Σ and Π are larger for a ligand with smaller $\Sigma\sigma$. The correlations previously found for electron-withdrawing substituents are revealed to be extended in electron-releasing ones. The bonding parameters for complex **7** are out of the range of the diagram, although $\Sigma\sigma$ corresponds to the values of the parameters around **8**. This discrepancy will be discussed below. The results are explained in terms of inductive (field) and conjugative (resonance) effects[13] of the substituents.

For a phthalocyanine with electron-releasing substituents, the inductive effect gives a shift of every MO to higher energy compared to the corresponding MO for the unsubstituted phthalocyanine. The energy shift of a given MO should increase with the absolute value of $\Sigma\sigma$. Several MO's are to be considered. The destabilization of the σ-donating MO's causes the increase in the σ donicity to iron $d_{x^2-y^2}$ that lies at higher energy. Thus, Σ should increase with increasing electron-releasing ability of the substituent. Similarly, the destabilization of the π-donating $e_g(\pi)$ orbitals and π-accepting $e_g(\pi^*)$ orbitals causes the increase in Π: the π-interacting iron $d_{yz,zx}$ orbitals lie between $e_g(\pi)$ and $e_g(\pi^*)$. The highest occupied a_{2u} orbital, too, π-donates via the symmetry-allowed interaction with the empty iron $4p_z$ orbital. The destabilization of a_{2u} also causes the increase in Π. It is obvious from the correlations shown in Figure 4 that the inductive effect is at work.

The second effect of substitution is the conjugation of p orbitals of the atoms of the substituents with orbitals of the ring. Shelnutt and Ortiz[13] have systematically investigated UV/vis spectra of metalloporphyrins and determined relative energy splittings of the frontier orbitals on the basis of the four-orbital model. They have found that the energy of the affected HOMO orbital, either a_{2u} for meso substitution or a_{1u} for pyrrole substitution, for copper porphyrins increases relative to that for copper porphine and that the more electron-withdrawing substituents cause a larger destabilization of the affected orbital. This result can never be explained by the inductive mechanism because it predicts an increase in stabilization, not destabilization, of a given MO with electron-withdrawing ability. Shelnutt and Ortiz have explained the relationship in terms of conjugation of the substituents with the ring, assuming that the more electron-withdrawing a substituent, the more the substituent carbons become conjugated with the ring. The filled a_{1u} and a_{2u} orbitals are relatively close to the filled p orbitals of the substituent α-carbons. Therefore, the filled ring orbitals are destabilized by mixing with substituent-carbon p orbitals that lie at lower energy than a_{1u} and a_{2u}.

The same kind of argument applies for the present case. The σ-donating MO's are not expected to be influenced by the conjugative effect in the first approximation. For a substituent with α-carbon, -nitrogen, or -oxygen, the $e_g(\pi^*)$ level is apparently far from empty or filled 2p orbitals of the substituent, but the filled $e_g(\pi)$ orbitals are relatively close to the filled 2p orbitals. Therefore, the filled $e_g(\pi)$ orbitals are stabilized by conjugation with substituent 2p orbitals that lie at higher energy than $e_g(\pi)$, forcing Π to decrease. The destabilization of a_{2u} by the conjugative effect causes the increase in π donicity to iron $4p_z$, since the relative energies of the a_{2u} and substituent 2p orbitals mentioned above for the porphyrins are reasonably adopted for the present phthalocyanines. The conjugative effect depends on the relative energies and the charge distributions of the interacting orbitals and hence on the respective substituents. For chloro-substituted 13, the conjugation of filled 3p orbitals and $e_g(\pi^*)$ should also be taken into cosideration. In the case of unsubstituted 1, the conjugation is not permitted because suitable p orbitals are not available. Thus, the conjugative mechanism modifies Π in diverse ways depending upon the type of the substituents.

The σ-donating MO's are not expected to be influenced directly by the conjugative effect. However, the change in the charge distributions of the affected π-interacting orbitals may result in the secondary inductive effect on the σ-donating orbitals. The deviations of the values of Σ and Π from linear relationships to $\Sigma\sigma$ in Figure 4 appear to reflect the conjugative effect.

As mentioned above, the Mössbauer parameters for complexes 6 and 8 seem to be particularly anomalous in Figure 2. However, the values of the bonding parameters in Table II and Figure 4 indicate that neopentoxy groups in 6 are, in fact, electron releasing. Neopentoxy groups in 6 increase the occupancies of the iron 3d and 4s orbitals through the σ and π bonds, compared with electron-withdrawing substituents. A larger 3d occupancy causes a larger δ; the larger 4s occupancy, on the contrary, causes a smaller δ. The small δ for 6 in Figure 2 is believed to reflect the predominance of the effect of the large 4s occupancy, and the large ΔE_Q the large $3d_{x^2-y^2}$ occupancy caused by the strong σ donicity. Although the sum of the Hammett σ constants can not be calculated for 8, the values of the bonding parameters are reasonable. The points for 8 are located at the positions of corresponding Σ and Π on the least-squares fitted lines in Figure 4. The points correspond to $\Sigma\sigma$ of 0.6 and indicate that the C_4H_4-fused ring is weakly electron withdrawing. The large δ for 8 in Figure 2 is believed to reflect the predominance of the effect of the small 4s occupancy, and the small ΔE_Q the small $3d_{x^2-y^2}$ occupancy. Thus, the bonding parameters have proved to represent the σ- and π-bonding properties of the macrocyclic ligands, in spite of the rather irregular set of the Mössbauer data.

The abnormally small values of the bonding parameters for 7 are unexpected; they result from the abnormally small value of ΔE_Q (Table II). If the substituent were a phenyl sulfoxide group instead of a phenylthio group, the electron-withdrawing ability would be so high as to correspond to the small values of Σ and Π. However, the close agreement between the calculated and found values of the elemental analysis and the narrow line widths of the Mössbauer spectra (the average width at 4.4 K is 0.29 mm s^{-1}) are items of evidence against the possibility that the complex studied is an undesired compound. The present argument tacitly assumes that the ground-state configuration[9,14-18] remains the same for all the complexes studied, probably $^3E_g[(d_{xy})^2(d_{yz},d_{zx})^3(d_{z^2})^1]$. If the iron in 7 has an alternative configuration $^3A_{2g}[(d_{xy})^2(d_{yz},d_{zx})^2(d_{z^2})^2]$, the observed small ΔE_Q is accounted for: the latter configuration has a more negative contribution to ΔE_Q.

Conclusion

Two kinds of bonding parameters, Σ and Π, were calculated from Mössbauer parameters, δ and ΔE_Q. The orders of Σ and Π are in good correlation with the sum of the Hammett σ constants, $\Sigma\sigma$, of the substituents. The results are explained in terms of inductive and conjugative effects of the substituents.

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