The Ge–O–Ge band in (hpGeO)$_x$ is, like its counterpart in (PcGeO)$_x$, both broad and relatively strong. The breadth of the band in both compounds can be attributed to the coupling of vibrations and provides further evidence for the polymeric nature of (hpGeO)$_x$ and (PcGeO)$_x$.

Examination of the data in this paper on the frequencies of the germanium–halogen and –oxygen vibrations reveals an interesting fact, namely, that for comparable bands the hemiporphyrazine band consistently occurs at a higher frequency. This suggests that in the hemiporphyrazines the *trans* groups are bound more tightly. Supporting this conclusion are the relative positions of the O–H and O–D stretching bands of hpGe(OH)$_2$, hpGe(OD)$_2$, PcGe(OH)$_2$, and PcGe(OD)$_2$ (strengthening of the Ge–O bond should weaken the O–H bond and *vice versa*).

Also supporting this conclusion are the powder pattern data for the polymers (PcGeO)$_x$ and (hpGeO)$_x$. Previously the 3.50-A line in the pattern of (PcGeO)$_x$ has been interpreted in terms of a Ge–O bond length of 1.75 A.[20] A similar interpretation of the 3.40-A line in the pattern of (hpGeO)$_x$ yields a Ge–O bond length of 1.70 A and this somewhat shorter bond length again suggests that the *trans* groups are held more tightly in the hemiporphyrazines.

Just why the *trans* group bonds in the hemiporphyrazines are stronger than those in the phthalocyanines is not completely clear. However, the data with regard to the aromaticity of the two macrocycles developed in this paper and the data on bond lengths and molecular shapes developed by Knox, Speakman, Templeton, and Robertson[12–16,21] and their co-workers provide some basis for an answer. It seems reasonable to suggest that, while the four central nitrogen atoms in the phthalocyanine ring are bound strongly and uniformly to the germanium atom, this is not the case in the hemiporphyrazines. Here it appears likely that the pyridine rings retain much of their original character and that their nitrogen atoms are relatively weakly bound to the germanium atom. If so, this would naturally lead to stronger *trans* group bonds.

Infrared Spectrum of Metal-Free Hemiporphyrazine.—Some controversy has existed in the past concerning the assignment of the N–H stretching vibration in the infrared spectrum of metal-free phthalocyanine.[22,23] Because of this, the spectra of hpH$_2$ and hpD$_2$ are of interest. Little difficulty attaches to the assignment of the N–H vibrations in these compounds, since hpH$_2$ shows a sharp band at 3452 cm^{-1} and a broad, strong band at 574 cm^{-1} while hpD$_2$ shows what are quite apparently the counterparts of these bands at 2569 and 417 cm^{-1}. Assignment of the high-frequency bands to N–H and N–D stretching modes and the low-frequency bands to the corresponding bending modes is thus unambiguous.

Reaction Chemistry.—Enough germanium hemiporphyrazines have now been made so that it is clear that the chemistry of this series of compounds is quite similar to that of the germanium phthalocyanines[24,25] (and the silicon and tin phthalocyanines for that matter). However, the parallel is not complete, the hemiporphyrazine ring being considerably more subject to chemical attack than the phthalocyanine ring.

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A Mössbauer-Effect Study of Some Iron–Phthalocyanine Derivatives

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The ^{57}Fe Mössbauer spectra of phthalocyanineiron(II) and several of its derivatives have been measured at temperatures between 77 and 423°K. Diamagnetic adducts of phthalocyanineiron(II) with several organic bases show quadrupole split spectra, and the peak separation varies with base strength. The electric field gradient arises from anisotropic covalent bonding. The spectra observed from phthalocyanineiron(II) and phthalocyaninechloroiron(III) are discussed in terms of their possible electronic structures.

Introduction

Phthalocyanine and its metal derivatives are of considerable interest both because of their novel geometry and because of their structural similarity to the biologically important porphyrins. Iron-containing compounds are of particular importance in the latter respect and their structures may be investigated by Mössbauer spectroscopy. Several such studies of haemo-

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globin and its derivatives have been reported,[2,3] but apart from the parent compound[4] the chemically more accessible iron phthalocyanines have received little attention. In an attempt to obtain further insight into the bonding situation in compounds containing a metal ion surrounded by a square of coplanar nitrogen atoms, we have measured the ^{57}Fe Mössbauer spectra of several iron containing phthalocyanines. In each case we obtain values of the isomer shift and of the quadrupole splitting. The former is related to the s electron density at the nucleus. The latter is proportional to the electric field gradient and is sensitive to the symmetry of the nuclear environment.

Experimental Section

Phthalocyanineiron(II) was prepared from metal-free phthalocyanine and purified by sublimation in a stream of nitrogen.[5] Phthalocyaninebis(pyridine)iron(II)[6] and the related picoline compounds were prepared by extracting phthalocyanineiron(II) with the appropriate base for 24 hr. Excess solvent was removed by distillation under reduced pressure, and the crystals which separated were collected, washed with water and alcohol, and dried in air.

Phthalocyaninebis(imidazole)iron(II)[7] was prepared by fusion of a 50:1 mixture of imidazole and phthalocyanineiron(II) in a stream of nitrogen at temperatures just below the boiling point of the base (~240°) for 4 hr. After filtration, the remaining imidazole was removed by extraction with alcohol.

Phthalocyaninechloroiron(III) was prepared by aerial oxidation[6] of phthalocyanineiron(II) in concentrated hydrochloric acid at 90°.

Magnetic susceptibilities were measured at room temperature using a Gouy balance. The results for phthalocyanineiron(II) and phthalocyaninechloroiron(III) were in agreement with values obtained by Lever.[8] The remaining compounds are diamagnetic.

The Mössbauer spectra of the phthalocyanine derivatives were measured using a spectrometer which has been described in detail by Whitfield and Vickermann.[9] A ^{57}Co in Pd source rigidly attached to an electromechanical transducer is vibrated at a frequency of 30 cps and at such an amplitude as to give a sweep of velocities from −3 to +3 mm/sec with respect to a stationary absorber. The absorber consists of a thin layer of the compound to be studied containing 20–25 mg of iron/cm^2 of cross section. The detector is a thin NaI crystal and the spectra are accumulated in a 400-channel RIDL analyzer used in time mode. An electronic gating circuit is used to synchronize the motion of the source and the channel advance of the analyzer. Spectra were determined over a range of temperatures between 77 and 423°K and peak positions were determined with an accuracy of ±0.02 mm/sec. The isomer shifts and quadrupole splittings are listed in Table I. The isomer shifts are quoted relative to the center of the sodium nitroprusside doublet. In Figures 1 and 2 are shown the spectra obtained from phthalocyanineiron(II) and phthalocyaninebis(imidazole)iron(II), respectively.

TABLE I

MÖSSBAUER PARAMETERS FOR PHTHALOCYANINE–IRON DERIVATIVES

Compound	Temp, °K	ΔE_Q, mm/sec (±0.02)	Isomer shift, mm/sec (±0.02)
Phthalocyanineiron(II)	77	2.71	0.77
	195	2.65	0.74
	295	2.67	0.68
	423	2.58	0.60
Phthalocyaninebis(pyridine)iron(II)	77	1.89	0.62
	195	2.00	0.58
	295	2.05	0.53
Phthalocyaninebis(β-picoline)iron(II)	77	1.81	0.61
	195	1.88	0.60
	295	1.95	0.55
Phthalocyaninebis(γ-picoline)iron(II)	195	1.89	0.58
	295	1.96	0.55
Phthalocyaninebis(α-picoline)iron(II)	195	1.94	0.60
	295	2.01	0.56
Phthalocyaninebis(imidazole)iron(II)	77	1.71	0.63
	195	1.76	0.59
	295	1.79	0.54
Phthalocyaninechloroiron(III)	77	2.52	0.64
	195	2.52	0.61
	295	2.51	0.54

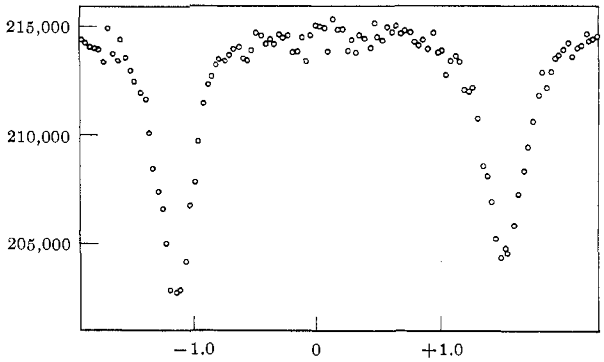

Figure 1.—The ^{57}Fe Mössbauer spectrum of phthalocyanineiron(II).

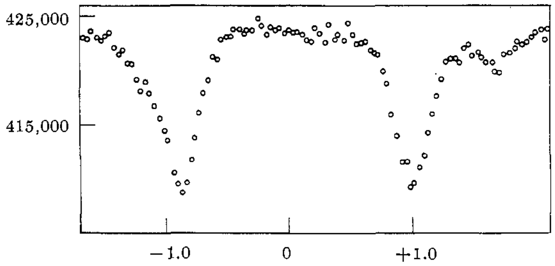

Figure 2.—The ^{57}Fe Mössbauer spectrum of phthalocyaninebis(imidazole)iron(II).

Discussion

We shall first discuss general features relevant to all the compounds and then discuss the individual results. The microsymmetry of the metal environment is D_{4h} and the metal orbitals transform as shown.

a_{1g}	b_{1g}	b_{2g}	e_g	a_{2u}	e_u
s, d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}, d_{yz}	p_z	p_x, p_y

If we consider only orbitals on the four surrounding nitrogen atoms, the π orbitals span e_g, a_{2u}, and b_{2u}. The σ orbitals span a_{1g}, b_{1g}, and e_u. There are no π orbitals in the molecular plane and d_{xy} is formally nonbonding

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since the σ and π representations do not include b_{2g}. The relative energies of the d orbitals have been the subject of much discussion.[10,11] The situation has recently been reviewed by Lever,[8] who concludes that the order $b_{2g} < e_g < a_{1g} < b_{1g}$ is generally favored. The position of d_{z^2} depends strongly on the degree of axial perturbation in the particular molecule.

Ferrous Phthalocyanine.—The magnetic moment of this complex ($\mu_{\text{eff}} = 3.49$ BM, 294°K) is high for a spin-paired ($S = 1$) state, and it was suggested that this might be due to thermal admixture of a low-lying $S = 2$ state.[12] However, the complex obeys a Curie–Weiss law and the magnetic moment is virtually temperature independent.[8] It would thus appear that there are no low-lying excited states. This conclusion is reinforced by the Mössbauer results. The quadrupole splitting is virtually independent of temperature in contrast to the situation in octahedral high-spin ferrous[13] or low-spin ferric[14] complexes where the presence of low-lying excited states produces a strong temperature variation.

Sixfold-Coordinated Complexes.—The axial perturbation of the coordinating ligands raises the energy of d_{z^2} and these complexes are diamagnetic with d-electron configuration $(b_{2g})^2(e_g)^4$. The most striking feature of the Mössbauer results is the magnitude of the quadrupole splitting. The value for the bis(pyridine) compound is even greater than that for sodium nitroprusside and is much larger than that of other low-spin Fe(II) complexes. If covalency effects are neglected the predicted splitting for low-spin d^6 complexes is zero even in the presence of a tetragonal distortion. It is clear that the large splittings observed must arise from anisotropic covalent bonding. A simple way to allow for this is to define bonding coefficients k_b and k_e for the b_{2g} and e_g, orbitals.[15] The predicted EFG is

$$q = 2(k_b^2 - k_e^2)q',\ q' = \frac{4}{7}\langle r^{-3}\rangle$$

As we have seen d_{xy} is nonbonding whereas d_{yz} and d_{xz} may π bond with the phthalocyanine ring. Thus $k_b = 1$ and $k_e < 1$. q is nonzero and positive. We have thus far ignored the ligands in our considerations. It is clear that they are of some importance because the observed splitting decreases as the basicity of the donor increases. This suggests that we should also consider the effects of π bonding to the ligands. The situation is now somewhat modified because the ligand has only twofold symmetry—a pyridine ring may π bond with d_{yz} or d_{xz} but not with both simultaneously. The question arises as to whether the aromatic rings of the two ligands are parallel or perpendicular to one another. If they are coplanar then the e_g orbitals become split and d_{xz} and d_{yz} have different bonding coefficients. This would induce more asymmetry in the system than if the rings were staggered and would lead to a nonzero value for η, the asymmetry parameter of the electric field gradient. Similar situations occur in the diamagnetic compounds oxyhaemoglobin and haemoglobin carbon monoxide.[3] The former has only a single π^* orbital of the O_2 molecule involved in bonding and shows a large quadrupole splitting of 2.2 mm/sec at 4°K; CO has a pair of antibonding π orbitals which can simultaneously interact with d_{xz} and d_{yz} and the splitting in its haemoglobin complex is 0.36 mm/sec. These observations indicate that delocalization to the ligands is more important than delocalization to the phthalocyanine ring in producing an electric field gradient at the iron nucleus. They also suggest by analogy with the haemoglobin derivatives that the ligands are in an eclipsed configuration in the compounds we have studied. As was noted by Lang and Marshall,[3] the observed splitting is roughly equivalent to the presence of a single hole in d_{yz}.

Our analysis of the results suggests that delocalization from ferrous iron occurs more readily to pyridine than to the more basic ligands. This conclusion is in agreement with measurements of the π-electron affinities of substituted pyridines[16] and with the stability of various addition complexes of ferrous porphyrins.[17]

The observation that π-electron delocalization is less effective in the imidazole complex with phthalocyanineiron(II) than in the pyridine and the picoline complexes is of some interest in connection with the imidazole pump model of electron transport in certain biological systems proposed by Urry and Eyring.[18] A complex between ferrous porphyrin and imidazole is postulated as the biological carrier implicated in the cytochrome chain. The model requires a facile exchange of imidazole groups between adjacent iron atoms and the intermediate involved is structurally very similar to the phthalocyanine complex.

Our results at various temperatures show that the quadrupole splitting observed for the octahedrally coordinated complexes decreases as the temperature is lowered. As discussed earlier the presence of low-lying excited states is implied but this would seem to be ruled out by the observation that the compounds are diamagnetic at room temperature. An unexplained temperature variation has recently been observed for oxyhaemoglobin[3] but there the splitting increases on cooling. A possible explanation for our compounds is that as the temperature is lowered, contraction of the lattice forces the donor ligands to take up a distorted configuration less favorable for π bonding. A determination of the crystal structure would be of some interest in this respect.

The sensitivity of the quadrupole splitting to the nature of the donor ligands is not reflected in the isomer shifts which are identical within experimental

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error and are close to those observed for other diamagnetic Fe(II) complexes.

Phthalocyaninechloroiron(III).—The oxidation state of the iron in this compound has been shown to be three by quantitative oxidation,[19] and it should have a spin of $^{3}/_{2}$. The magnetic moment is low and on the basis of a careful study of its temperature dependence, it has been suggested that dimeric iron–iron interactions occur.[8] No magnetic splitting was observed in the Mössbauer spectrum at 77°K, but one might hope to do so at lower temperatures. The absence of any temperature variation in the quadrupole splitting suggests that no significant depopulation of excited electronic states is occurring in the temperature range covered.

The only other well-authenticated iron(III) compound with a quartet ground state is $Fe[S_2CN(C_2H_5)_2]_2Cl$. The crystal structure has recently been determined[20] and discrete molecules are present. The Mössbauer spectrum of this compound at room temperature shows a quadrupole split doublet with ΔE_Q = 2.54 mm/sec and an isomer shift of +0.64 mm/sec. Similar results have been obtained by Wickman and Trozzolo[21] for the dipropyl and dimethyl derivatives. The quadrupole splitting is almost identical with that observed for phthalocyaninechloroiron(III), but the isomer shift is 0.10 mm/sec more positive. A more detailed comparison is not meaningful because the structure of the dithiocarbamate complex is distorted with the Fe atom 0.63 A above the plane of the four sulfur atoms, whereas that of the phthalocyanine is unknown.

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Raman Study of Aqueous Metal Oxalate Complexes and Related Oxalates[1]

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Raman spectra were measured of concentrated oxalate solutions of Zn(II) and Mg(II). Spectra of the tris complexes were obtained in both cases, and for Zn(II) the bis complex was also detected. No indication of monodentate coordination was observed. For the equilibrium $Zn(C_2O_4)_2^{2-} + C_2O_4^{2-} \rightleftarrows Zn(C_2O_4)_3^{4-}$, an equilibrium quotient of 3.6 ± 0.6 M^{-1} was determined at 43° in the ionic strength range 8.9–10.2 *M*. Raman intensities and depolarization ratios were quantitatively measured for the three complexes and, for comparison, for oxalate ion, oxalic acid, and dimethyl oxalate. From the intensities of M–O stretching modes, the coordination was shown to be principally ionic (covalent bond orders *ca.* $^{1}/_{4}$). Intensities of high-frequency oxalate bands suggest that considerable coupling is apparent, possibly enhanced by increased planarity of oxalate ion on coordination.

Introduction

The oxalate ion represents a simple example of a bidentate, charged ligand. Because of its electronic structure, it presents not only the obvious problems of whether its complexes are essentially ionic, but whether extensive electronic rearrangements may occur on coordination. A Raman spectrophotometric study should not only answer the question of what species are present in solution but also give information on both the character of the metal–oxygen coordination and the subsequent bonding changes within the coordinated ligand. For these reasons the present study was undertaken. The metal ions Zn^{2+} and Mg^{2+} were chosen because of solubility considerations. Of the common divalent cations, only these give colorless oxalate solutions of sufficient concentration for careful Raman studies.

Experimental Section

Analytical reagent grade chemicals were used throughout. Solutions of oxalate complexes were prepared by dropwise addition with vigorous stirring of a concentrated solution of either $Zn(NO_3)_2$ or $Mg(NO_3)_2$ to a solution saturated with $K_2C_2O_4 \cdot H_2O$ and containing an excess of this solid. By maintaining a temperature of *ca.* 40° (the temperature at which all spectra were run), a solution containing as high as 1.0 *M* total Zn(II) and as low as 2.6 *M* total oxalate could be prepared which showed no precipitation for at least 1 day. With Mg in place of Zn(II), the maximum total metal ion concentration so obtainable was 0.4 *M* at a minimum total oxalate concentration of 2.4 *M*. In order to avoid troublesome H_2O Raman bands, some solutions were prepared in 99.9% D_2O, but it was not necessary to remove the H_2O from the initial hydrated salts. Efforts to prepare solutions of suitable concentrations of oxalate complexes of Cd(II), Hg(II), and Mn(II) for Raman studies were not successful.

Stoichiometric oxalate concentrations were determined by standard permanganate titration, and Zn^{2+} or Mg^{2+} concentrations were determined by EDTA titration, after oxidation of the oxalate, using Eriochrome T as indicator.[2] In analyzing dimethyl oxalate solutions, hydrolysis was effected by heating with KOH

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[1] From the Ph.D. thesis of E. C. Gruen (Procter and Gamble predoctoral fellow) and supported by the Office of Saline Water, U. S. Department of the Interior.

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