The *cis*- and *trans*-effects in Carbonyl Complexes of Bis(dimethylglyoximato)iron(II)

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Mössbauer spectra of the complexes $[Fe(Hdmg)_2L_2]$ and $[Fe(Hdmg)_2L(CO)]$ (H_2dmg = dimethylglyoxime, L = pyridine or 1-methylimidazole) have been measured between 4.2 and 295 K, and in applied magnetic fields at 4.2 K. Changes in isomer shifts and quadrupole splittings on carbonylation are similar to those observed in haemochromes. In all four complexes studied the principal component V_{zz} of the electric field gradient is positive, and the asymmetry parameter $\eta > 0.5$. Replacement of an axial amine by CO is shown to result in perturbations of the iron–nitrogen bonding both *cis* and *trans* to the site of substitution.

DIOXIME complexes of iron(II), $[Fe(dioximate)_2L_2]$ (L = Lewis base), have been employed as convenient low molecular weight model compounds for the biologically important haems. These complexes are diamagnetic and contain low-spin iron(II) (d^6). *X*-Ray crystallographic studies of $[Fe(Hchd)_2(im)_2]$ [1] and $[Fe(Hdmg)_2(im)_2]$ [2] (H_2chd = 1,2-cyclohexanedione dioxime, H_2dmg = dimethylglyoxime, and im = imidazole) have shown that the dioxime ligands co-ordinate to iron in an essentially planar fashion, with *trans* imidazole groups. Thus, these compounds are structurally related to (diamine)iron(II)–porphyrin and –phthalocyanine complexes, although strictly speaking they lack a four-fold rotation axis and the point-group symmetry at iron is no higher than D_{2h}.

Several Mössbauer spectroscopic investigations of bis(amine)bis(dioximato)iron(II) complexes have been reported.[3-6] Dale *et al.*[3] studied the series $[Fe(Hchd)_2L_2]$ using a variety of different amines L as axial ligands, whilst Sasaki and Shigematsu[4] investigated bis(pyridine)- and bis(imidazole)-iron(II) complexes of four different dioximes. More recently, Shafranski *et al.*[5] have examined dimethyl- and diphenyl-glyoximatoiron(II) species with pyridine and 3- and 4-substituted pyridines in axial positions. Where comparisons are possible, agreement amongst the various sets of Mössbauer parameters is generally satisfactory. One might also note that for a given axial base, complexes of $Hdmg^-$ and $Hchd^-$ give very similar Mössbauer parameters.

In bis(amine)porphyrinatoiron(II) complexes and in $[Fe(pc)(pip)_2]$ (H_2pc = phthalocyanine and pip = piperidine) replacement of one of the axial amines by a carbonyl group results in a pronounced decrease in both the Mössbauer isomer shift δ and quadrupole splitting $|\Delta E_Q|$.[7,8] Qualitatively similar differences were also observed by Dale *et al.*[3] between the Mössbauer parameters of $[Fe(Hchd)_2(im)_2]$ and $[Fe(Hchd)_2(im)(CO)]$. However, Morpurgo and Mosini[9] have published Mössbauer data for 12 $[Fe(Hdmg)_2L(CO)]$ complexes which appear to show an opposite trend for the quadrupole splittings. In four cases direct comparisons can be made with the data of Shafranski *et al.*[5] for the corresponding $[Fe(Hdmg)_2L_2]$ species and in three other cases somewhat less direct comparisons with the $[Fe(Hchd)_2L_2]$ complexes[3] are possible. In every case the carbonyl derivative is reported[9] to have a *larger* quadrupole splitting than the corresponding diamine.

In connexion with our continuing studies of carbonyl haemochromes and related species[8,10] it is important to establish whether the dimethylglyoxime derivatives are in fact exceptional or if the data of Morpurgo and Mosini[9] are in error. To this end we report here Mössbauer measurements on $[Fe(Hdmg)_2L_2]$ and $[Fe(Hdmg)_2L(CO)]$, where L = pyridine (py) or 1-methylimidazole (mim). The complexes have also been examined at 4.2 K in applied magnetic fields to determine the signs of the electric field gradients (e.f.g.s) and magnitudes of the asymmetry parameters, η, in these derivatives. These data provide the first conclusive evidence that replacement by CO of an axial amine perturbs the iron–ligand bonds both *cis* and *trans* to the site of substitution.

RESULTS

^{57}Fe Mössbauer data for the complexes are given in Table 1. As a check on the internal consistency of our results, spectra for all the species were recorded twice at liquid nitrogen temperature using different spectrometers and different velocity transducers. In each case these independent measurements gave δ and $|\Delta E_Q|$ values which were identical to within ± 0.01 mm s^{-1}. Moreover, δ and $|\Delta E_Q|$ values at 4.2 K were obtained both from zero-field spectra and from spectra recorded in applied magnetic fields. In fitting the latter (see later), δ, $|\Delta E_Q|$, and η were allowed to vary, and in no case did the optimum values of isomer shift and quadrupole splitting so obtained differ by more than 0.02 mm s^{-1} from those measured in zero field.

For $[Fe(Hdmg)_2(py)_2]$ our data are in excellent agreement with those of Shafranski *et al.*,[5] both at room temperature and at 80 K, and our values at the latter temperature also agree well with those quoted by Sasaki and Shigematsu[4] at *ca.* 100 K. The only significant disagreement amongst the three sets of measurements for this complex occurs with the data at 300 K, where the values of Sasaki and Shigematsu[4] for both δ and $|\Delta E_Q|$ are somewhat higher than the other two data sets. Although Mössbauer data for [Fe-

TABLE 1

^{57}Fe Mössbauer parameters (mm s^{-1}) of the complexes. Values of δ are relative to metallic iron

Complex	T/K	δ [a]	ΔE_Q	Γ_1	Γ_2	Ref. [b]
$[Fe(Hdmg)_2(py)_2]$	300	0.24	1.78			4
	300	0.20	1.67			5
	295	0.21	1.70	0.31	0.32	
	~100	0.26	1.73			4
	80	0.28	1.69			5
	78	0.27	1.71	0.29	0.29	
	4.2	0.18 [c]	1.71	0.30	0.30	
$[Fe(Hdmg)_2(im)_2]$	300	0.27	1.31			4
	~100	0.31	1.29			4
$[Fe(Hdmg)_2(mim)_2]$	295	0.23	1.38	0.26	0.25	
	78	0.30	1.34	0.26	0.26	
	4.2	0.19 [c]	1.30	0.26	0.26	
$[Fe(Hdmg)_2(py)(CO)]$	298	0.23 [d]	1.77			9
	295	−0.01	1.21	0.29	0.30	
	78	0.06	1.19	0.28	0.29	
	4.2	−0.01 [c]	1.19	0.28	0.28	
$[Fe(Hdmg)_2(mim)(CO)]$	295	0.01	1.17	0.28	0.29	
	78	0.08	1.14	0.30	0.31	
	4.2	−0.02 [c]	1.14	0.28	0.28	

[a] Measured with source at room temperature unless stated otherwise. [b] This work unless stated otherwise. [c] Measured with source at 4.2 K. [d] Relative to $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$; subtract 0.27 mm s^{-1} to convert to iron reference.

$(Hdmg)_2(mim)_2]$ have not been published previously, our measurements for this complex are, as expected, similar to those of Sasaki and Shigematsu [4] for $[Fe(Hdmg)_2(im)_2]$.

Both carbonyl derivatives show substantially smaller values of isomer shift and quadrupole splitting than those exhibited by the parent bis-amines. Changes in both parameters upon carbonylation are entirely analogous to those observed by Dale *et al.* between $[Fe(Hchd)_2(im)_2]$ and $[Fe(Hchd)_2(im)(CO)]$. The $|\Delta E_Q|$ value for $[Fe(Hdmg)_2(py)(CO)]$ found here, which is nearly temperature-independent, is *ca.* 0.6 mm s^{-1} smaller than that reported for this compound by Morpurgo and Mosini.[9] On the other hand, the discrepancy in isomer shift values appears to be much smaller. Unfortunately, Morpurgo and Mosini [9] failed to quote the reference point for their isomer shift data, but did state that $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ was used as the spectrometer calibrant. If we assume this complex also provided their zero-velocity reference for isomer shifts, then their δ value (relative to metallic iron) for $[Fe(Hdmg)_2(py)(CO)]$ at room temperature is −0.04 mm s^{-1}, compared to the present value of −0.01 mm s^{-1}.

The care we have exercised in recording our Mössbauer spectra, the fact that identical isomer shift and quadrupole splitting parameters were obtained at 80 K using two completely independent spectrometers as well as at 4.2 K from zero-field and applied-field spectra, and the lack of any pronounced temperature dependence of $|\Delta E_Q|$, all give us confidence that the present data are correct and that those of Morpurgo and Mosini are in error. As the quadrupole splittings of all the other carbonyl derivatives reported by

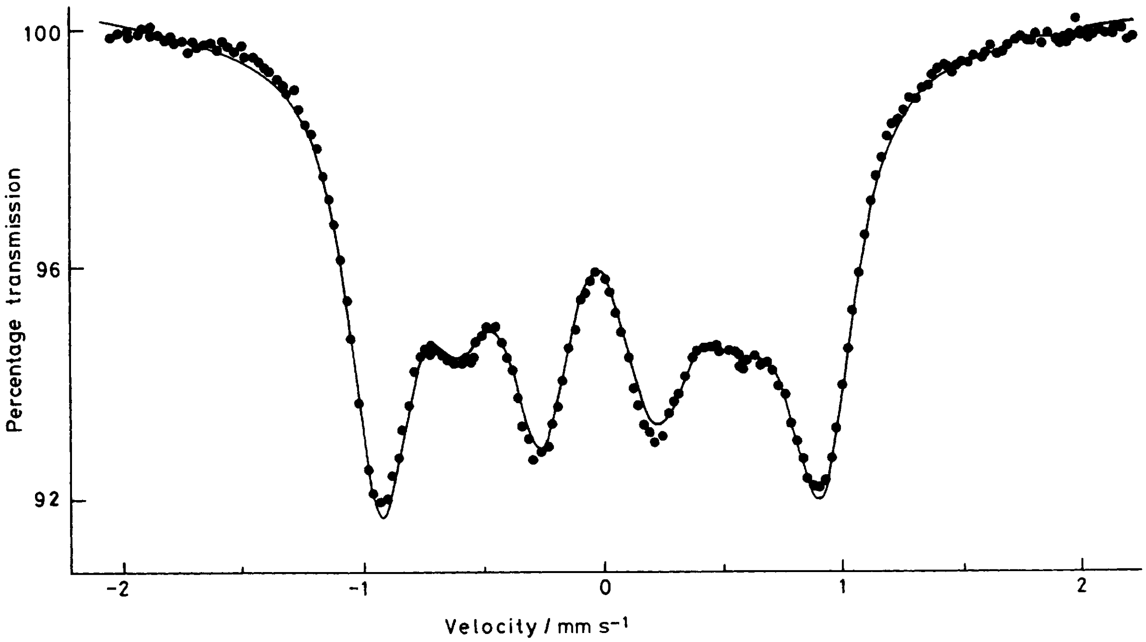

FIGURE Mössbauer spectrum of $[Fe(Hdmg)_2(mim)(CO)]$ measured at 4.2 K in a longitudinal applied magnetic field $H_{\text{appl.}}$ = 2.77 T. The calculated curve (——) is based on the parameter values: $\delta = -0.02$ mm s^{-1}, $\Delta E_Q = +1.14$ mm s^{-1}, $\eta = 0.75$, and $\Gamma = 0.28$ mm s^{-1}

these authors are larger than that quoted for [Fe(Hdmg)$_2$(py)(CO)], we suspect a large systematic error in their data. Although we are not aware of the source of such an error, it may be pointed out that since the isomer shifts are small, a systematic error in calibration of the Doppler velocity scale would produce a much larger error in $|\Delta E_Q|$ than in δ, as observed.

The Mössbauer spectra of the four complexes studied here in longitudinal applied magnetic fields are all characterized by having fairly large η values. Dale *et al.*[11] measured the Mössbauer spectra of [Fe(Hchd)$_2$L$_2$] (L = im or NH$_3$) in transverse applied fields of 3.0 T, and stated that in both cases η was close to unity. However, no attempt was made to fit the spectra by computer simulation and the signs of V_{zz}, the principal component of the e.f.g. tensor, were not specified. Lang and Dale[12] subsequently carried out a computer fit of the spectrum of [Fe(Hchd)$_2$(im)$_2$] determined at 4.2 K in a transverse field of 6.0 T, and quoted an η value of 0.98 with $V_{zz} > 0$. For the complexes examined here, computer fitting of the spectra also showed V_{zz} to be positive in every case.

The present results are the first applied-field Mössbauer data to be reported for any [Fe(dioximate)$_2$(L)(CO)] derivative. The spectrum of [Fe(Hdmg)$_2$(mim)(CO)] is illustrated in the Figure. The asymmetry parameters are slightly smaller in both carbonyl complexes than in the corresponding bis-amines, but are still substantial. In their discussion of the e.f.g.s in [Fe(Hdmg)$_2$(L)(CO)] complexes, Morpurgo and Mosini[9] have erroneously assumed that $\eta = 0$. This would be true only if the two nitrogen atoms of each dioximate ligand were precisely equivalent, which of course they are not.[1,2]

DISCUSSION

There are several points concerning the present data that call for interpretation and discussion, *e.g.* the signs of the field gradients and magnitudes of the asymmetry parameters in the diamine derivatives, and how these quantities, as well as the isomer shifts, change when one of the axial amines is replaced by CO.

It should be pointed out that the orientation of the e.f.g. tensor relative to the molecular axes is not known, nor are *X*-ray crystallographic data available for the present complexes. We shall approximate the effective point-group symmetry at iron in the diamine complexes as D_{2h}; although the true symmetry is undoubtedly lower than this, this approximation will not materially affect our conclusions. We assume that the dioximate ligands lie essentially in the *xy* plane with the amine bases along the *z* axis. This is a natural choice of axes, and the one made previously by Dale *et al.*[3,11]

The two independent parameters of the e.f.g. tensor in the bis-amine complexes investigated here, as well as those in the [Fe(Hchd)$_2$L$_2$] complexes examined previously,[11,12] are fully consistent with *X*-ray structural data for [Fe(Hdmg)$_2$(im)$_2$] (1)[2] and [Fe(Hchd)$_2$(im)$_2$] (2).[1] In both the latter molecules the bonds between iron and the nitrogen atoms of the axial imidazole ligands [1.99 (1) and 2.05 Å (2)] are substantially longer than those between iron and the nitrogen atoms of the dioximate moieties [1.89 and 1.92 Å (1); 1.91 and 1.97 Å (2)]. Thus there should be more metal character in the bonding orbital involving the iron $d_{x^2-y^2}$ orbital than in the bonding orbital formed from d_{z^2}. Since the $d_{x^2-y^2}$ orbital makes a positive contribution to the e.f.g. and the d_{z^2} orbital a negative contribution, one expects on this basis that V_{zz} will be positive, as observed. As Dale *et al.*[3] have pointed out, an increase in σ-donor strength of the axial ligands should decrease V_{zz}, and the smaller ΔE_Q in [Fe(Hdmg)$_2$(mim)$_2$] than in [Fe(Hdmg)$_2$(py)$_2$] is consistent with the lower pK_a value for pyridine.

This σ-bonding argument ignores the six electrons in the iron orbitals of $b_{2g}(d_{xy})$ and $e_g(d_{xz}, d_{yz})$ symmetry. The former is a non-bonding orbital and can legitimately be ignored, whereas electrons in the e_g orbitals can interact with vacant π^* orbitals on the ligands. As electrons in the e_g orbitals contribute negatively to the e.f.g., any iron$\rightarrow$ligand π donation will merely make V_{zz} more positive and will increase the quadrupole splitting.

In discussing the large η values found for [Fe(Hchd)$_2$L$_2$] (L = im or NH$_3$), Dale *et al.*[11] stated 'The difference in the ligand field produced by a nitrogen atom double-bonded to an oxygen atom as opposed to a nitrogen atom single-bonded to a hydroxyl group is almost certainly important.' Lang and Dale[12] subsequently commented that the η value of 0.98 in the imidazole complex indicated that 'the hydrogen bonding in this compound is highly anisotropic.' These two statements seem to be merely two different ways of describing the same phenomenon. The molecular structure of [Fe(Hdmg)$_2$(im)$_2$][2] shows O–H distances of 1.0 and 1.5 Å, so that the O–H bonds are indeed very asymmetric. The two N–O distances are also significantly different (1.365 and 1.408 Å), the shorter N–O distance being associated with the longer O–H bond length, and it is reasonable to assume that there is some double-bond character in the shorter N–O bond. These differences in the O–H and N–O bonds are reflected in different equatorial Fe–N distances (see above). Thus one could also consider that the large asymmetry parameters result from anisotropy of the bonding orbitals involving the iron $d_{x^2-y^2}$ and/or d_π orbitals.

Dale *et al.*[3] have argued that in these dioximate complexes an increase in axial ligand σ donation should decrease V_{zz}, whilst an increase in axial ligand π acceptance should increase V_{zz}. Since CO is generally considered to be a weaker σ-donor and stronger π-acceptor than an amine, these considerations lead one to expect an increase in $|\Delta E_Q|$ on replacing an axial amine by CO, whereas the opposite is in fact observed. Underlying these arguments is the tacit assumption that substitution of one axial ligand by another causes only a negligible perturbation of the remaining bonds to iron. In view of the present results and previous data for porphyrinatoiron(II) carbonyl complexes,[7,8] this assumption seems to be unjustified, at least when one of the axial ligands is CO. Indeed, unless there is substantial perturbation of one or more of the remaining iron–ligand bonds, the only way to account for the decrease in quadrupole splitting in terms of σ and π bonding properties is to assume that CO is both a stronger σ-donor and weaker π-acceptor than an amine.

We therefore accept the notion that replacement of an axial amine by CO perturbs the other iron–ligand bonds, and consider possible mechanisms by which such perturbation could produce the observed changes in Mössbauer parameters.

It is usually considered[13] that the valence contribution to the e.f.g., $q_{\text{val.}}$, can be expressed in terms of effective populations n_i of the various iron $3d$ orbitals by equation (1), where R is a Sternheimer antishielding

$$q_{\text{val.}} = \tfrac{4}{7}(1 - R)\langle r^{-3}\rangle [n_{x^2-y^2} + n_{xy} - n_{z^2} - \tfrac{1}{2}(n_{xz} + n_{yz})] \quad (1)$$

factor and $\langle r^{-3}\rangle$ the expectation value of $1/r^3$ taken over the $3d$ radial function. [In the presence of bonding interactions the radial extents of the various d orbitals will differ, and each n_i in equation (1) should more properly be weighted by its own appropriate $\langle r_i^{-3}\rangle$ value.] Ignoring lattice effects the quadrupole splitting is given by equation (2), with $V_{zz} = e\,q_{\text{val.}}$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$.

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

The diagonal elements V_{ii} of the e.f.g. tensor in the principal axis system are conventionally labelled such that $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$. To decrease $|\Delta E_Q|$ one requires either an enhanced electron density in those iron orbitals that make a negative contribution to $q_{\text{val.}}$ (*i.e.*, d_{z^2}, d_{xz}, d_{yz}), a diminished electron density in the iron $d_{x^2-y^2}$ orbital, or both. Since the Laplacian of the electrostatic potential vanishes, knowledge of η and the sign and magnitude of ΔE_Q are sufficient completely to specify all three principal components of the e.f.g., and η provides valuable information on departures of the system from axial symmetry. The isomer shift is a scalar quantity and measures the total s-electron density at the iron nucleus. The isomer shift δ will decrease both with an overall increase in ligand→iron σ donation and an overall increase in iron→ligand back π donation, and it is likely that σ effects will dominate.[3]

Binding of a CO ligand by iron may result in perturbations either *cis* or *trans* to the Fe–CO bond. We shall make the reasonable assumption here that CO is a better π-acceptor than an amine. (*i*) *trans*-Effect: if electron density in the iron d_π orbitals is withdrawn towards the CO group, the positive charge on the iron nucleus may be partially deshielded from the remaining axial amine. This might result in a contraction of the Fe–N bond *trans* to the CO ligand, and an increased σ donation from this axial amine to iron. (*ii*) *cis*-Effect: withdrawal by CO of electron density from the iron d_π orbitals may be compensated by increased forward π donation into these orbitals from the filled p_z orbitals on the nitrogen atoms of the dioximate ligands. To prevent the removal of too much electron density from these nitrogen atoms, this increased π donation would presumably be accompanied by a reduced N→Fe σ donation, thereby decreasing the metal character of the bonding orbital involving $d_{x^2-y^2}$.

Although seemingly plausible, the *trans*-effect argument given above appears to be at variance with X-ray crystallographic data for bis(amine)- and carbonylamine-porphyrinatoiron(II) complexes.[14-17] Such data are quite limited, but suggest that replacement of an amine by a carbonyl ligand lengthens (by up to *ca.* 0.1 Å), rather than shortens, the remaining Fe–N axial bond. In the present context a more significant feature than this Fe–N bond lengthening is that the Fe–C bonds in the carbonyl derivatives, which range in length from 1.61 to 1.77 Å,[15,16] are much shorter than the Fe–N bonds they replace (typically 2.00 ± 0.05 Å), so that the sum of the axial bond lengths is less than in the diamine complexes. Similar short Fe–C (1.730 Å) and long *trans* Fe–N bonds (2.088 Å) have also been found in the case of a [14]-annulene macrocyclic ligand,[18] and may be expected to occur in the present derivatives. Regardless of any assumptions about the σ and π bonding capabilities of the ligands, a shortening of the mean axial bond length should place more electron density near iron along the z axis in the carbonyl complexes, and result in a smaller $|\Delta E_Q|$ as observed. If this charge density has appreciable s character, δ should also be decreased.

A *trans*-effect of this type, resulting in shorter mean axial bond lengths for the carbonyl derivatives, seems capable of rationalising, at least qualitatively, the trends found for both δ and $|\Delta E_Q|$. Of course, this does not necessarily mean that *cis*-effects are unimportant. As soon as we turn our attention to the asymmetry parameters it becomes clear that changes in η upon carbonylation are explicable only in terms of a *cis*-effect.

As the e.f.g. tensor is traceless, a decrease in V_{zz} caused by replacing one axial ligand with another must always be matched by an identical decrease in $|V_{xx} + V_{yy}|$. In the absence of any *cis*-effect this substitution should cause no change in η, and a given fractional change in V_{zz} should be accompanied by the same fractional change in each of $|V_{xx}|$ and $|V_{yy}|$. However, in both cases the carbonyl derivative has a smaller η than the corresponding diamine, and hence the e.f.g. anisotropy in the xy plane has diminished. This may be seen more clearly from an examination of the e.f.g. tensor components listed in Table 2. In particular it should be noted that carbonylation causes a greater decrease in $|V_{yy}|$ than in $|V_{zz}|$, and an *increase* in $|V_{xx}|$.

As detailed structural information for these complexes is lacking, it is not possible to specify the relative orientation of the e.f.g. principal axis system to the molecular axes. Nor is it clear at this time why carbonylation produces a much larger decrease in $|\Delta E_Q|$ with pyridine as axial ligand rather than 1-methylimidazole. Nevertheless, it seems evident that substitution of an amine by CO in these dioximate complexes causes significant changes in all the remaining Fe–N bonds, and that a proper interpretation of the Mössbauer parameters requires a consideration of both *cis*- and *trans*-effects. This is likely to be true for porphyrinatoiron(II) derivatives as well,[8] although in that case verification of *cis*-effects on the basis of Mössbauer data alone is hampered by the effectively axial symmetry ($\eta \simeq 0$) of the complexes.

TABLE 2

Components of the e.f.g. tensors for the complexes, determined in longitudinal applied magnetic fields $H_{appl.}$ at 4.2 K

Complex	$H_{appl.}$/T	ΔE_Q/ mm s^{-1}	η	V_{xx}	V_{yy}	V_{zz}
					mm s^{-1}	
$[Fe(Hdmg)_2(py)_2]$	2.82	+1.71	0.73	−0.22	−1.36	1.58
$[Fe(Hdmg)_2(mim)_2]$	3.20	+1.30	0.92	−0.05	−1.10	1.15
$[Fe(Hdmg)_2(py)(CO)]$	2.82	+1.19	0.55	−0.25	−0.88	1.13
$[Fe(Hdmg)_2(mim)(CO)]$	2.77	+1.14	0.75	−0.13	−0.92	1.05

EXPERIMENTAL

Preparations.—All the complexes were prepared using procedures reported in the literature.[19] However, the carbonyl derivatives were dried in a stream of CO and stored under a CO atmosphere. All complexes gave satisfactory analytical data, and the electronic spectra were in excellent agreement with the parameters reported by Pang and Stynes.[19] The carbonyl stretching frequencies (Nujol mulls) were at 1 978 cm^{-1} for $[Fe(Hdmg)_2(mim)(CO)]$ and at 1 985 cm^{-1} for $[Fe(Hdmg)_2(py)(CO)]$.

Mössbauer Spectra.—Powder samples of the complexes were loaded into nylon cells which were then sealed with epoxy resin, these operations being performed in a glove-box under an appropriate atmosphere (N_2 for the bis-amine complexes and CO for the carbonyl derivatives).

Spectra were recorded with a 50-mCi * ^{57}Co(Rh) source using spectrometers and cryostats previously described.[20] The Doppler velocity scale was calibrated with a metallic iron-foil absorber, and isomer shifts are quoted relative to the centroid of the iron spectrum.

Spectra measured in zero magnetic field were fitted to Lorentzian lineshapes by least-squares techniques, and no constraints were imposed on the fitting parameters. Spectra obtained at 4.2 K in longitudinal applied magnetic fields were least-squares fitted on a conversational terminal using a suitably modified [21] version of a program originally described by Lang and Dale.[12] Lorentzian linewidths were fixed at the mean values observed at 4.2 K in zero-field, and the parameters that were allowed to vary were δ, $|\Delta E_Q|$, sign of V_{zz}, and η.

* Throughout this paper: 1 Ci = 3.7×10^{10} Bq.

This work was supported in part by the Natural Sciences and Engineering Research Council. We thank Mrs. A. Sallos and Ms. B. Ruhl for valuable technical assistance.

[1/1297 *Received, 12th August,* 1981]

REFERENCES

[1] C. K. Prout and T. J. Wiseman, *J. Chem. Soc.*, 1964, 497.

[2] K. Bowman, A. P. Gaughan, and Z. Dori, *J. Am. Chem. Soc.*, 1972, **94**, 727.

[3] B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, *Trans. Faraday Soc.*, 1968, **64**, 620.

[4] Y. Sasaki and T. Shigematsu, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3590.

[5] V. N. Shafranski, V. N. Zubarev, R. A. Stukan, K. I. Turta, and D. D. Buburbuz, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 260.

[6] R. A. Stukan, K. I. Turta, A. V. Ablov, V. N. Zubarev, and A. M. Gol'dman, *Zh. Neorg. Khim.*, 1976, **21**, 286.

[7] W. M. Connor and D. K. Straub, *Inorg. Chem.*, 1976, **15**, 2289.

[8] B. R. James, J. R. Sams, T. B. Tsin, and K. J. Reimer, *J. Chem. Soc., Chem. Commun.*, 1978, 746.

[9] G. O. Morpurgo and V. Mosini, *J. Chem. Soc., Dalton Trans.*, 1974, 2233.

[10] K. J. Reimer and J. R. Sams, unpublished work.

[11] B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, *Trans. Faraday Soc.*, 1968, **64**, 3011.

[12] G. Lang and B. W. Dale, *Nucl. Instrum. Methods*, 1974, **116**, 567.

[13] G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc. A*, 1970, 956.

[14] S.-M. Peng and J. A. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 8032.

[15] J. L. Hoard in 'Porphyrins and Metalloporphyrins,' ed. K. M. Smith, Elsevier, Amsterdam, 1975, ch. 8.

[16] G. B. Jameson and J. A. Ibers, *Inorg. Chem.*, 1979, **18**, 1200.

[17] J. L. Hoard, personal communication, quoted in ref. 16.

[18] V. L. Goedken, S.-M. Peng, J. Molin-Norris, and Y. Park, *J. Am. Chem. Soc.*, 1976, **98**, 8391.

[19] I. W. Pang and D. V. Stynes, *Inorg. Chem.*, 1977, **16**, 590.

[20] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, 1969, **8**, 95; J. R. Sams and T. B. Tsin, *ibid.*, 1975, **14**, 1573.

[21] J. S. Haynes, A. R. Hume, J. R. Sams, and R. C. Thompson, *Chem. Phys.*, in the press.