Correlations between Spectral Parameters of some Carbonylbis(dimethylglyoximato) (substituted pyridine)iron(II) Complexes

By **Giorgio O. Morpurgo** * and **Valeria Mosini**, Istituto Chimico, Università di Roma, Italy

A series of carbonylbis(dimethylglyoximato)(substituted pyridine)iron(II) complexes, $[Fe(Hdmg)_2(X)CO]$ (I; X = substituted pyridine), has been prepared and analysed, and visible, near u.v., i.r., and Mössbauer spectra have been measured in the solid state. Two charge-transfer (c.t.) bands of the reflectance spectra are assigned to electronic transitions from the metal atom to molecular orbitals of Hdmg and CO, respectively, on the basis of their dependence on p*K* values of X. Of the two Mössbauer parameters, the isomer shift, δ, and the quadrupole splitting, ΔE_Q, the first appears to be linearly correlated with p*K* values of the ligand X, while the second correlates linearly with the CO stretching frequency. It appears that delocalization of d_{xz} electrons on the CO group dominates the ΔE_Q values, through the mediating influence of the σ-donor power of X (in one series) and the π-acceptor power of the bases (for the remaining complexes).

Iron(II) dioxime complexes, $[Fe(diox)_2(X)Y]$, of C_{4v} microsymmetry around the central iron atom (X, Y = bases such as pyridine, imidazole, hydrazine, *etc.*) have been extensively studied, as these low-molecular-weight metal complexes resemble, in some respects, those of iron porphyrins. However, very little attention has been devoted to complexes which have CO as one of the axial ligands. Recently, L. Vaska *et al.* reported some results on the reversible decarboxylation of *trans*-$[Fe(Hdpg)_2(X)CO]$ complexes [Hdpg = bidentate diphenylglyoximato(1—); X = pyridine, substituted pyridine, or imidazole].[1] In order to justify the use of such complexes as models for CO derivatives of naturally occurring iron compounds, the properties of carbonyl(dioximato)-iron compounds need to be explained in terms of their electronic structures. In this study the preparation, spectral properties, and Mössbauer parameters of a series of Fe^{II} complexes, $[Fe(Hdmg)_2(X)CO]$ [I; Hdmg = bidentate dimethylglyoximato(1—); X = pyridine or substituted pyridines], are reported and discussed.

EXPERIMENTAL

Materials.—The salt diammonium iron(II) bis(sulphate) hexahydrate, dimethylglyoxime (H_2dmg), pyridine (py), 2-, 3-, and 4-methylpyridine (2-Mepy, *etc.*) were R.P. reagent, supplied by C. Erba. 3- and 4-Aminopyridine ($3-NH_2py$, *etc.*), 3- and 4-cyanopyridine (3-CNpy, *etc.*), and 3,5-dichloropyridine ($3,5-Cl_2py$) were purchased from Fluka A.G., 3- and 4-acetylpyridine (3-MeCOpy) from Baker, and 3-bromopyridine (3-Brpy) and 3,4-dimethylpyridine ($3,4-Me_2py$) from Schuchardt.

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[1] L. Vaska and T. Yamaji, *J. Amer. Chem. Soc.*, 1971, **93**, 6673.

Preparations.—Complexes. Solid samples of the complexes [Fe(Hdmg)$_2$(X)CO], (I), were prepared as follows. A solution (100 cm^3) of 2·6 × 10^{-3}M-H_2dmg and 1·95 × 10^{-2}M-py or -substituted pyridine, in water–dioxan (7 : 3 v/v), were deaerated by prolonged bubbling of dinitrogen.† After saturation with carbon monoxide, a 1·3 × 10^{-2}M-Fe[NH_4]$_2$[SO_4]$_2$,6H_2O solution (10 cm^3) at pH 4 was added. The pH was then increased to 7 by addition of sodium hydroxide. A reddish brown precipitate formed and was collected, washed with distilled water, and dried. Complexes (I) are stable when kept in the dark in a desiccator, and no decomposition was detected even after 1 a, in contrast to [Fe(cdiox)$_2$X$_2$] (cdiox = cyclohexanedione dioxime) which slowly oxidize unless kept under an inert atmosphere.[2] Satisfactory analyses were obtained for all the complexes (Table 1).

TABLE 1

Analyses (%) of the complexes [Fe(Hdmg)$_2$(X)CO], (I) *

Base (X)	C	H	N
py	45·6 (42·8)	5·4 (4·8)	15·3 (17·8)
3-Mepy	44·1 (43·8)	5·1 (5·1)	17·9 (17·2)
4-Mepy	44·2 (43·8)	5·2 (5·1)	16·7 (17·2)
3-NH$_2$py	38·9 (41·2)	4·8 (4·9)	20·1 (20·6)
4-NH$_2$py	40·1 (41·2)	4·8 (4·9)	19·8 (20·6)
3-CNpy	42·3 (43·1)	4·3 (4·3)	19·8 (20·1)
4-CNpy	43·5 (43·1)	4·1 (4·3)	19·7 (20·1)
3-MeCOpy	44·9 (44·2)	4·9 (4·8)	15·6 (16·1)
4-MeCOpy	45·5 (44·2)	5·4 (4·8)	15·4 (16·1)
3-Brpy	35·6 (35·7)	4·0 (3·8)	15·2 (14·9)
3,5-Cl$_2$py	34·9 (36·4)	3·8 (3·6)	15·1 (15·0)
3,4-Me$_2$py	45·3 (45·7)	5·6 (5·4)	17·1 (16·5)

* Calculated values are given in parentheses.

Complexes (I) are sparingly soluble in most of the common organic solvents, where they dissolve without decomposition only if the solvents are saturated with carbon monoxide. The order of solubility is approximately: $CHCl_3 \simeq CHBr_3 \simeq$ MeOH $\simeq$ EtOH $\simeq Me_2CO \simeq HCONMe_2 \simeq$ tetrahydrofuran $\simeq Me_2SO \gg C_6H_6 \simeq$ dioxan $\simeq Me_2O \simeq$ toluene $\gg CCl_4$.

Pyridinium iodides. These compounds were prepared by reaction of the appropriate pyridine with methyl iodide in ethanol, and were purified by repeated crystallization from ethanol in the presence of activated charcoal, which was found effective in eliminating tri-iodide and other impurities. All the u.v. and visible spectra of these compounds were measured at 25 °C in methylene chloride solution, where the pyridinium salts are completely associated.[3] The band-maximum frequencies were found to be in substantial agreement with values reported in literature. When the bands were very close to each other the spectra were resolved with a curve analyser.

Spectroscopic Measurements.—Powder-reflectance spectra were measured with a Beckman DK-2 spectrophotometer equipped with a reflectance unit. The relevant data are given in Table 2. I.r. spectra of the complexes were obtained in Nujol mulls with a Beckman IR-7 spectrophotometer. Table 2 gives $\bar{\nu}$(CO) values for all the complexes. Frequencies were read from the wavenumber drum, not from the chart paper. The maximum error was 1 cm^{-1} in $\bar{\nu}$(CO). Mössbauer spectra were recorded at room temperature, with a ^{57}Co-in-Cu source. The spectrometer was calibrated using $Na_2[Fe(CN)_5NO],2H_2O$ as standard. All complexes contained *ca.* 5 mg cm^{-2} of natural iron, except the 3-Brpy derivative for which no signal could be detected.

TABLE 2

p*K* Values and polarographic one-electron reduction potentials (*E*/V, against Hg pool) of pyridines; absorption bands (10^3 cm^{-1}) in powder reflection spectra and wavenumber of C–O bond (cm^{-1}) of the complexes [Fe(Hdmg)$_2$(X)CO]

X	p*K*	*E*	Band (A)	Band (B)	$\bar{\nu}$(CO)
(1) 3,5-Cl$_2$py	0·7	−1·39	20·8		2 013
(2) 3-CNpy	1·3	−1·45	20·7		2 020
(3) 4-CNpy	1·8	−1·21	20·6		(2 005) [a]
(4) 3-Brpy	2·8	(−1·53) [b]	20·2	26·4	2 009
(5) 3-MeCOpy	4·8	−1·22	19·6		2 003
(6) py	5·2	−1·88	19·7	24·6	2 018
(7) 3-Mepy	5·7	−1·89	19·5	24·2	2 010
(8) 4-Mepy	6·0	−1·99	19·5	23·8	2 000
(9) 3-NH$_2$py	6·1	−2·02	19·1	23·7	1 992
(10) 3,4-Me$_2$py	6·5	−2·04	19·2	23·6	1 997
(11) 4-MeCOpy	6·6	−1·05	19·1		1 994
(12) 4-NH$_2$py	9·1		18·2		2 002

[a] The band is broad and of low intensity. [b] A plot of log $I/(I_d - I)$ against *E* where *I* is the diffusion current, I_d the limiting diffusion current, gave a straight line of gradient corresponding to the transfer of only 0·5 electron. This anomalous behaviour was not further investigated.

Polarographic Measurements.—Polarographic-reduction waves of pyridines (10^{-3}M) were measured in 95% dimethylformamide with 5% H_2O, using 5 × 10^{-2}M-tetraethylammonium iodide as supporting electrolyte.[4] The instrument used was a Sargent model XXI polarograph, the cell being thermostatted at 25 °C. The cathode was a Hg-pool electrode to which the reduction potentials of Table 2 are referred. The potentials were not corrected for the *IR* decrease.

RESULTS

Reflectance Spectra.—Most of the complexes showed a reflectance spectrum similar to those in Figure 1, which is characterized by three absorption regions: at 19 000, 24 000, and *ca.* 34 000 cm^{-1}, the latter being very ill defined. In some complexes the 24 000 cm^{-1} absorption appeared as a

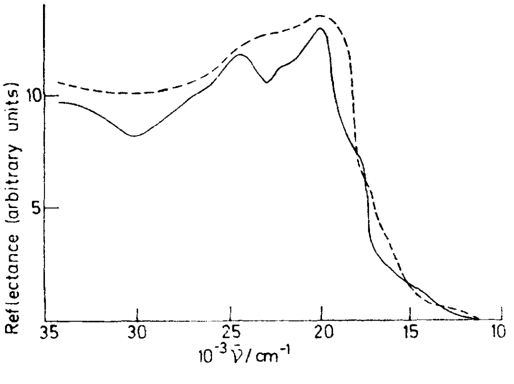

FIGURE 1 Reflectance spectra of the complexes [Fe(Hdmg)$_2$(py)CO] (——) and of [Fe(Hdmg)$_2$(3-MeCOpy)CO] (— — —)

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† 1M = 1 mol dm^{-3}.

[2] P. Day and N. Sanders, *J. Chem. Soc.* (*A*), 1969, 2303.

[3] R. A. Mackay, J. R. Landolph, and E. J. Poziomek, *J. Amer. Chem. Soc.*, 1971, **93**, 5026.

[4] C. Parkanyi and R. Zahradnik, *Bull. Soc. chim. belges*, 1964, **73**, 57.

shoulder on the 19 000 cm^{-1} band. Wavenumbers of the bands are reported in Table 2. The overall features of the spectra are very similar to those of complexes such as [Fe(cdiox)$_2$X$_2$] (X = pyridine or substituted pyridine) [2] which show absorption bands at *ca.* 19 000 [band (A)], 25 000 [band (B)], and 35 000 cm^{-1} [band (C)], the first being assigned to Fe^{II}$\rightarrow$oxime and the second and third to Fe^{II}$\rightarrow$py charge transfer (c.t.).[2] However, such as assignment could not be extended straightforwardly to our spectra, because, while the reflectance spectra of the bis(pyridine) complexes are very similar to their solution spectra, this is not the case for the present complexes. Solution spectra of complexes (I) were shifted to higher energy, and the two-band system appeared at *ca.* 25 000 cm^{-1}. A band at *ca.* 24 000 cm^{-1} was reported for [Fe(Hdpg)$_2$(X)CO] solutions.[1]

The data of Table 2 indicate that band (A) shifts to lower energy with increasing p*K* value of the co-ordinated pyridine, according to the equation $\tilde{\nu}_A/10^3\ \mathrm{cm^{-1}} = -0{\cdot}30\mathrm{p}K + 21{\cdot}17$. This behaviour is close to that of band (A) of the complexes [Fe(cdiox)$_2$X$_2$]; as a consequence band (A) should be assigned to metal ($3d_{yz}$)† $\rightarrow$ in-plane ligand (Hdmg) c.t.[2,5-7]

Band (B), which, in the bis(pyridine) complexes shifts to higher energy with electron-donating substituents, moved in the opposite direction in our complexes according to the equation $\tilde{\nu}_B/10^3\ \mathrm{cm^{-1}} = -0{\cdot}82\mathrm{p}K + 28{\cdot}8$; it cannot, then, be assigned to c.t. from iron(II) to pyridine, but is probably c.t. from the iron $3d_{xz}$ orbital to CO.[8] Since the complexes contain a substituted pyridine ligand, Fe^{II}$\rightarrow$py(π^*) c.t. would also be expected to occur approximately in the same energy range [2] as band (B). It may lie under the envelope together with band (B), although it is striking that it was not observed even in complexes containing a substituted pyridine ligand with high p*K*, where the separation between the two c.t. bands should be at a maximum. An alternative explanation could be that in the solid the d_{xz} atomic orbital is stabilized by interaction with one of the two π^* orbitals of CO and, more weakly, by one of the π^* orbitals of pyridine. Since this stabilization is more marked than in the presence of two pyridine groups, the Fe^{II}$\rightarrow$py(π^*) c.t. is shifted to higher energy. Using arguments analogous to those of Day and Sanders [2] it would be predicted that in solution, where the plane of the pyridine molecule could be oriented differently, both the d_{xz} and d_{yz} electrons are better stabilized by the axial ligands, thus making c.t. to the oxime more difficult.

Band (C), which is at the limit of the frequency range covered in this work, is certainly difficult to assign. It was broader and weaker than the corresponding band of the bis(pyridine) complexes, which was assigned to a second c.t. to pyridine.[2] In the light of these considerations and of the discussion about band (B), we tentatively assign band (C) as an envelope of c.t.s to pyridine.

I.r. spectra.—All complexes (I) were characterized by an i.r. band in the region of 2 000 cm^{-1}, which is attributed to the C–O stretching frequency. The data are given in Table 2. No correlation was found between $\tilde{\nu}$(CO) and the p*K* values of the co-ordinated pyridines. Previously, relations between $\tilde{\nu}$(CO) and p*K* have been found. They were explained either assuming that the base *trans* to the CO molecule has only an inductive effect, or that additional π-interaction of the base with the metal atom is important.[9] In the latter case the donor properties of the ligand are modified by a synergic effect which is also proportional to its σ-donor properties as measured by the p*K* value. In the present case neither of the two mechanisms can be used to explain the experimental results.

Mössbauer Spectra.—Together with attempts to interpret Mössbauer parameters on the basis of theoretical arguments, a more empirical approach is often used.[10-12] The latter is usually based on correlations, in a series of closely related compounds, either between δ (the isomer shift) and ΔE_Q (the quadrupole splitting) [13-15] or between one of these and some other parameter, such as binding energy,[16] position in the spectrochemical series,[17] or the electronegativity of the ligands.[18] Mössbauer parameters for complexes (I) are listed in Table 3.

TABLE 3

Charge-transfer bands ($E_t/10^3$ cm^{-1}) of substituted *N*-methylpyridinium iodides in methylene chloride at 25 °C, and Mössbauer parameters, δ and ΔE_Q, of the corresponding [Fe(Hdmg)$_2$(X)CO]

X	E_{t1}	E_{t2}	δ mm s^{-1}	ΔE_Q mm s^{-1}	Estimated error mm s^{-1}
(1) 3,5-Cl$_2$py	22·98	30·39	0·28	1·91	±0·04
(2) 3-CNpy	22·98	27·60	0·26	1·83	±0·02
(3) 4-CNpy	20·22	30·30	0·24	2·05	±0·04
(4) 3-Brpy	25·31	32·25			
(5) 3-MeCOpy	24·15	29·24	0·22	2·02	±0·02
(6) py	26·88	35·08	0·23	1·77	±0·02
(7) 3-Mepy	27·77	34·00	0·21	1·95	±0·02
(8) 4-Mepy	28·73	35·71	0·17	2·05	±0·04
(9) 3-NH$_2$py	29·94	39·00	0·19	2·12	±0·04
(10) 3,4-Me$_2$py	28·98	35·08	0·20	2·10	±0·04
(11) 4-MeCOpy	22·52	32·57	0·19	2·16	±0·02
12) 4-NH$_2$py	36·90		0·17	1·98	±0·04

The isomer shift. No linear correlation between δ and ΔE_Q was found. Deviations from linearity are expected when the ligands are not pure σ-donors or pure π-acceptors,[10] or when a ligand alters the geometry around the iron atom more than others.[12] The isomer shift is a measure of the total *s*-electron density at the iron nucleus and it would be expected to decrease with increasing σ-donor and π-acceptor power of the axial ligand. In most cases the separate influences of σ- and π-bonding are difficult to assess. However, in the present study a linear correlation was found between δ and pyridine p*K* values (Figure 2). The gradient of the line indicates that $\psi_s(0)$, the nuclear *s* density, increases with σ-donor power of the axial pyridine, through

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† *y* Is the axis bisecting the C–C central bond of the two Hdmg groups, and *z* the axial direction as in ref. 5.

[5] G. De Alti, V. Galasso, A. Bigotto, and G. Costa, *Inorg. Chim. Acta*, 1969, **3**, 533.

[6] M. Griffith and M. G. Mellon, *Analyt. Chem.*, 1947, **19**, 1017.

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[8] P. Day and N. Sanders, *J. Chem. Soc.* (*A*), 1967, 1536.

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[16] I. Adams and J. M. Thomas, *J.C.S. Chem. Comm.*, 1972, 751.

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[18] J. Danon in 'Chemical Application of Mössbauer Spectroscopy,' eds. V. I. Goldanskii and R. H. Herber, Academic Press, New York, 1968, ch. 3.

interaction between the orbital of *s* symmetry of the axial base and the axial d^2sp^3 hybrids of the iron atom. This does not mean that π-bond variations are of little importance for complexes (I), but apparently the δ parameter is more sensitive to L $\longrightarrow$ M electron transfer than to back donation by d^6 electrons into vacant orbitals of π-symmetry.[13]

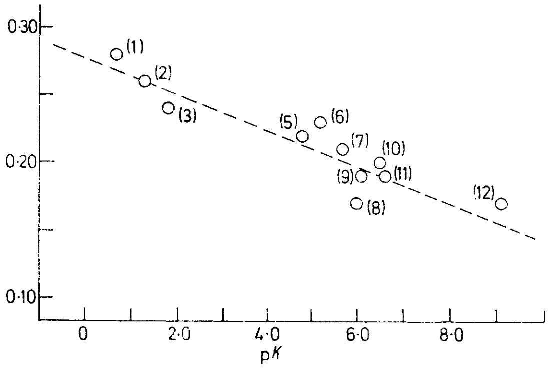

FIGURE 2 Plot of Mössbauer isomer shifts, δ, against pyridine pK values (numbers refer to compounds listed in Table 2)

The quadrupole splitting. The quadrupole splitting ΔE_Q for a nucleus of quadrupole moment Q in an electric field gradient q is given by equation (1), where q may be considered as the sum of the contributions (q_i) made by the individual electrons of the valence shell and of the effect due to external charges. By disregarding this latter effect the contribution due to the valence electrons is given by equation (2), where n is the effective population of the various d orbitals and K is defined as in ref. 11. For *trans*-isomers $\eta = 0$, and for complexes (I) q is expected to be positive:[10] this assumption is fully justified on the basis of the results obtained. The quadrupole splitting can be related to the symmetry of the electronic environment of the central atom. Thus for a perfectly symmetrical octahedral low-spin Fe^{II} (t_{2g}^6) complex, no quadrupole splitting can be observed since $q_{\text{val}} = 0$. In a complex of C_{4v} microsymmetry, q_{val} will be different from zero, and its value will depend on the effective population, '*n*,' of the *d* orbitals. This latter effect will depend on the electron donating or withdrawing power of the ligand. If the charge density on the metal due to the in-plane ligand is assumed constant, then, to a first approximation, only the electron population of the d_{z^2}, d_{xz}, and d_{yz} atomic orbitals contribute to q_{val}. If the donor strength of an axial ligand is progressively increased, n_{z^2} also increases, while q_{val} decreases; on the other hand, if the π-acceptor properties of an axial ligand increase, the electrons of the d_{xz} and d_{yz} orbitals become delocalized, the populations n_{xz} and n_{yz} decrease, and both q_{val} and ΔE_Q increase. Thus, ΔE_Q is proportional to the difference between the π-acceptor and σ-donor properties of the axial ligands.

$$\Delta E_Q = \tfrac{1}{2}e^2qQ(1 + \tfrac{1}{3}\eta^2)^{\frac{1}{2}} \qquad (1)$$

$$q_{\text{val}} = K[n_{xy} - \tfrac{1}{2}(n_{xz} + n_{yz})] + K(n_{x^2-y^2} - n_{z^2}) \qquad (2)$$

In principle, the stretching frequency ν(CO) is also affected by the same factors as ΔE_Q.[19] The matter, however, is still controversial, as mentioned above. We found a linear correlation between ΔE_Q and $\tilde{\nu}$(CO) (Figure 3), indicating that the bond order between carbon and oxygen decreases as ΔE_Q increases. The correlation found suggests that we can use $\tilde{\nu}$(CO) values for predicting approximate ΔE_Q values, at least for complexes (I). However, whether σ-donor or π-acceptor power, or both, is the main factor affecting the two parameters is still obscure.

Of the two factors, σ-donor power can be taken as proportional to pK, the base strength, and to σ_H, the Hammett substituent constants. We observed that σ_H, in turn, varies linearly with the change in σ-electron population of the nitrogen atoms of the substituted pyridines.[20] The π-acceptor power would be expected to depend on the energy of the lowest π^* antibonding orbitals, which, in the case of pyridines, transform as b_1 and a_2 in the C_{2v} group. The π^* orbitals were considered for the substituted pyridines and corresponding pyridinium iodides. The latter show two electronic absorption bands E_{t1} and E_{t2} (at higher energy) which, being assigned to transitions from the highest-occupied molecular orbital of iodide to vacant b_1 and a_2 m.o.s of the pyridinium ion respectively, allow an estimate of their electron affinities.[21] It has been reported that E_{t1} linearly correlates with σ_H, the calculated charge on the nitrogen atom (Q_N), and the polarographic half-wave potentials. The data indicate that the lower the donor power the more stable is b_1. No such correlations have been found for E_{t2}.[3,21,22]

Data on pyridine and substituted pyridines are more scarce. The polarographic potentials (E) relative to one-electron reduction (Table 2) have been associated with energies [4,23] of the lowest unoccupied m.o., b_1. On this basis it is possible to divide the pyridines into two groups: one which includes pyridine, methyl-substituted pyridines, and 3-NH$_2$py, which are reduced by two electrons in a single wave at *ca.* $-2{\cdot}0$ V, and a group of more easily reducible compounds whose first one-electron reversible polarographic wave falls in the range $-(1{\cdot}0$—$1{\cdot}5)$ V. A good linear relation [Figure 4(*a*)] was found by plotting ΔE_Q values against E of the second group of pyridines. The order in which the complexes appear in the plot is the same as that

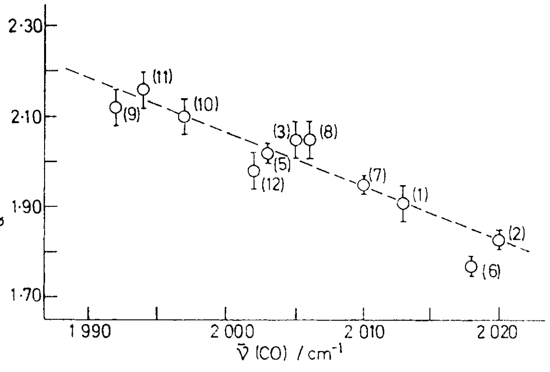

FIGURE 3 Plot of Mössbauer quadrupole splittings, ΔE_Q, against CO stretching wavenumbers

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[19] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2953, and refs. therein.

[20] T. K. Wu, *J. Chem. Phys.*, 1969, **51**, 3622.

[21] R. A. Mackay and E. J. Poziomek, *J. Amer. Chem. Soc.*, 1972, **94**, 4167.

[22] E. M. Kosower and J. A. Skorcz, *Adv. Mol. Spectroscopy*, 1962, 413.

[23] L. Bellugi, M. Bossa, and G. O. Morpurgo, unpublished work.

on the ΔE_Q against $\bar{\nu}$(CO) plot. However, this would indicate that low CO frequencies are produced by low-lying b_1 orbitals. A possible explanation of this discrepancy is that instead ΔE_Q correlates with the a_2 orbital which also varies linearly with E as b_1, but in the opposite direction. This is supported by the fact that a reasonable correlation exists between E and E_{t2} in this group of compounds, and by m.o. calculations.[23] The importance of a_2 in determining the π-acceptor power of the axial base might be related to a deviation of its molecular plane from the *xz* plane of the complex. A deviation of *ca.* 4° has been found in a bis-(imidazole) complex.[24] In the case of a carbonylruthenium *meso*-porphyrin imidazole complex the base was proposed to form, as a limiting case, a π-bonded sandwich compound.[25]

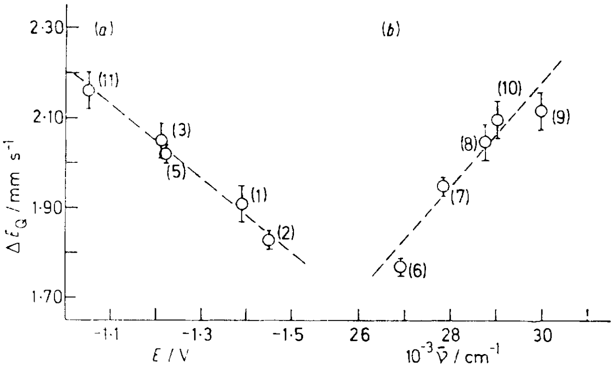
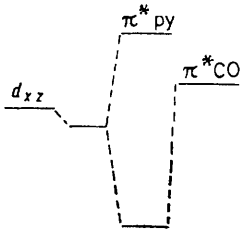


FIGURE 4 Plot of Mössbauer quadrupole splittings, ΔE_Q, against: (*a*) polarographic one-electron reduction potentials of pyridines; (*b*) the wavenumber of the first c.t. band of some pyridinium iodides

The qualitative energy diagram below summarizes the above discussion: as the π-acceptor power of the pyridine is progressively increased, it is expected that the energy of the $3d_{xz}$ metal orbital will decrease with concomitant decrease of the interaction with CO π-orbitals. The latter effect is apparently much more important, in the sense that the comparatively small stabilization of the orbitals due to the base is amplified *via* the interaction with the carbonyl π-system. A case similar to the present one, as far as the importance of the π-bond on variations in ΔE_Q is concerned, is that of the ion [Fe(CN)$_5$NO]$^{2-}$ for which formula (2) can be applied when considering only n_{xy}, n_{xz}, and n_{yz} orbital populations.[26]



Considering the high energy of the b_1 and a_2 orbitals in the group of axial ligands which includes pyridine, methyl-substituted pyridines, and aminopyridines (4-NH$_2$py is not polarographically reducible, and E_{t2} cannot be detected in the spectrum of the corresponding pyridinium salt), it is hardly surprising that π-acceptor power plays a less-important role. For these bases it is probable that ΔE_Q depends mainly on the σ-donor power, as suggested by the plot in Figure 4(*b*). A significant deviation from this relation is that of 4-NH$_2$py for which formation of a hydrogen bond, −N−H · · · O=C−, might be postulated. The positive gradient can be viewed as indicating that the main factor affecting the charge symmetry is delocalization of $3d_{xz}$ electrons on π-orbitals of CO, which increases with the σ-donor strength of the axial base. Though, *a priori*, a clear cut distinction between the σ- and π-effects of bases cannot be expected, in some cases it has been already suggested, *e.g.* for porphyrin–iron(II)–pyridine complexes.[27]

Since complexes (I) give similar spectral parameters, arising from entirely different electron properties of X, it would appear to be advisable to determine if such ' levelling effects ' also manifest themselves in the reactivity of these complexes, *e.g.* in changes in the activation energy of the decarbonylation reactions, once similarities in behaviour between the solid state and solution has been ascertained.

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