Transition Metal Complexes of Nitrogen-containing Ligands. Part 13.[1] Mössbauer Spectra of Carbonyliron Complexes containing Cyclic Diazene Ligands

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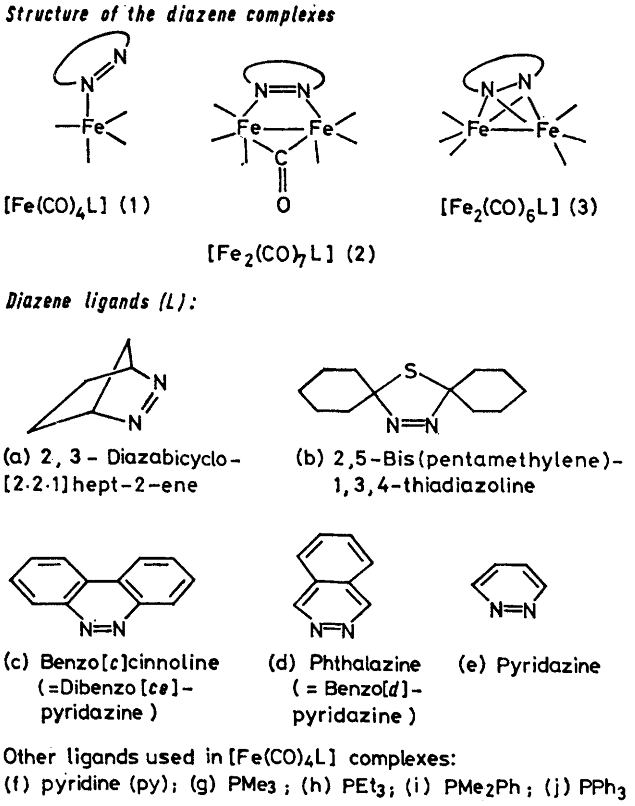
Room-temperature Mössbauer parameters are reported for carbonyliron complexes of the types [Fe(CO)$_4$L], [Fe$_2$(CO)$_7$L], and [Fe$_2$(CO)$_6$L] where L is a cyclic diazene ligand. The data for the mononuclear [Fe(CO)$_4$L] complexes are compared with those of organophosphane complexes of the same type.

IRON-57 Mössbauer studies of uncharged tetracarbonyliron complexes, [Fe(CO)$_4$L], published since the original work of Collins and Pettit,[2] have been confined to cases in which L is either a tertiary phosphorus, arsenic, or antimony ligand,[3-6] or an olefin.[7,8] In these complexes the Group 5 ligands replace an axial CO in the trigonal bipyramid of the [Fe(CO)$_5$] parent, while the olefins occupy an equatorial position. The ensuing local co-ordination symmetries for the Fe(CO)$_4$ moieties are thus C_{3v} in the former and C_{2v} in the latter complexes. This difference becomes essential in efforts to establish the dependence of the Mössbauer isomer shift S and electric quadrupole splitting ΔE_Q on the nature of the ligand L. Indeed, the approximately linear correlations between S and ΔE_Q suggested so far [2,5-7] differ even in their sign. This has left the influence of the donor–acceptor properties of the ligands on the Mössbauer parameters rather controversial.



Scheme explaining symbols and abbreviations. The notation for the complex types (1)—(3) and the diazene ligands L = a—e is identical with the one used in ref. 9

To clarify this matter it seemed desirable to obtain further data, particularly on axially substituted complexes with ligands whose properties differ substantially from those of the tertiary phosphanes. In the course of extended work [9] on carbonyliron complexes containing cyclic azo-compounds [(a),(b)] and 1,2-diazenes [(c)—(e)] we have therefore recorded the Mössbauer spectra of some complexes [(1d)—(1f), according to the Scheme given above] in which the axial ligand L is bound to iron through the lone electron pair of a nitrogen atom. For comparison, several phosphane-substituted complexes (1g)—(1j) have also been studied under identical conditions, *i.e.* at room temperature and with a source of ^{57}Co in Rh. Reasonably good agreement with earlier Mössbauer results was found in those cases where such data were available, *e.g.* for L = PEt$_3$ (1h) [2] and PPh$_3$ (1j).[2-6]

In addition to the mononuclear [Fe(CO)$_4$L] complexes (1), some binuclear complexes of the types [Fe$_2$(CO)$_7$L] (2) and [Fe$_2$(CO)$_6$L] (3) containing diazene ligands have been studied. The Mössbauer parameters of all the complexes are compiled in the Table, together with the CO stretching frequencies. In Figure 1 the quadrupole splittings are plotted against the isomer shifts for all the complexes listed in the Table.

RESULTS AND DISCUSSION

For the 14.4-keV Mössbauer resonance of ^{57}Fe, decreasing values of the isomer shift S reveal an increasing s-electron density $\rho(0)$ at the iron nucleus. The S values found for our [Fe(CO)$_4$L] complexes therefore show that $\rho(0)$ is higher in the organophosphane complexes (1g)—(1j) than in the complexes containing nitrogen ligands (1d)—(1f). The higher charge density at the iron nucleus may result from the higher σ-donor capacity of the organophosphanes or from their stronger π-acceptor behaviour, which withdraws d electrons by d_π–p_π backbonding and thus reduces the screening of the *s*-electron density. Actually, both mechanisms are expected to contribute, but their relative importance is unknown.

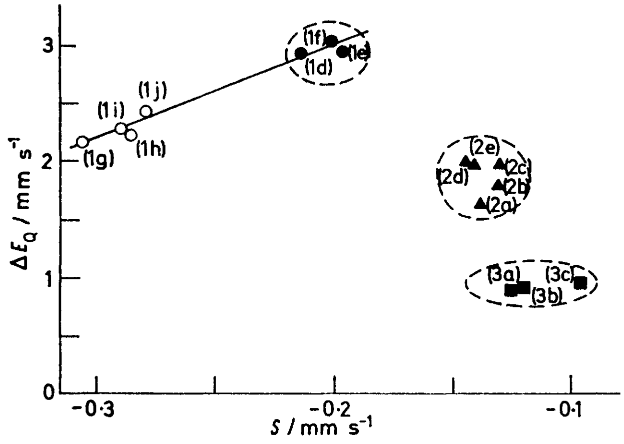


FIGURE 1 Plot of the electric-quadrupole splitting ΔE_Q against the isomer shift *S* for the three types of carbonyliron complexes studied. The isomer shift is given with respect to a source of ^{57}Co in Rh

A significant difference between the π-acceptor properties of the organophosphane ligands (g)—(j) and those containing nitrogen (d)—(f) can be assessed from the CO stretching frequencies of the [Fe(CO)$_4$L] complexes (Table and Figure 2). For the local symmetry C_{3v} of the Fe(CO)$_4$ fragment one expects three i.r.-active vibrational modes, namely $2A_1 + E$. The low-frequency absorption at *ca.* 1 920 cm^{-1} (see Figure 2) is certainly attributable to the doubly degenerate (E) vibrational mode involving the antisymmetric stretching vibration of the three equatorial CO ligands, while the absorption at *ca.* 2 040 cm^{-1} arises mainly from the symmetric $A_1(2)$ equatorial stretching motion.[10,11] The remaining $A_1(1)$ band represents essentially the stretching vibration of the single CO ligand on the three-fold axis, opposite to L. This frequency should be sensitive to the nature of L because the axial CO competes directly with L for the *d* electrons used in metal-to-ligand backbonding. Indeed the data (Table) show that the two absorption bands representing mainly vibrations of the equatorial CO ligands do not depend significantly on the nature of the ligand L, whereas the frequency of the stretching vibration of the axial CO

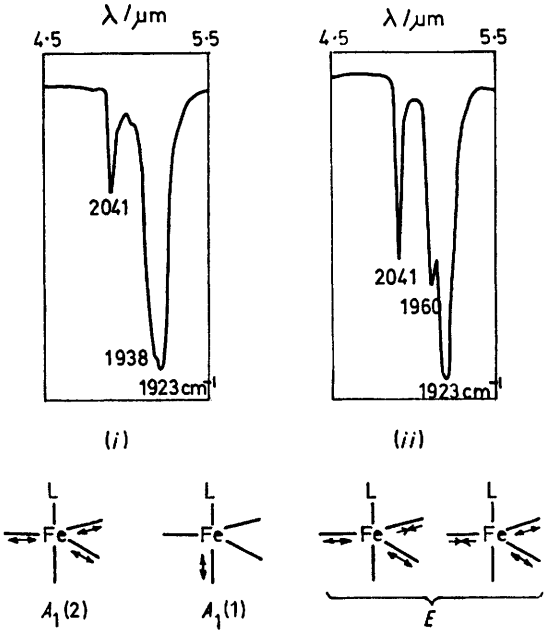


FIGURE 2 Carbonyl-region i.r. spectra of two [Fe(CO)$_4$L] complexes showing the dependence of the $A_1(1)$ absorption frequency on the nature of the ligand L. In both cases the band at 2 041 cm^{-1} is the $A_1(2)$ absorption, while the degenerate E-type band lies at 1 923 cm^{-1}. L = pyridazine (*i*) and PMe$_2$Ph (*ii*). [In non-polar solvents (hexane) the diazene complexes (1d) and (1e) possess four ν(CO) absorptions, in contrast to the expectation for C_{3v} symmetry. This has been ascribed to the existence of different conformers in solution (*cf.* A. Albini and H. Kisch, *Topics Current Chem.*, 1976, **65**, 105)]

Room-temperature Mössbauer parameters and CO stretching frequencies for the carbonyliron complexes. The values of the isomer shift *S* are given relative to the ^{57}CoRh source. To convert them into values relative to iron metal 0.110 mm s^{-1} must be added to these values. The electric-quadrupole splitting ΔE_Q is the full doublet separation

Complex	S / mm s^{-1}	ΔE_Q / mm s^{-1}	CO stretching bands (cm^{-1}) [a]			
[Fe(CO)$_4$L]						
(1d)	−0.214(5)	2.93(3)	2 041	1 937 (sh)	1 924	
(1e) [b]	−0.197(8)	2.97(2)	2 041	1 938 (sh)	1 923	
(1f) [b]	−0.195(5)	3.04(3)	2 042	1 927		
(1g)	−0.305(8)	2.18(2)	2 034	1 954	1 918	
(1h)	−0.285(3)	2.22(1)	2 036	1 957	1 919	
(1i)	−0.288(8)	2.29(1)	2 041	1 960	1 923	
(1j)	−0.279(1)	2.43(1)	2 037	1 957	1 924	
[Fe$_2$(CO)$_7$L]						
(2a)	−0.139(4)	1.64(1)	2 050	1 999, 1 977, 1 963		1 799 [c]
(2b)	−0.131(5)	1.80(1)	2 062	2 009, 1 996, 1 963		1 812 [c]
(2c)	−0.130(3)	1.99(1)	2 041	1 997, 1 975, 1 957		1 788 [c]
(2d)	−0.144(15)	2.01(3)	2 037	1 987, 1 964, 1 945		1 772 [c]
(2e) [b]	−0.141(5)	2.00(3)	2 043	1 987, 1 969, 1 950		1 779 [c]
[Fe$_2$(CO)$_6$L] [d]						
(3a) [b]	−0.125(2)	0.91(1)	2 058	2 009	1 977	
(3b)	−0.122(2)	0.92(1)	2 061	2 015	1 969	
(3c) [b]	−0.096(4)	0.99(1)	2 058	2 017	1 973	

[a] In tetrahydrofuran. [b] The molecular structure is known from X-ray determinations.[14–16,22,23] [c] Attributable to the bridging CO ligand. [d] The ' aromatic ' ligands pyridazine (e) and phthalazine (d) do not form [Fe$_2$(CO)$_6$L]-type complexes.[9]

ligand is higher in the organophosphane complexes [(1g)—(1j): 1 954—1 960 cm^{-1}] than in the complexes containing nitrogen ligands [(1d)—(1f): 1 927—1 938 cm^{-1}]. The spectra plotted in Figure 2 illustrate this behaviour very clearly. Thus the organophosphanes are obviously more successful in withdrawing electrons from the metal than the nitrogen ligands. This argument fits well into the model used by Carroll *et al.*,[5] who explained the isomer shifts in complexes containing phosphorus, arsenic, and antimony ligands in terms of a dominant σ-donor effect that is synergistically enhanced by π-acceptor bonding.

In the $[Fe(CO)_5]$ parent the electric-quadrupole coupling constant, and hence the electric-field gradient at the iron nucleus, is known to be positive.[12] This shows the dominance of the positive contributions from the electron density of the *d* and *p* electrons in the equatorial plane of the bipyramid, relative to the negative contributions from the axial electrons. When an apical CO is replaced by a ligand L having stronger (weaker) σ-donor capacity than CO, the *d*- and *p*-electron density along the molecular axis is enhanced (reduced) and, consequently, one expects the electric-quadrupole splitting ΔE_Q to become smaller (larger) than in the parent complex. This expectation is born out by the experimental data, which yield $\Delta E_Q = 2.58$ mm s^{-1} for $[Fe(CO)_5]$,[12,13] compared to *ca.* 2.3 mm s^{-1} for the substituted complexes with tertiary phosphane ligands and 3.0 mm s^{-1} for those with ligands containing nitrogen (Table).

Considering these results one can readily understand[6] the approximately linear correlation between the isomer shift and the quadrupole splitting with a positive gradient as indicated in Figure 1. This relation is essentially the same as the one reported by Carroll *et al.*[5] and Parish,[6] but the pyridine and diazene ligands extend the range beyond that of the earlier studies. Notably, this correlation cannot be expected to hold for the substitution of a ligand in the equatorial plane of the $[Fe(CO)_5]$ bipyramid. The different molecular symmetry should not greatly influence the dependence of the isomer shift on the donor–acceptor properties of the ligand, but the electric-quadrupole splitting is expected to change in the opposite direction than for axial substitution. This, indeed, explains the negative gradient of the correlation found by Korecz and Burger[7] for $[Fe(CO)_4L]$ complexes where L is an olefin bound in an equatorial position. The correlation, with a negative gradient, deduced originally by Collins and Pettit[2] for an ensemble containing complexes of both geometries would thus seem ' most fortuitous ', as has been pointed out previously.[5,8] The present results for the axially substituted complexes with ligands containing nitrogen [(1d)—(1f)] contradict this correlation more clearly than previous data.[5,6]

While the cyclic diazenes behave as unidentate two-electron ligands L in $[Fe(CO)_4L]$ complexes, they are symmetrically bound to both iron atoms in the binuclear structures $[Fe_2(CO)_7L]$ and $[Fe_2(CO)_6L]$. In all cases the Mössbauer spectra show that there is only one type of iron atom. The binuclear complexes can formally be considered as derivatives of $[Fe_2(CO)_9]$ with either two or three carbonyl bridges replaced by the diazene, which then functions as a four- or six-electron ligand. Complexes of type (2) and (3) are, indeed, prepared from $[Fe_2(CO)_9]$, but the i.r. spectra of the reaction mixtures in the CO stretching region show that mononuclear $[Fe(CO)_4L]$ is formed as an intermediate.[9]

The heptacarbonyldi-iron complexes (2) are structurally related to the mononuclear tetracarbonyliron complexes (1). According to the *X*-ray structure[14] of the pyridazine complex $[Fe_2(CO)_7(N_2C_4H_4)]$ (2e), the binuclear molecule consists of two approximately trigonal-bipyramidal moieties where the nitrogen atoms of the bridging pyridazine occupy apical positions and one equatorial CO group is shared as a bridging ligand. The hexacarbonyldi-iron complexes (3), on the other hand, contain a distorted diferradiazatetrahedrane skeleton, where the nitrogen–nitrogen axis is perpendicular to the Fe–Fe bond.[15,16]

The Mössbauer parameters of the three types of carbonyliron complexes (1)—(3) containing cyclic diazene ligands fall into characteristic regions as indicated in Figure 1. The limited number of binuclear complexes studied so far does not permit one to comment on possible correlations between isomer-shift and quadrupole-splitting data. This, however, does not impair the usefulness of Mössbauer spectroscopy as a fingerprint method during the preparation of new related carbonyliron compounds.

The isomer shifts measured for the binuclear complexes of types (2) and (3) show that the *s*-electron density $\rho(0)$ is systematically lower than in the mononuclear $[Fe(CO)_4L]$ complexes (Figure 1). It is tempting to ascribe this to the reduced number of CO acceptor ligands, of which there are 4, 3.5, and 3 per iron atom in (1), (2), and (3) respectively. However, the electron density of $[Fe_2(CO)_9]$ is even lower than in any of the complexes of type (2) and (3),[12,17] indicating that the relative isomer shifts in the different types of complex (1)—(3) are not accessible to a simple explanation.

It is remarkable that the isomer shifts *S* vary very little (0.01—0.04 mm s^{-1}) between complexes of types (2) and (3). This small variation is reminiscent of the report that the isomer shifts of the bis(μ-phosphido)-complexes $[Fe_2(CO)_8(\mu\text{-}PMe_2)_2]^n$ ($n = 0$, -1, or -2) are also surprisingly similar,[18] indicating little alteration in the charge distribution around the iron nuclei. It has been suggested[19] that the metals should be considered as ' charge transmitters ' which, qualitatively speaking, takes into account that the total electron density is distributed over the whole cluster system and, if necessary, is preferentially trapped in the carbonyl electron sinks. A similar mechanism might explain the fact that the isomer shift varies only slightly on going from type (2) to type (3) complexes.

EXPERIMENTAL

All the complexes studied can be synthesized in solution by the reaction of $[Fe_2(CO)_9]$ with the ligand L. The

$[Fe(CO)_4L]$ complexes containing phthalazine (1d),[20] pyridazine (1e),[21,22] and pyridine (1f)[23] were prepared in benzene and recrystallized three to five times from n-hexane at −78 °C. Complexes (1g)—(1j) (*cf.* references given in refs. 5 and 24) were obtained by stirring a suspension of $[Fe_2(CO)_9]$ in benzene in the presence of the organophosphane and recrystallized from tetrahydrofuran–hexane. The triphenylphosphane complex $[Fe(CO)_4(PPh_3)]$ (1j) was separated from $[Fe(CO)_3(PPh_3)_2]$ by vacuum sublimation at 150—160 °C. The $[Fe_2(CO)_7L]$ complexes (2a)—(2e) are all described in ref. 9. The $[Fe_2(CO)_6L]$ complexes (3a),[9,25,26] (3b),[25] and (3c)[9,26] are formed as by-products during the synthesis of the corresponding $[Fe_2(CO)_7L]$ complexes which decarbonylate at elevated temperatures.[9]

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