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## MÖSSBAUER STUDIES OF SOME HEXA-COORDINATE IRON(II) COMPLEXES

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### Summary

Mössbauer parameters are analysed in terms of the point-charge model and compared with the CN stretching frequency values for a number of low-spin iron(II) complexes.

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### Introduction

Isocyanides and phosphines are well known to behave as good  $\sigma$ -donor and  $\pi$ -acceptor ligands. A number of hexa-coordinated low-spin iron(II) complexes of the types  $[\text{FeCl}(\text{CNR})_{5-n}\text{L}_n]$ ,  $[\text{Fe}(\text{CNR})_3\text{L}_3](\text{ClO}_4)_2$ , and  $\text{FeCl}_2(\text{CNR})_4$  ( $\text{L} = \text{PPh}(\text{OEt})_2$  or  $\text{PPh}_3$ ;  $\text{R} = \text{alkyl or aryl group}$ ;  $n = 3, 2, 0$ ) have been recently prepared [1]. The presence of an anionic ligand and the nature of the neutral ligands seem to be more important than steric hindrance in determining the stability and the formulae of these compounds [1].

This paper reports Mössbauer parameters for these complexes. The Mössbauer quadrupole splitting ( $QS$ ) and centre shift ( $CS$ ) can be very useful in investigating structure and bonding in the solid state. Furthermore, the  $QS$  of hexa-coordinated low-spin iron(II) complexes can help to characterize *cis* and *trans* isomers while the  $CS$  can be related to the bonding ability of the ligands, so that the two parameters give complementary informations on the nature of  $\nu$ - and  $\pi$ -bonding.

### Experimental

The compounds reported in Table 1 were prepared as perchlorate salts by published methods [1].

The spectra were recorded at liquid nitrogen temperature (measured tem-

perature 85 K) with the  $^{57}\text{Co}$  in Pt source and the spectrometer described earlier [2].

All the absorbers contained ca. 5 mg/cm<sup>2</sup> of natural iron. The reproducibility was 0.01 mm/sec. The calibration was by means of hyperfine structure of iron foil enriched in  $^{57}\text{Fe}$  isotope and with sodium nitroprusside, to which isomer shifts (mm/sec) were referred.

The absorbers were powders compressed between aluminized Mylar foils in aluminum containers. Metallic indium was used to fix the container in the hole of the cooling system. The temperature was measured by a constantan-iron thermocouple. Mössbauer parameters were evaluated by the least squares method [3].

The IR spectra of free isocyanides in methylene chloride were recorded with a Perkin-Elmer 621 spectrophotometer.

Attempts to determine the sign of  $QS$  of compound II (Table 1), by using the magnetic field technique, at room temperature were unsuccessful [4]. The degeneracy of the nuclear levels was poorly removed in an applied longitudinal magnetic field of 20 kOe.

## Results and discussion

The Mössbauer parameters (mm/sec) are summarized in Table 1, along with the  $\nu(\text{CN})$  stretching frequencies ( $\text{cm}^{-1}$ ) of coordinated and free isocyanides.

The  $QS$  ratios of complexes XII, XI, and X (1.73/1/0.88) are very close to those predicted by the point-charge model (2/-1/1) for the *trans*-, *cis*- $\text{FeA}_4\text{B}_2$  and  $\text{FeA}_5\text{B}$  species [5]. Consequently, a *cis*-structure can be assigned to the red complex XI, while the violet compound XII has a *trans*-structure. The experimental  $QS$  values, at 80 K, for the complexes *trans*-, *cis*- $\text{FeCl}_2(4\text{-MeOC}_6\text{H}_4\text{NC})_4$  and  $[\text{FeCl}(4\text{-MeOC}_6\text{H}_4\text{NC})_5]\text{ClO}_4$  are: +1.59; -0.83; +0.70 mm/sec, respectively

TABLE 1

MÖSSBAUER PARAMETERS (mm/sec) AND  $\nu(\text{CN})$  FREQUENCIES OF IRON(II) COMPLEXES DISCUSSED IN THIS PAPER

Compound <sup>a</sup>	CS	QS	$\nu(\text{CN})$ ( $\text{cm}^{-1}$ ) <sup>b</sup> compound		$\nu(\text{CN})$ ( $\text{cm}^{-1}$ ) free isocyanide
(I) $[\text{FeCl}(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2\text{L}_3]\text{ClO}_4$	0.25	(+) 0.55	2153 s	2100 s	2129 <sup>c</sup>
(II) $[\text{FeCl}(2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC})_2\text{L}_3]\text{ClO}_4$	0.30	(+) 0.75	2142 s	2104 s	2123
(III) $[\text{FeCl}(2\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2\text{L}_3]\text{ClO}_4$	0.32	(+) 0.44	2151 s	2103 s	2126
(IV) $[\text{FeCl}(\text{C}_6\text{H}_5\text{NC})_2\text{L}_3]\text{ClO}_4$	0.34	(+) 0.54	2157 s	2107 s	2130
(V) $[\text{FeCl}(4\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_2\text{L}_3]\text{ClO}_4$	0.38	(+) 0.62	2142 s	2094 s	2128
(VI) $[\text{FeCl}(4\text{-CH}_3\text{OC}_6\text{H}_4\text{NC})_2\text{L}_3]\text{ClO}_4$	0.46	(+) 0.51	2156 s	2113 s	2128
(VII) $[\text{Fe}(\text{C}_6\text{H}_5\text{NC})_3\text{L}_3](\text{ClO}_4)_2$	0.20	0.38	2204 s	2170 s	2145
(VIII) $[\text{FeCl}(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_3\text{L}'_2]\text{ClO}_4$	0.37	0.74	2164 m	2125 s	2129 <sup>c</sup>
(IX) $[\text{FeCl}(\text{C}_6\text{H}_5\text{NC})_2]\text{ClO}_4$	0.20	(+) 0.80	2214 w	2173 s	2130
(X) $[\text{FeCl}(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_5]\text{ClO}_4$	0.29	(+) 0.78	2216 w	2173 s	2129 <sup>c</sup>
(XI) $\text{FeCl}_2(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_4$ <sup>d</sup> (red)	0.45	(-) 0.89	2193 w	2151 s	2129 <sup>c</sup>
(XII) $\text{FeCl}_2(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_4$ <sup>d</sup> (violet)	0.44	(+) 1.54			2129 <sup>c</sup>

<sup>a</sup> L = PPh(OEt)<sub>2</sub>, L' = PPh<sub>3</sub>. <sup>b</sup> Only the principal bands are listed here. <sup>c</sup> From ref. 6. <sup>d</sup> Prepared as reported in ref. 7.

[8,9]. The sign to the *QS* data of the complexes IX-XII are assigned by analogy. Assuming the partial quadrupole splitting (p.q.s.) of  $\text{Cl}^-$  ( $-0.30$  mm/sec) [9] as the reference value, a p.q.s. of  $-0.70$  mm/sec is calculated from the *QS* of compounds IX-XII for both ligands  $4\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$  and  $\text{C}_6\text{H}_5\text{NC}$ . This value is in agreement with that of  $-0.69$  mm/sec reported for the isocyanide ligands [10].

From IR and PMR data a *cis*-geometry was assigned to compounds I-IV [1]. On this basis and with the p.q.s. previously reported, a positive sign for the *QS* values of these compounds is predicted by the point-charge approximation.

The axial ligand field and the preferential delocalization of the electrons in certain directions are responsible for the *QS*. A positive field gradient means that the electrons form a pancake shaped environment around the iron nucleus. This is reasonable because the strong charge on the Z axis due to the  $\text{Cl}^-$  ion and the axial ligand, compresses the electrons in the XY plane. In addition the strong  $\pi$ -acceptor ability of isocyanide and phosphine ligands in the XZ and YZ orbitals leads to more delocalisation of these non-bonding electrons than of the XY non-bonding electrons (i.e.,  $N_{XZ-YZ} > N_{XZ} = N_{YZ}$ ). Thus there is an excess of negative charge in the XY plane near the iron nucleus giving a positive field gradient.

From the PMR and IR data a *cis*-structure has been suggested for compound VII [1]. The calculated *QS* value for such a structure is zero on the basis of the point-charge approximation [11], while the experimental value is  $0.38$  mm/sec. However, this value is the minimum in the set, and can be explained by assuming that the structure of the compound deviates from octahedral microsymmetry. Because of the unknown sign, the point-charge model does not allow a unique assignment of the structure.

The *CS* data reported in Table 1 are within the usual range for iron(II) hexacoordinated low-spin complexes. A closer look reveals the following features; the *CS* values increase from compound I to compound VI, so that the  $\sigma + \pi$  bonding ability of the isocyanide ligands increases in the reverse order. The relatively small values seem to indicate that the  $\sigma$ -donor properties contribute predominantly to the bonding of the isocyanide ligands. This general predominance of the  $\sigma$ -donor properties of the isocyanide ligands is also supported by the IR data. The symmetric  $\nu(\text{CN})$  frequencies for the complexes are higher than those for the corresponding free isocyanide ligands.

As for complex VII, the *CS* value is consistent with previous suggestion that  $\sigma$ -donor ability of the cyclohexyl isocyanide is higher than that of the alkyl isocyanides [1]. The increase in the *CS* from the complex X to the complexes XI and XII can be related to the  $\pi$ -donation of  $\text{Cl}^-$  ligand, which increases the shielding and decreases the *s*-electron density in the last two complexes. The *CS* value of IX is smaller than that of X; the corresponding value of I is also smaller than that of X, while that of compound IV is higher than that of compounds IX and X.

The  $\nu(\text{CN})$  frequencies of the complexes IX and X are about  $86\text{ cm}^{-1}$ , and those of the complexes I and IV are about  $26\text{ cm}^{-1}$  higher than the corresponding frequencies in the free isocyanide ligands. This can be attributed to the presence of the phosphine ligands L, which decrease the  $\sigma$ -donor ability of the isocyanides. On the other hand, the *CS* data for the same complexes indicate that the  $\pi$ -acceptor properties of the 4-methylphenyl isocyanide increase from the complex X to the compound I and for the phenyl isocyanide decrease from

the derivative IX to the derivative IV. Similar observations hold when the complex VI is compared with the corresponding chloropentakis(4-methoxyphenyl isocyanide)iron(II).

It is evident that CS data provide a useful tool for determining the  $\pi$ -acceptor ability of isocyanide ligands in these complexes.

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