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MÖSSBAUER STUDIES OF SOME NEW HEXACOORDINATE IRON(II) COMPLEXES WITH ISOCYANIDES, PHOSPHINES AND HALIDES

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Summary

Mössbauer parameters have been determined, at 80 K, for some new complexes of the type $[FeX(CNR)_{5-n}L_n]ClO_4$ (n = 3, 2, 0; X = Br^-, I^-; L = $PhP(OEt)_2$; R = 4-$CH_3C_6H_4$, 2-$CH_3C_6H_4$, C_6H_5, 4-$NO_2C_6H_4$, 4-$CH_3OC_6H_4$, 2,6-$(CH_3)_2C_6H_3$ and $[FeX_2(4\text{-}CH_3C_6H_4NC)_4]$. Treatment by the point-charge model has been carried out to rationalize quadrupole splitting and centre shift values for chloro, bromo and iodo derivatives. The structural assignments, by pqs parameters, are consistent with X-ray and IR data.

Introduction

A number of hexacoordinate low-spin iron(II) complexes of the type $[FeX(CNR)_{5-n}L_n]ClO_4$, $[FeX_2(CNR)_4]$ (L = $PPh(OEt)_2$, PPh_3; R = aryl group; n = 3, 2, 0; X = Cl^-) have been recently prepared [1]. Some information on the molecular and electronic structure of the chloro derivatives has been reported [2]. The molecular structures of $[FeCl(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$ [3] and $[FeCl(4\text{-}CH_3C_6H_4NC)_3(PPh_3)_2]FeCl_4$ [4] have been determined by X-ray analysis.

This paper reports analytical data, Mössbauer parameters, IR and PMR data for the corresponding bromo and iodo derivatives as a study of the molecular and electronic structure of the halide complexes. The pqs * values have been used

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* pqs = partial quadrupole splitting.

for structural predictions, and the pcs * and IR data to explain the bonding properties of the ligands [5—10].

Experimental

The solvents were purified, dried, and distilled under a stream of nitrogen. Reagent grade $FeX_2 \cdot 6\ H_2O$ was dried in a vacuum oven under nitrogen at 110°C or by treatment with 2,2-dimethoxypropane. Diethyl phenylphosphonite was prepared by the method of Rabinowitz et al. [11]. Substituted phenyl isocyanides were obtained by the phosgene method [12] or by an improved Hofman carbylamine synthesis [13].

The chloro derivatives were prepared by a published method [1]. The bromo- and iodo-bis(isocyanide)tris(diethylphenylphosphonite)-iron(II) perchlorates, (see Table 1) were prepared analogously from anhydrous $FeBr_2$ or FeI_2.

The bromotris(4-methylphenylisocyanide)bis(triphenylphosphine)iron(II) perchlorate was prepared by adding 4-methylphenyl isocyanide (50 ml, 42 mmol) to a mixture of anhydrous $FeBr_2$ (10 mmol), triphenylphosphonite (12.5 g, 45 mmol) and 50 ml of anhydrous acetone. The exothermic reaction was allowed to proceed without cooling. After 1 h, anhydrous lithium perchlorate (1.03 g, 10 mmol) was added and the mixture was concentrated. Precipitation was effected by addition of alcohol/ether, and the complexes were recrystallized from acetone/alcohol.

The $[FeX_2(4\text{-}CH_3C_6H_4NC)_4]$ compounds were obtained by Malatesta's method [14].

The new bromo and iodo complexes of Table 2 were stable as solids and in organic solvents. The elemental analyses are not sensitive to contamination by iron(III). A purification of the recrystallized compounds was carried out by chromatography on silica gel using ethanol as eluent.

IR spectra of dichloromethane solutions were recorded on a Perkin—Elmer 621 spectrophotometer. Of the two typical bands of uncoordinated perchlorate ion, the one at 1050—1170 cm^{-1} is masked by strong absorptions in this region due to the phosphine ligands; the other, at 630 cm^{-1}, is always present. The absence of absorption in the 1600—1800 cm^{-1} region indicates that bridging isocyanides are absent. The far-infrared spectra were recorded on a Beckman IR 11 instrument in the 80—500 cm^{-1} region.

PMR measurements were made with Hitachi Perkin—Elmer, Bruker HFX-10 and Varian HR-220 instruments using TMS as internal reference. Conductivities of 10^{-3} M solutions of the complexes in nitrobenzene, at 25°C, were measured with a LKB bridge.

Mössbauer spectra were recorded at 80 K by a constant-acceleration spectrometer using a ^{57}Co in Pt matrix source at room temperature. The velocity scale was calibrated with a 99.99% ^{57}Fe foil. The centre shift values were referred to nitroprusside. The reproducibility was 0.01 mm s^{-1}. The absorber densities were 4—6 mg natural iron per cm^2. Attention was paid to obtain absorbers with a high degree of homogeneity.

600 Channels of the 4096-MCA were used. The contents were collected by a teletype tape punch and by an X—Y recorder. A representative experimental

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* pcs = partial centre shift.

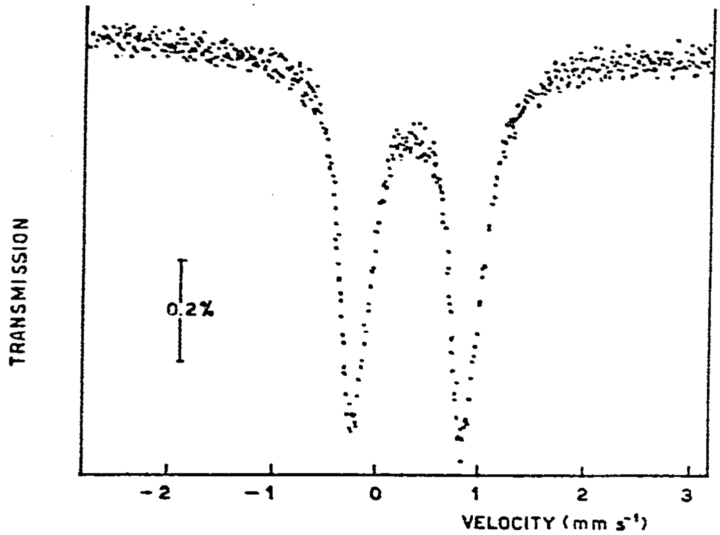


Fig. 1. Mössbauer spectrum of [FeBr(2,6-$(CH_3)_2C_6H_3NC)_2L_3]ClO_4$.

spectrum is shown in Fig. 1. All spectra were fitted without constraints, to two Lorentzian line shapes by a modified version of the program [15] adapted for the CDC Cyber 76 computer. The computed full width ranges from 0.28 to 0.35 mm s^{-1}. The most part of the spectra was asymmetric; the average ratio is less than 1.1 for random polycrystalline samples.

Results and discussion

The relation $CS = 0.21 + \Sigma_i(\text{pcs})_i$ [5] is used to rationalize the measured centre shift of Table 1. The employed pcs values, at 80 K in mm s^{-1}, are: $Cl^- = 0.10$, $Br^- = I^- = 0.13$, 4-$CH_3OC_6H_4NC = 0.00$, $PPh_3 = 0.07$ [9]. A working value of 0.01 mm s^{-1}, comparable to $P(OEt)_3 = 0.04$ and $P(OMe)_3 = 0.03$ mm s^{-1} [9] is assigned to the unknown pcs of the $PhP(OEt)_2$ ligand. To derive an average pcs for 4-$CH_3C_6H_4NC$ we use the three compounds X of Table 1: a value of −0.02 mm s^{-1} is found. The pcs values of 2-$CH_3C_6H_4NC$, C_6H_5NC, 4-$NO_2C_6H_4NC$, 2,6-$(CH_3)_2C_6H_3NC$ are unknown, and working value of −0.02 mm s^{-1} is assumed for all three ligands.

The predicted centre shift values are in brackets in Table 1. These are in agreement with measured centre shift values: the $|CS_{\text{obs.}} - CS_{\text{cal.}}|$ differences are less than 0.11 mm s^{-1} for all halide derivatives of Table 1.

The point-charge model is used to rationalize the quadrupole splitting data. The employed pqs data, at 80 K in mm s^{-1}, are: $Cl^- = -0.30$, $Br^- = -0.28$, $I^- = -0.29$, 4-$CH_3OC_6H_4NC = -0.70$, $PPh_3 = -0.53$ [9]. The value of −0.63 mm s^{-1}, the value of pqs of $P(OEt)_3$ [9], is assigned to the unknown pqs of the $PhP(OEt)_2$ ligand. We use the three compounds X of Table 1 to derive an average pqs value for 4-$CH_3C_6H_4NC$: a value of −0.70 mm s^{-1} is found. Because the pqs values for 4-$CH_3OC_6H_4NC$, 4-$CH_3C_6H_4NC$, C_6H_5NC ligands are −0.70 mm s^{-1}, we assume, tentatively, this value for the unknown pqs of the 2-$CH_3C_6H_4NC$, C_6H_5NC, 4-$NO_2C_6H_4NC$, 2,6-$(CH_3)_2C_6H_3NC$ ligands.

TABLE 1

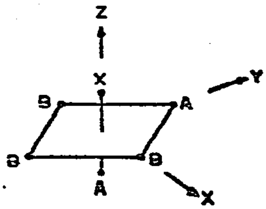
OBSERVED AND CALCULATED (IN PARENTHESES) MÖSSBAUER PARAMETERS AT 80 K

	Compound [a]	CS (mm s^{-1})			QS (mm s^{-1})		
		X = Cl [b]	X = Br	X = I	X = Cl [b]	X = Br	X = I
I	$[FeX(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	0.25	0.25	0.25	0.55	0.59	0.56
		(0.31)	(0.34)	(0.34)	(+0.60)	(+0.64)	(+0.62)
II	$[FeX(2\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	0.32	0.30	0.25	0.44	0.54	0.52
		(0.31)	(0.34)	(0.34)	(+0.60)	(+0.64)	(+0.62)
III	$[FeX(C_6H_5NC)_2L_3]ClO_4$	0.34	0.29	0.23	0.54	0.64	0.67
		(0.31)	(0.34)	(0.34)	(+0.60)	(+0.64)	(+0.62)
IV	$[FeX(4\text{-}NO_2C_6H_4NC)_2L_3]ClO_4$	0.38	0.25	−0.29	0.62	0.75	0.56
		(0.31)	(0.34)	(0.34)	(+0.60)	(+0.84)	(+0.62)
V	$[FeX(4\text{-}CH_3OC_6H_4NC)_2L_3]ClO_4$	0.46	0.29	0.31	0.51	0.67	0.61
		(0.35)	(0.38)	(0.38)	(+0.60)	(+0.64)	(+0.62)
VI	$[FeX(2,6\text{-}(CH_3)_2C_6H_3NC)_2L_3]ClO_4$	0.30	0.24	—	0.75	1.07	—
		(0.31)	(0.34)		(+0.80)	(+0.87)	
VII	$[FeX(4\text{-}CH_3C_6H_4NC)_3L'_2]ClO_4$	0.37	0.32	—	0.74	0.85	—
		(0.40)	(0.43)		(−0.75)	(−0.77)	
VIII	$[FeX(4\text{-}CH_3C_6H_4NC)_5]ClO_4$	0.29	0.25	0.29	0.78	0.75	0.92
		(0.22)	(0.25)	(0.25)	(+0.80)	(+0.84)	(+0.82)
IX	$[FeX_2(4\text{-}CH_3C_6H_4NC)_4]$	0.45	0.44	0.34	0.89	0.78	0.76
		(0.34)	(0.40)	(0.40)	(−0.80)	(−0.84)	(−0.82)
X	$[FeX_2(4\text{-}CH_3C_6H_4NC)_4]$	0.44	0.32	0.38	1.54	1.68	1.70
		(0.34)	(0.40)	(0.40)	(+1.60)	(+1.68)	(+1.64)

[a] L = $PPh(OEt)_2$, L′ = PPh_3. [b] From ref. 2.

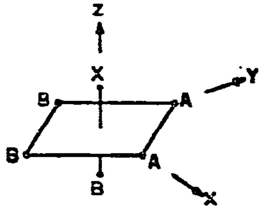
For $[\mathrm{FeXA_2B_3}]^+$ complexes I—VI three geometrical isomers are possible with the following EFG expressions:

I, *mer*-isomer



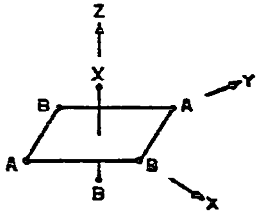
$$V_{XX} = \{3[B]-[X]-2[A]\}e$$
$$V_{YY} = \{[A]-[X]\}e$$
$$V_{ZZ} = \{2[X]+[A]-3[B]\}e$$

II, *fac*-isomer
II, *fac*-isomer



$$V_{XX} = \{[A]-[X]\}e$$
$$V_{YY} = \{[A]-[X]\}e$$
$$V_{ZZ} = \{2[X]-2[A]\}e$$

III, all-*trans*-isomer



$$V_{XX} = \{3[B]-2[A]-[X]\}e$$
$$V_{YY} = \{4[A]-3[B]-[X]\}e$$
$$V_{ZZ} = \{2[X]-2[A]\}e$$

In order to preserve the convention $|V_{ZZ}| \geqslant |V_{YY}| \geqslant |V_{XX}|$, for the three isomers of $[\mathrm{FeX(4\text{-}CH_3C_6H_4NC)_3L'_2}]\mathrm{ClO_4}$ ($X = \mathrm{Cl^-}, \mathrm{Br^-}$), the choice of the axis is $\begin{pmatrix} X & Y & Z \\ Z & X & Y \end{pmatrix}$.

The calculated η and *QS* values for the isomers of the halides I—VII are reported in Table 2 with the measured splittings for comparison purpose. Some structural assignments may be made from Table 2, taking ±0.20 mm $\mathrm{s^{-1}}$ as satisfactory agreement between observed and predicted *QS* magnitudes [9,10].

By structural use of the pqs, the compounds $[\mathrm{FeX(4\text{-}CH_3C_6H_4NC)_2L_3}]\mathrm{ClO_4}$ ($X = \mathrm{Cl^-}, \mathrm{Br^-}, \mathrm{I^-}$), $[\mathrm{FeX(2\text{-}CH_3C_6H_4NC)_2L_3}]\mathrm{ClO_4}$ ($X = \mathrm{Cl^-}, \mathrm{Br^-}, \mathrm{I^-}$), $[\mathrm{FeX(C_6H_5NC)_2L_3}]\mathrm{ClO_4}$ ($X = \mathrm{Cl^-}, \mathrm{Br^-}$), $[\mathrm{FeX(4\text{-}CH_3OC_6H_5NC)_2L_3}]\mathrm{ClO_4}$ ($X = \mathrm{Cl^-}, \mathrm{I^-}$), $[\mathrm{FeI(4\text{-}NO_2C_6H_5NC)_2L_3}]\mathrm{ClO_4}$ have *mer*-structures (cf. Table 2). For $[\mathrm{FeI(C_6H_5NC)_2L_3}]\mathrm{ClO_4}$ comples a *mer*-structure is also suggested. The $[\mathrm{FeBr(4\text{-}CH_3OC_6H_4NC)_2L_3}]\mathrm{ClO_4}$, $[\mathrm{FeCl(4\text{-}NO_2C_6H_4NC)_2L_3}]\mathrm{ClO_4}$ compounds have not all-*trans*-structure but probably a *mer*-structure.

It is not possible, by Mössbauer data alone, to define the geometrical arrangement of $[\mathrm{FeBr(4\text{-}NO_2C_6H_4NC)_2L_3}]\mathrm{ClO_4}$ from the small differences between predicted and measured quadrupole splitting (cf. Table 2). However IR measurements seem to exclude the all-*trans*-structure (cf. Table 3).

The Mössbauer structural prediction for $[\mathrm{FeCl(4\text{-}CH_3C_6H_4NC)_2L_3}]\mathrm{ClO_4}$ is consistent with the recent X-ray analysis (cf. Fig. 2). Bond angles, in the iron environment of this compound, show small departures from ideal octahedral geometry as they are in the range 85.70—95.40° [3]. IR data in solution, suggesting a *cis*-arrangement for the two isocyanide ligands [1], are consistent with the

(Continued on p. 334)

TABLE 2

CALCULATED QUADRUPOLE SPLITTINGS (mm s^{-1}) AND η VALUES FOR THE THREE ISOMERS OF THE $[FeXA_2B_3]ClO_4$ COMPOUNDS

Compound [a]	Measured	Structure I		Structure II	Structure III	
		QS	η	*QS*	*QS*	η
$[FeCl(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	0,55	+0,60	0,35	+0,80 [b]	+0,84 [b]	0,52
$[FeBr(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	0,59	+0,64	0,35	+0,84 [b]	+0,87 [b]	0,50
$[FeI(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	0,56	+0,62	0,34	+0,82 [b]	+0,85 [b]	0,51
$[FeCl(2\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	0,44	+0,60	0,35	+0,80 [b]	+0,84 [b]	0,52
$[FeBr(2\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	0,54	+0,64	0,33	+0,84 [b]	+0,87 [b]	0,50
$[FeI(2\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	0,52	+0,62	0,34	+0,82 [b]	+0,85 [b]	0,51
$[FeCl(C_6H_5NC)_2L_3]ClO_4$	0,54	+0,60	0,35	+0,80 [b]	+0,84 [b]	0,52
$[FeBr(C_6H_5NC)_2L_3]ClO_4$	0,64	+0,64	0,33	+0,84 [b]	+0,87 [b]	0,50
$[FeI(C_6H_5NC)_2L_3]ClO_4$	0,67	+0,62	0,34	+0,82	+0,85	0,51
$[FeCl(4\text{-}NO_2C_6H_4NC)_2L_3]ClO_4$	0,62	+0,60	0,35	+0,80	+0,84 [b]	0,52
$[FeBr(4\text{-}NO_2C_6H_4NC)_2L_3]ClO_4$	0,75	+0,64	0,33	+0,84	+0,87	0,50
$[FeI(4\text{-}NO_2C_6H_4NC)_2L_3]ClO_4$	0,56	+0,62	0,34	+0,82 [b]	+0,85 [b]	0,51
$[FeCl(4\text{-}CH_3OC_6H_4NC)_2L_3]ClO_4$	0,51	+0,60	0,35	+0,80 [b]	+0,84 [b]	0,52
$[FeBr(4\text{-}CH_3OC_6H_4NC)_2L_3]ClO_4$	0,67	+0,64	0,33	+0,84 [b]	+0,87 [b]	0,50
$[FeI(4\text{-}CH_3OC_6H_4NC)_2L_3]ClO_4$	0,61	+0,62	0,34	+0,82 [b]	+0,85 [b]	0,51
$[FeCl(2,6\text{-}(CH_3)_2C_6H_3NC)_2L_3]ClO_4$	0,75	+0,60	0,35	+0,80	+0,84	0,52
$[FeBr(2,6\text{-}(CH_3)_2C_6H_3NC)_2L_3]ClO_4$	1.07	+0,64 [b]	0,33	+0,84 [b]	+0,87	0,50
$[FeCl(4\text{-}CH_3C_6H_4NC)_3L'_2]ClO_4$	0,74	+1,01 [b]	0,53	+0,46 [b]	−0,75	0,24
$[FeBr(4\text{-}CH_3C_6H_4NC)_3L'_2]ClO_4$	0.85	+1.05	0.50	+0,50 [b]	−0.77	0.32

[a] η = 0 unless otherwise shown. [b] $\| QS_{\text{meas.}}| - |QS_{\text{calc.}}\| > 0{,}20$ mm s^{-1} (tolerance limit).

TABLE 3

ν(CN) STRETCHING FREQUENCIES OF COORDINATED AND FREE ISOCYANIDES IN CH_2Cl_2 SOLUTION AND ν(FeX) FAR-INFRARED STRETCHING FREQUENCIES (cm^{-1})

Compound	Coordinated isocyanides[a]						Free isocyanides[c]
	X = Cl[b]	ν(FeCl)	X = Br	ν(FeBr)	X = I	ν(FeI)	
$[FeX(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	2153s 2110s	240	2157s 2115s	164	2151s 2114s	135	2129
$[FeX(2\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	2150s 2104s	239	2153s 2107s	165	2147s 2108s	137	2126
$[FeX(C_6H_5NC)_2L_3]ClO_4$	2157s 2107s	244	2154s 2110s	166	2151s 2112s	141	2130
$[FeX(4\text{-}NO_2C_6H_4NC)_2L_3]ClO_4$	2142s 2094s	238	2145s 2097s	161	2138s 2096s	130	2128
$[FeX(4\text{-}CH_3OC_6H_4NC)_2L_3]ClO_4$	2156s 2113s	241	2157s 2118s	160	2154s 2118s	131	2128
$[FeX(2,6\text{-}(CH_3)_2C_6H_3NC)_2L_3]ClO_4$	2142s 2097s	237	2154w 2113s	159	— —	—	2123
$[FeX(4\text{-}CH_3C_6H_4NC)_3L'_2]ClO_4$	2164m 2125s	238	2170w 2129s	160	— —	—	2129
$[FeX(4\text{-}CH_3C_6H_4NC)_5]ClO_4$	2216w 2173s	—	2212w 2169s	—	2210w 2163s	—	2129
$[FeX_2(4\text{-}CH_3C_6H_4NC)_5]$	2193w 2151s	—	2193w 2150sh	—	2190w 2146s	—	2129

[a] Only the principal bands are listed here. [b] From ref. 1. [c] From ref. 2.

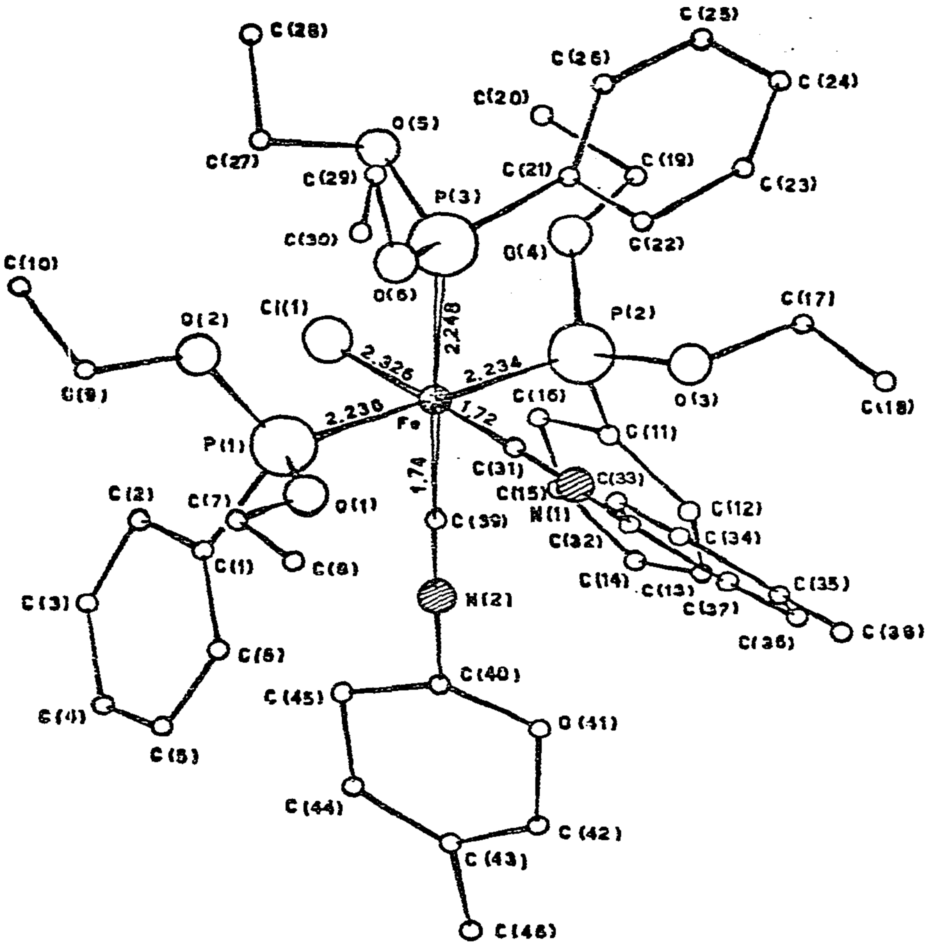


Fig. 2. Clinographic projection of the structure of $[FeCl(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$ with bond lengths in the coordination polyhedron.

structural assignment. Probably all the compounds I—V, for which the Mössbauer spectroscopy indicate a *mer*-structure, are isostructural. The IR spectra of the chloro derivatives I—V show two strong absorptions of roughly equal intensity (Table 4) attributed to the symmetric and antisymmetric stretching modes of the CN's indicating a *cis*-isocyanide arrangement. The IR spectra of the bromo and iodo derivatives are similar (Table 3), but the band at the highest frequency is a little weaker than the other, perhaps because of molecular distortions.

No structure can be excluded for $[FeCl(2,6\text{-}(CH_3)_2C_6H_3NC)_2L_3]ClO_4$ but a *fac*-structure is suggested (cf. Table 2). In contrast the $[FeBr(2,6\text{-}(CH_3)_2\text{-}C_6H_3NC)_2L_3]ClO_4$ complex has all-*trans*-structure. The IR spectrum of the chloro derivative shows two strong absorptions of roughly equal intensities at 2142 and 2097 cm^{-1}. In the bromo derivative the same symmetric and antisymmetric frequencies are shifted to 2154 and 2113 cm^{-1} (cf. Table 3) with 1/20 ratio of the intensities. The predicted *fac*-structure for $[FeCl(2,6\text{-}(CH_3)_2C_6H_3NC)_2\text{-}$

$L_3]ClO_4$ and all-*trans*-structure for $[FeBr(2,6\text{-}(CH_3)_2C_6H_3NC)_2L_3]ClO_4$ accounts for the large magnitude of their measured quadrupole splittings with respect to derivatives I—VI of Table 1.

The $[FeCl(4\text{-}CH_3C_6H_4NC)_3L'_2]ClO_4$ derivative has an all-*trans*-structure (cf. Table 2). This Mössbauer prediction is in agreement with the results of X-ray analysis, with a small departure from ideal geometry [4]. The PMR data, showing two singlets (1/2) at τ 7.74 and 7.66 ppm due to the isocyanide protons, do not allow differentiation of the three isomers [1]. The *fac*-molecular structure appears to be excluded, and an all-*trans*-structure is indicated for the $[FeBr(4\text{-}CH_3C_6H_4NC)_3L'_2]ClO_4$ compound by the pqs criterion, as it is for the chloro derivative (cf. Table 2).

Within the limits of point-charge model, a positive sign may be assigned to all the measured quadrupole splitting values of compounds I—VI of Table 1, because all the calculated quadrupole splittings of the three isomers of the chloro, bromo and iodo derivatives have positive sign (cf. Table 2). This is in agreement with a previous assignment for the chloro derivatives [2]. A negative sign can be assigned to the measured *QS* of the chloro and bromo derivatives VII (cf. Table 2).

Calculated quadrupole splittings for the VIII and IX compounds are shown in brackets in Table 1. For comparison purpose also the predicted *QS* values of the compounds X are also listed. The results indicate a positive sign for the measured *QS* values of the compounds VIII, X and a negative sign for the quadrupole splittings of compounds IX (cf. Table 1) in agreement with a previous assignment for the chloro derivatives [2].

The measured *QS* ratios of chloro, bromo and iodo derivatives VIII, IX, X of Table 1 (0.88/1/1.73) [2], (0.69/1/2.15), (1.21/1/2.24), respectively, are close to those predicted by the point-charge model (1/—1/2) [6]. Consequently a *cis*-structure may be assigned to all the derivatives IX and a *trans*-structure to all the derivatives X. This assignment is consistent with IR data and with the measured quadrupole splittings of the similar compounds $[FeCl(4\text{-}CH_3OC_6H_4NC)_5]ClO_4$, *cis*- and *trans*-$[FeCl(4\text{-}CH_3OC_6H_4NC)_4]ClO_4$: +0.73, —0.78, +1.55 mm s^{-1}, respectively [8].

The predicted quadrupole splitting values for all the compounds are shown in brackets in Table 1. The agreement between the magnitudes of measured and calculated *QS* values is good: the differences $\|QS_{\text{obs.}}| - |QS_{\text{calc.}}\|$ are less than 0.13 mm s^{-1}.

In the ν(CN) frequencies region (Table 3) two bands indicating a *cis*-arrangement of two isocyanide ligands are always present. The frequencies are higher for the complexes than for the free ligands, indicating a higher bond order in the first case. This seems to indicate a weak π interaction Fe—CNR. The σ-bonding ability of the halogen ligand does not significantly influence the metal—isocyanide bond order. There is no evidence of a trend, and the differences going from the chloro to the bromo or iodo derivative are within the experimental error.

Although no similar complexes have been previously reported, a comparison with isostructural complexes of the first transition series [16], indicates that the differences in the ν(FeX) frequencies from the chloro to the bromo or to the iodo derivative are as expected. Similarly the nature of the isocyanide or phosphine ligands does not seem to influence the FeX frequencies, and thus the Fe—X bond order.

From Table 1 the *QS* trend increases on going from chloro to bromo and decreases from bromo to iodo complexes for compounds (I—V). In contrast the centre shift sequence varies: it is opposite to the *QS* sequence for compounds IV—VI, it is constant for compound I, and decreases for compounds II and III. The increase in the centre shift values for derivatives VIII, IX and X can be related to the π-donation of halides, which increases the shielding and decreases the *s*-electron density at the iron nucleus.

The centre shift values for compounds IX and X are large compared to the shifts for other complexes (cf. Table 1). This is probably due to increased shielding of the *s*-electrons by *d*-electrons,

TABLE 4

PHYSICAL PROPERTIES OF BROMO AND IODO DERIVATIVES

Complex	Color	M.p. [a] (°C)	Molar cond. [b]	Analysis Found (calcd.) (%)		
				C	H	N
$[FeBr(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	yellow	142	25.0	51.95 (51.92)	5.87 (5.59)	2.44 (2.93)
$[FeI(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	red	145	24.1	49.21 (49.72)	5.49 (5.35)	2.28 (2.52)
$[FeBr(2\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	yellow-orange	142	23.8	51.85 (51.92)	6.05 (5.59)	2.43 (2.63)
$[FeI(2\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	red-brown	148	24.8	49.83 (49.79)	5.70 (5.35)	2.35 (2.52)
$[FeBr(C_6H_5NC)_2L_3]ClO_4$	yellow-orange	131	23.7	50.31 (50.91)	5.26 (5.53)	2.54 (2.70)
$[FeI(C_5H_5NC)_2L_3]ClO_4$	red-brown	130	24.7	49.04 (48.79)	5.14 (5.11)	2.39 (2.58)
$[FeBr(4\text{-}NO_2C_6H_4NC)_2L_3]ClO_4$	yellow-orange	162	23.7	47.06 (46.93)	5.20 (4.74)	4.10 (4.98)
$[FeI(4\text{-}NO_2C_6H_4NC)_2L_3]ClO_4$	red-orange	165	23.8	44.99 (45.05)	4.68 (4.55)	4.46 (4.78)
$[FeBr(4\text{-}CH_3OC_6H_4NC)_2L_3]ClO_4$	yellow-orange	141	24.7	49.22 (50.40)	5.71 (5.43)	2.37 (2.56)
$[FeI(4\text{-}CH_3OC_6H_4NC)_2L_3]ClO_4$	red-brown	137	24.0	48.53 (48.32)	5.17 (5.16)	2.36 (2.45)
$[FeBr(2,6\text{-}(CH_3)_2C_6H_3NC)_2L_3]ClO_4$	yellow	146	23.4	52.36 (52.78)	5.74 (5.81)	2.39 (2.56)
$[FeBr(4\text{-}CH_3C_6H_4NC)_3L'_2]ClO_4$	orange	161	24.2	64.58 (64.85)	4.79 (4.62)	3.69 (3.78)
$[FeBr(4\text{-}CH_3C_6H_4NC)_5]ClO_4$	yellow	183	24.7	58.19 (58.59)	4.42 (4.30)	8.22 (8.53)
$[FeI(4\text{-}CH_3C_6H_4NC)_5]ClO_4$	yellow-orange	190	24.3	55.95 (55.35)	4.21 (4.06)	7.89 (8.07)
cis-$[FeBr_2(4\text{-}CH_3C_6H_4NC)_4]$	red	182	—	55.26 (56.16)	4.21 (4.09)	8.08 (8.19)
trans-$[FeBr_2(4\text{-}CH_3C_6H_4NC)_4]$	blue	210	—	55.60 (56.16)	3.93 (4.09)	8.04 (8.19)
cis-$[FeI_2(4\text{-}CH_3C_6H_4NC)_4]$	red	176	—	49.10 (49.38)	3.48 (3.63)	6.81 (7.20)
trans-$[FeI_2(4\text{-}CH_3C_6H_4NC)_4]$	green	192	—	48.84 (49.38)	3.56 (3.63)	6.96 (7.20)

[a] Melting points were determined in capillaries and uncorrected. [b] 10^{-3} *M* nitrobenzene solution at 25°C (cm^2/ohm mol).

TABLE 5

CHEMICAL SHIFTS (τ(ppm)) OF SOME BROMO AND IODO COMPLEXES

Compound [a]	Phenyl protons (phosphines and/ or isocyanide)	CH_2 (phos- phine)	CH_3 (isocyanide)	CH_3 (phosphine)
$[FeBr(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	2.7m 3.2m	6.0m	7.62s	8.68t 8.76t
$[FeI(4\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	2.7m 3.2m	5.9m	7.60s 7.65s	8.66t 8.74t
$[FeBr(2\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	2.5m 2.8m	6.0m	7.63s 7.93s	8.63t 8.78t
$[FeI(2\text{-}CH_3C_6H_4NC)_2L_3]ClO_4$	2.5m 2.9m	6.0m	7.58s 8.03s	8.61t 8.75t
$[FeBr(C_6H_5NC)_2L_3]ClO_4$	2.5m 2.7m	6.0m	— —	8.65t 8.73t
$[FeI(C_6H_5NC)_2L_3]ClO_4$	2.5m 2.7m	6.0m	— —	8.64t 8.73t
$[FeBr(4\text{-}CH_3OC_6H_4NC)_2L_3]ClO_4$	2.6m 3.1m	6.1m	6.16s—	8.68t 8.76t
$[FeI(4\text{-}CH_3OC_6H_4NC)_2L_3]ClO_4$	2.6m 3.1m	6.0m	6.12s 6.18s	8.65t 8.73t
$[FeBr(2,6\text{-}(CH_3)_2C_6H_3NC)_2L_3]ClO_4$	2.3m 2.9m	5.9m	— 7.93s	8.51t 8.67t
$[FeBr(4\text{-}CH_3C_6H_4NC)_3L'_2]ClO_4$	2.1m 2.6m 3.1m	—	7.64s 7.74s	— —
$[FeBr(4\text{-}CH_3C_6H_4NC)_5]ClO_4$	2.4d 2.7d —	—	7.62s 7.64s	— —
$[FeI(4\text{-}CH_3C_6H_4NC)_5]ClO_4$	2.4d 2.7d —	—	7.61s 7.64s	— —

[a] For the chemical shifts of the free ligands cf. ref. 1.

In Tables 4 and 5 are listed the physical properties, analyses and chemical shifts of some of the bromo and iodo derivatives.

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