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HEXACOORDINATED PENTAKIS(ISOCYANIDE)IRON(II) COMPOUNDS

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SUMMARY

New iron(II) compounds of formula $[FeL_5(ligand)](ClO_4)_2$ and $[FeL_5X]^+$, where L = *p*-tolyl isocyanide and X = Cl or Br, have been prepared by treatment of $[FeL_5OClO_3]ClO_4 \cdot H_2O$ with the appropriate halide or with the ligands alkyl CN, aryl CN, cyclohexyl NC, Ph_3P, Ph_3As or Ph_3Sb.

INTRODUCTION

The preparations of the complexes $[FeL_5(OClO_3)](ClO_4) \cdot H_2O$ (L = *p*-tolyl isocyanide) have been previously described[1]. Preliminary experiments showed that the monodentate perchlorate group can be easily replaced by neutral or negatively charged ligands, and we have now studied the reactions with ligands having donor atoms belonging to Group IV (isocyanide, carbon monoxide), Group V (phosphine, arsine, and stibine derivatives), Group VI (tetrahydrofuran, diphenyl sulphide, and thiourea), and Group VII (halide). The products are of the general type $[FeL_5(ligand)]^{n+}$ ($n = 1$ or 2), their properties throw light on the nature of the Fe(isocyanide)$_5^{++}$ entity.

RESULTS

Treatment of $[FeL_5(OClO_3)]^+$ with cyclohexyl isocyanide, alkyl cyanides, aryl cyanides, or the compounds Ph_3E, where E = P, As or Sb, in a refluxing chlorinated solvent gives new complexes according to the equation:

$$[FeL_5(OClO_3)]^+ + L' \rightarrow [FeL_5L']^{++} + ClO_4$$

When L' was thiourea or triphenyl-phosphite the products were intractable sticky solids with the expected IR spectrum.

The compounds containing neutral ligands are not available by other routes, but the halide complexes can be obtained from $[Fe(CNR)_4Cl_2]$ and sodium perchlorate[1].

Bidentate ligands gave a variety of results. Thus 1,2-bis(diphenylphosphino)ethane gave a bridged, binuclear complex, (XI), while the sebacodinitrile complex isolated, (VIII), had only one cyano group coordinated to the metal. In the case of acrylonitrile complex (IX), for which different types of bonding are possible, the IR

TABLE 1

ANALYTICAL AND OTHER DATA

Compound[a]	M.p. (°C)	Analysis found (calcd.) (%) C	H	N	mol. wt.[b,c]	Λ[d]
$[FeL_5(o\text{-}CH_3C_6H_4CN)](ClO_4)_2$	229	60.1	4.39	8.77	957	158
(I)		(59.81)	(4.24)	(8.87)	(904)	(1.42)
$[FeL_5(m\text{-}CH_3C_6H_4CN)](ClO_4)_2$	232	60.1	4.39	8.77	957	175
(II)		(60.39)	(4.21)	(8.78)	(942)	(0.60)
$(FeL_4(p\text{-}CH_3C_6H_4CN)](ClO_4)_2$	225	60.1	4.39	8.77	957	198
(III)	215	(59.36)	(4.30)	(8.83)	(954)	(0.45)
	decomp.					
$[FeL_5(p\text{-}FC_6H_4CN)](ClO_4)_2$	226	58.7	4.06	8.74	961	186
(IV)		(58.20)	(3.97)	(8.84)	(906)	(0.46)
$[FeL_5(2\text{-}C_{10}H_8CN)](ClO_4)_2$	200	61.65	4.23	8.46	993	170[e]
(V)	decomp.	(60.80)	(4.23)	(8.36)	(994)	(0.62)
$[FeL_5(C_6H_5CH_2CN)](ClO_4)_2$	230	60.1	4.39	8.77	957	184
(VI)	210	(59.44)	(3.99)	(8.89)	(978)	(0.42)
	decomp.					
$[FeL_5(CN_3CN)](ClO_4)_2$	131	57.25	4.32	9.53	880	177
(VII)		(57.19)	(4.50)	(9.20)	(900)	(0.42)
$(FeL_5(NC(CH_2)_8CN)](ClO_4)_2$	227	59.97	5.07	9.76	1004	190
(VIII)	decomp.	(59.93)	(4.73)	(9.49)	(1305)	(0.58)
$[FeL_5(CH_2{=}CHCN)](ClO_4)_2$[i]	143	57.8	4.26	9.50	893	156
(IX)		(57.97)	(4.25)	(9.24)	(1100)	(0.92)
$[FeL_5(PPh_3)](ClO_4)_2 \cdot CHCl_3$	226	57.90	4.17	5.72	1222	195
(X)	decomp.	(57.44)	(3.77)	(5.77)	(1275)	(0.49)
$[FeL_5(Ph_2PCH_2)_2FeL_5](ClO_4)_4$	230–3	61.3	4.52	6.74	1222	436
(XI)[a]	212	(61.91)	(4.58)	(6.51)	insol.	(0.131)
	decomp.					
$[FeL_5(AsPh_3)](ClO_4)_2$	189	60.7	4.36	6.10	1146	198[f]
(XII)	165	(61.06)	(4.58)	(6.44)	(1150)	(0.40)
	decomp.					
$[FeL_5(SbPh_3)](ClO_4)_2 \cdot 0.5CH_2Cl_2$	204	56.80	4.13	5.66	1235	
(XIII)		(57.23)	(4.21)	(5.46)	(1245)	
$[FeL_5(SbPh_3)](ClO_4)_2$[k]	195	58.3	4.18	5.86	1193	198
(XIV)		(58.65)	(4.01)	(5.73)	(1155)	(0.32)
$(FeL_5Cl)(ClO_4)$	186	61.7	4.51	9.0		96.3
(XV)		(62.11)	(4.50)	(9.02)		(0.48)
$(FeL_5Cl)(BPh_4)$	165	77.25	5.52	7.03		16.1[g,h]
(XVI)		(77.61)	(5.77)	(7.06)		(0.44)
$(FeL_5Br)(ClO_4)$	180–9	58.5	4.27	8.53		
(XVII)		(58.42)	(4.31)	(8.41)		
$[FeL_5(CNC_6H_{11})](ClO_4)_2$	ca. 220	59.45	4.75	8.86	949	186
(XVIII)[a]	decomp.	(59.60)	(4.50)	(8.89)	(936)	(0.63)

[a] All the compounds are yellow, except XI (white) and XVIII (ivory-white). [b] Found (calcd.). [c] Mechrolab osmometer in chloroform solution at 37°. [d] Ohm^{-1} cm^2 $mole^{-1}$ in CH_3NO_2 solution, at the molar concentration ($\times 10^{-3}$) given between brackets. [e] 263 Ohm^{-1} cm^2 $mole^{-1}$ (acetonitrile, 0.65×10^{-3} M). [f] 283 Ohm^{-1} cm^2 $mole^{-1}$ (CH_3CN, 0.51×10^{-3} M). [g] Nitrobenzene solution. [h] 101 Ohm^{-1} cm^2 $mole^{-1}$ (CH_3CN, 0.38×10^{-3} M). [i] O found 14.53, calcd. 14.53%. [k] O found 10.55, calcd. 10.70%.

TABLE 2

INFRARED DATA[a]

Compound	ν(CN) region		620–400 cm^{-1} region
	Nujol	$CHCl_3$	Nujol
(I)	2268 w, 2228 w (sh), 2190 s (br)	2267 w, 2202 s	614 s, 550 s (asym.), 497 s (asym.)
(II)	2280 w, 2190 s	2276 w, 2200 s	617 s, 565 m (sh), 556 s, 516 m, 499 s, 450 w
(III)	2275 w, 2227 w (sh), 2190 s	2274 w, 2227 w (sh), 2188 s	615 s, 563 s, 546 s, 516 m, 499 s
(IV)	2281 w, 2227 w (sh), 2192 s	2280 w, 2227 w (sh), 2200 s	615 s, 561 s, 545 s, 516 m, 499 s
(V)	2269 w, 2221 w (sh), 2188 s	2269 w, 2220 w (sh), 2193 s	614 s, 558 s, 542 m, 515 m, 499 s, 470 m
(VI)	2225 w (sh), 2180 s	2228 vw (sh), 2195 s	615 s, 571 s, 557 s, 510 w (sh), 498 s (asym.)
(VII)	2222 w (sh), 2183 s	2226 w (sh), 2193 s	615 s, 571 m, 557 s, 514 w (sh), 499 s, 430 w
(VIII)	2298 vw, 2210 w (sh), 2185 s (br)		616 s, 558 s, 514 m (sh), 499 s
(IX)		2281 vw, 2195 vs	615 s, 556 s, 515 m (sh), 500 s
(X)		2217 w, 2175 s	
(XI)[b]		2213 w, 2172 s	
(XII)	2218 w, 2186 s (br)	2218 w, 2174 s	616 s, 560 s, 517 w, 502 s, 496 m (sh), 469 m
(XIII)	2211 w, 2160 s	2212 w, 2170 s	
(XIV)		2212 w, 2170 s	614 s, 558 s, 524 w, 502 s, 493 m (sh), 448 m
(XV)		2216 w, 2170 s	615 s, 560 s (sh), 554 s, 515 m, 501 s, 493 m (sh), 470 w (br)
(XVI)	2209 w, 2166 s	2213 w, 2174 s	
(XVIII)		2241 w, 2211 m (sh), 2193 s	

[a] Perkin–Elmer 457 or 621 grating instrument. [b] In CH_2Cl_2.

evidence indicates that there is coordination through the nitrogen atom. The compound $[FeL_5(OClO_3)](ClO_4)\cdot H_2O$ in CH_2Cl_2 did not react either at room temperature or under reflux with carbon monoxide, tetrahydrofuran, diphenyl sulphide, or succinic anhydride.

The reactions were usually carried out in chlorinated solvents in which the starting material is stable; some other solvents, including cold alcohol, react with the starting complex* while others interfere with the isolation of the products.

The formulae of the compounds obtained were primarily established by elemental analysis and molecular weight determinations (see Table 1); molar conductance data (Table 1), and spectroscopic evidence (Tables 2 and 3) provided additional evidence. The properties of $(FeL_6)(ClO_4)_2$ and of $[FeL_5(p\text{-}CH_3C_6H_4CN)](ClO_4)_2$ are quite distinct, and there is no question of an isocyanide-cyanide isomerization.

The complexes obtained are quite stable, as solids and in solution. For example, the complex $[FeL_5(NCCH_2Ph)](ClO_4)_2$ was recovered from a chloroform solution through which HCl had been bubbled; while the complex $[FeL_5(NCC_{10}H_8)](ClO_4)_2$ (V), did not react in refluxing CH_2Cl_2 with another donor such as Ph_3Sb.

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* Work in progress.

TABLE 3

^{1}H NMR DATA[a]

Compound	Solvent	Chemical shift τ (ppm)
(I)	CH_2Cl_2	7.57 s (15 H); 7.43 s (3 H); 2.1–2.9 m (24 H)
(II)	CH_2Cl_2	7.59 s (18 H); 2.1–2.9 m (24 H)
(III)	$CDCl_3$	7.67 s (18 H); 2.0–2.9 m (24 H)
(IV)	CH_2Cl_2	7.59 s (15 H); 2.15–2.85 m (24 H)
(V)	CH_2Cl_2	7.64 s; 1.9–2.9 m
(VI)	CH_2Cl_2	7.62 s; 2.25–2.85 m
	$CDCl_3$	7.63 s (15 H); 5.60 s (2 H); 2.20–2.90 m (24 H)
(VII)	CH_2Cl_2	7.56 s; 7.44 s
(VIII)	$CDCl_3$	8.95–8.1 (broad); 7.63 s; ca. 7 (broad), 2.05–2.85 m
(IX)[b]	$CDCl_3$	7.63 s; 3.66 and 3.46; 2.9–2.1 m
(XII)[c]	$CDCl_3$	7.70 s (15 H); 2.3–3.0 m (35 H)
(XIII)	$CDCl_3$	7.67 s (15 H); 4.73 s (1 H); 2.1–2.9 M (35 H)
(XIV)	$CDCl_3$	7.64 s (15 H); 2.1–2.9 m (35 H)
(XV)	$CDCl_3$	7.63 s (more intense) and 7.61 s (15 H); 2.57 q (20 H)
(XVI)	$CDCl_3$	7.71 s (more intense) and 7.66 s (15 H); 2.4–3.2 m (40 H)
(XVII)	$CDCl_3$	7.60 s (15 H); 2.58 q (20 H)
(XVIII)	$CDCl_3$	ca. 8.5 and 8.0 broad; 7.63 s; 2.58 q.

[a] Perkin-Elmer R-10 instrument operating at 33° and 60 MHz, TMS as internal standard; s singlet, q quartet also m multiplet. [b] The spectrum was recorded in CH_2Cl_2 with similar results. [c] No additional signal to τ 30.

The new nitrile containing complexes are much more stable than other nitrile complexes[2,3], which easily lose the RCN molecule even in the solid state: even prolonged pumping (0.1 mm) did not alter the composition of the compounds listed in Table 1.

Infrared and NMR spectra

For all the compounds except (XVI) the IR spectrum showed two strong absorption bands typical of a perchlorate group having tetrahedral symmetry, at ca. 1080 (broad) and 615 cm^{-1}, whereas in the starting complex splitting arising from the lower C_{3v} symmetry was evident.

A $[Fe(CNR)_5X]^{++}$ cation would be expected to have three IR active ν(CN) stretching vibrations ($2A_1+E$). In fact, three vibrations were present only in the case of $[FeL_5(C_6H_{11}NC)](ClO_4)_2$, for which only a single CN stretching frequency was expected; a single frequency is found with $[FeL_6]^{++}$ and can be associated with the local symmetry characteristics of the $Fe(CN-)_6$ framework.

The occurrence of several ν(CN) vibrations can be attributed to the differing electronic effects of the *p*-tolyl and cyclohexyl group, which give rise to differing electron densities in the $RN{=}C{\rightarrow}Fe$ bonds; this will give rise to a lower symmetry which ought to be octahedral than would be expected for a simpler structure.

For each of the compounds listed in Table 2, only one, strong, ν(CN) vibration and a shoulder were observed. This strong vibration was found in the range, 2202–2160 cm^{-1}, in which the ν(CN) of the starting material falls. The value of ν(CN) for the free ligand is lower, 2136 cm^{-1}, and the shift observed indicates that there is a negligible amount of π-back donation from the metal to the isocyanide ligands. The ν(CN) frequencies in our compounds are lower than those in $Ph_3B \cdot CNPh$ (2225

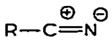
cm^{-1}) and $Ph_3B \cdot CNC(CH_3)_3$ (2275 cm^{-1})[4], in which no π-back donation is possible: these complexes have a higher formal oxidation state and a smaller number of isocyanide ligands than in the iron complexes.

The ν(CN) bands are often broad and asymmetric in the new complexes even in solution. The complexes containing halide, Ph_3P, Ph_3As or Ph_3Sb show the lowest ν(CN) values, and those containing an organic cyanide the highest values, in agreement with the lower π-accepting ability of the latter ligand. The nature of the organic radical in the nitrile molecule does not much affect the ν(CN) frequency, which is found at 2194 ± 2 when R is aliphatic and in a slightly wider range when R is aromatic.

The N≡C stretching frequency of the coordinated nitrile is present in nearly all cases as a weak band between 2269 and 2305 cm^{-1}, showing that the ligand has maintained its identity. The ν(N≡C) band is not detectable in the acetonitrile or phenylacetonitrile complex, (VII) and (VI), and the presence of the cyanide ligand was indicated by the analytical and NMR data. The ν(C≡N) frequency was 42–60 cm^{-1} greater than in the free ligand; a similar increase was observed for other nitrile derivatives[2,5] and indicates coordination through the nitrogen atom. The extent of the increase suggests that the contribution of the canonical form (A) compared with that of the canonical forms (B) is larger in the complexed than in the free ligand.

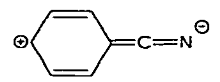
$R-C\equiv N$

(A)

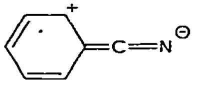


$R-\overset{\oplus}{C}=\overset{\ominus}{N}$

(B)



(B')



(B")

The intensity of the ν(N≡C) is probably mainly attributable to the most polar structures, *i.e.* (B), (B'), and (B"), the already weak band of the free nitrile becomes even weaker on coordination, and so may escape detection, especially when R is aliphatic.

All the complexes have typical bands in the 580–400 cm^{-1} region, where the in plane deformation Fe–C≡N and the stretching vibration Fe–C are found; these bands are not much affected by the nature of the sixth ligand.

The NMR spectra of all the complexes show the required singlet absorption due to the p-CH_3 group (τ ca. 7.6) and the multiplet or pseudoquartet due to the aromatic protons of the isocyanide ligand, in addition to the signal(s) due to the sixth ligand. However, the *m*- and *p*-tolyl cyanide complexes do not show separate signals for the CH_3 groups of cyanide and isocyanide ligands, probably because of overlapping. This overlapping does not occur with the *o*-tolyl cyanide complex (I), in which the resonance from the o-CH_3 group is moved downfield, probably by a long range effect.

CONCLUSION

The available data strongly indicate that the FeL_5^{++} entity must be considered a strong Lewis acid. Indeed the parent $[FeL_5(OClO_3)]^+$ ion gives very stable complexes by reaction with ligands which can give strong σ-bonds (nitrile, halide, Ph_3P, Ph_3As, Ph_3Sb, isocyanide); if the ligand has two different donor groups (acrylonitrile) coordination takes place via the σ-donor groups. Though carbon monoxide does not react under comparable conditions, reactions with other π-acceptor ligands (olefins, acetylenes) are being investigated.

EXPERIMENTAL

Melting points, analytical and conductivity data are presented in Table 1, infrared data in Table 2, and NMR data in Table 3. Evaporation was always carried out under reduced pressure. Some typical preparations are described below.

Pentakis(p-tolyl isocyanide)(2-naphthyl cyanide)iron(II) perchlorate (V)

Perchloratopentakis(*p*-tolyl isocyanide)iron(II) perchlorate hydrate, (XIX)[1], (0.4825 g) and 2-naphthyl cyanide (0.275 g) were refluxed in CH_2Cl_2 for 7 h. The pale yellow solution was evaporated to dryness, the residue was washed repeatedly with ether, was crystallized from CH_2Cl_2/ether to give the analytical sample. The other nitrile containing compounds were prepared similarly and crystallized from the same mixed solvent or from CH_2Cl_2/benzene (VII).

Pentakis(p-tolyl isocyanide)(triphenylphosphine)iron(II) perchlorate (X)

Triphenylphosphine (0.220 g) and compound (XIX) (0.641 g) in chloroform (50 ml) were refluxed for 4 h. Ethyl ether was added to the resulting pale yellow mixture and the precipitate was washed with ether. The analytical sample was obtained by crystallization from $CHCl_3$/ether (0.584 g). The IR spectrum showed an additional strong band at ca. 750 cm^{-1}, typical of clathrated chloroform.

Compounds (XI), (XII) and (XIII) were obtained similarly in CH_2Cl_2, and were crystallized from CH_2Cl_2/benzene, in the case of (XI) and (XII), or from CH_2Cl_2/ether, (XIII); the latter gave the solvent-free compound (XIV) after pumping at 64°/0.1 mm for 23 h.

Pentakis(p-tolyl isocyanide)bromoiron(II) perchlorate (XVII)

Compound (XIX) (0.600 g) and lithium bromide (0.061 g) were mixed in acetone (30 ml). After 3 h stirring, the mixture was evaporated to dryness. The residue was extracted with methylene chloride, and the crude product (0.405 g) was precipitated with toluene. The analytical sample was obtained after additional purification from CH_2Cl_2/toluene and twice from CH_2Cl_2/ether.

Pentakis(p-tolyl isocyanide)chloroiron(II) tetraphenylborate (XVI)

Violet tetrakis(*p*-tolyl isocyanide)dichloroiron(II) (0.9 g) was dissolved in methanol (10 ml) and sodium tetraphenylborate (1.2 g) in methanol (10 ml) was added. The filtered yellow precipitate was extracted with methanol (300 ml), and the extract was concentrated (ca. 20 ml) and filtered. The yellow crystals were washed with additional methanol (50 ml) to yield the analytical sample.

Pentakis(p-tolyl isocyanide)(cyclohexyl isocyanide)iron(II) perchlorate (XVIII)

Cyclohexyl isocyanide (0.1188 g) in CH_2Cl_2 was added to a solution of (XIX) (0.932 g) in the same solvent (20 ml). The solution was refluxed 3 h, allowed to stand overnight, and then evaporated to dryness. The residue was washed with diethyl ether (3 x 15 ml) then dissolved in methylene chloride and reprecipitated with ether. The pale-yellow crude product (0.437 g) was crystallized twice from CH_2Cl_2/ether to yield the ivory-white analytical sample. The preparation and the analysis of (XVIII) were repeated with identical results.

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