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NEW ISOCYANIDE COMPLEXES OF IRON(II)*

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SUMMARY

Attempts to prepare the reported four-coordinate complex $[FeL_4](ClO_4)_2$ led to isolation of the diamagnetic complexes $[FeL_6](ClO_4)_2$, $[FeL_5(OClO_3)](ClO_4)\cdot H_2O$, $[FeL_5(H_2O)](ClO_4)_2\cdot H_2O$ and $[FeL_5Cl](ClO_4)$ (L = isocyanide). These, together with the related compounds $[FeL_6](BPh_4)_2$ and $FeL_4Cl_2\cdot HgCl_2$, were characterized by IR and NMR spectra.

INTRODUCTION

Diamagnetic four-coordinated iron(II) complexes are uncommon. It was therefore decided to reinvestigate the compounds described in the literature as $[FeL_4](ClO_4)_2$[2] and $FeL_4X_2\cdot HgX_2$[3] (L = isocyanide; X = halogen), which could possibly be of this type. The latter compound was successfully prepared as described by Malatesta[3], but in our hands attempts to obtain the perchlorate gave $[FeL_6](ClO_4)_2$ or $[FeL_5(H_2O)](ClO)_4\cdot H_2O$, $[FeL_5(OClO_3)](ClO_4)\cdot H_2O$, where L is *p*-tolyl isocyanide.

RESULTS AND DISCUSSION

The reaction between *p*-tolyl isocyanide and iron(II) perchlorate was found to be very sensitive to the conditions employed, and, especially, to the solvent used. Direct reaction of pure *p*-tolyl isocyanide[4] and iron(II) perchlorate, without solvent, afforded some dark, oily tar and a crystalline, stable complex, $[Fe(CNC_7H_7)_6](ClO_4)_2$ (I); the related tetraphenylborate (II) was also obtained. Hexa-coordinated iron (II) alkyl isocyanide complexes are well-known[5]; they can be obtained by alkylation of hexacyanoferrate(II) with alkyl iodide or sulphate. This route cannot be used to obtain hexakis(aryl isocyanide)iron(II) derivatives, owing to the lack of suitable reactive aromatic halides. Since other iron(II) salts, such as halide or sulphate, do not afford[5] $[FeL_6]^{++}$ derivatives, but rather FeL_4X_2 or $FeL_2(SO_4)$, the presence of a

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weakly or non-coordinating anion seems to be a necessary condition for obtaining hexa-coordinated iron(II) isocyanide complexes.

The perchlorate (I) was identified by analyses, molecular weight, and conductivity; it is quite insoluble in water, in contrast with the $[FeL_4](ClO_4)_2$ previously described[2]. The infrared spectrum showed the two bands typical of tetrahedral perchlorate ion (F_2 at 1085, broad, vs; F_2 at 615, s) and all the bands typical of the ligand. The CN stretching frequency was observed at 2195 cm^{-1} ($CHCl_3$; CaF_2 windows) as a single sharp band, consistent with octahedral symmetry. The value found vor ν(CN) in the complex (I) is lower than the value found for the stronger band reported[6] for $[Fe(CNMe)_6]Cl_2$ (2234 vs, 2197 w, nujol), in agreement with the lower π-acceptor character of methyl isocyanide compared with that of aromatic isocyanides.

TABLE 1

ANALYTICAL AND OTHER DATA

Compound	M.p. (°C) Colour	Analyses found (calcd.) (%)			
		C	H	N	Fe
$[FeL_6](ClO_4)_2$[a] (I)	250 Ivory	60.69 (60.2)	4.40 (4.39)	8.88 (8.78)	
$[FeL_6](BPh_4)_2$ (II)	175 (dec.) White	81.90 (82.5)	5.73 (5.43)	5.92 (5.98)	
$[FeL_5(OClO_3)](ClO_4)\cdot H_2O$[a] (III)	158[d] Yellow	55.87 (56.0)	4.25 (4.32)	8.07 (8.15)	6.50 (6.54)
$[FeL_5(H_2O)](ClO_4)_2\cdot H_2O$[b] (IV)	132 Yellow	54.87 (54.8)	4.51 (4.46)	8.02 (7.98)	6.29 (6.37)
$[FeL_5Cl]ClO_4$ (V)	186 Yellow	62.1 (61.8)	4.50 (4.50)	9.02 (9.00)	
$FeL_4Cl_2\cdot HgCl_2$ (VI)	180 Red	43.93 (44.3)	3.20 (3.23)	6.35 (6.46)	6.90 (6.94)
trans-FeL_4Cl_2 (VII)	[e] Violet	64.78 (64.7)	4.57 (4.72)	9.40 (9.43)	
$[n\text{-}Bu_4N]HgCl_3$[c] (VIII)	78 White	34.93 (35.0)	6.50 (6.55)	2.29 (2.55)	

[a] Mol.wt. in chloroform solution, Mechrolab Osmometer at 37°: found for (I) 992, calcd. 956.8; found for (III) 943, calcd. 857.8. [b] O found 17.17, calcd. 18.28%. [c] Cl found 17.55, calcd. 19.4%. [d] See text. [e] It changes into the orange, *cis*-isomer on heating and decomposes at *ca.* 130°.

The presence of two infrared active CN stretching vibrations in the methyl isocyanide complex, which is definitely octahedral[7], may be due to solid state splitting, or was in agreement with other published results: three strong bands have been observed[8] in chloroform solution for $Cr(CNC_7H_7)_6$. The preparation[9] of the latter complex was repeated, and the red compound, m.p. 152°, was obtained. Although the compound was purified by crystallization from chloroform/ethanol, the chloroform solution was found to be markedly unstable, so that the three bands reported cannot be assigned to $Cr(CNC_7H_7)_6$; therefore the additional band observed in [Fe-

$(CNCH_3)_6]^{++}$ is likely to be due to solid state splitting.

However, the main conclusions reached on the basis of the solution spectrum of the chromium complex cannot be rejected: a very strong and very broad band (Table 2) was observed by us in nujol mull, the complex being insufficiently soluble or stable in all the solvents tried.

TABLE 2

ABSORPTION IN THE 2000–2300 cm^{-1} REGION AND NMR DATA

Compd.	Medium	IR data[a] (cm^{-1})	NMR data[b], τ (ppm)
(I)	Nujol	2190 s	7.61; 2.29–2.69[e]
	Chloroform	2195 s	
(II)	Nujol	2190 s	
(III)	Nujol	2185 s, 2174 sh	7.53; 2.35–2.69[f]
	Chloroform	2190 s, asymm	
	Nitrobenzene	2191 s, asymm	
	Acetonitrile	2187 s	
(IV)	Nujol	2188 s, 2093 s	7.65, 7.89; 4.3; 2.15–3.15
(V)	Nujol	2216 w, 2155 s, br	7.61[g]; 2.35–2.80
	Chloroform	2216 w, 2170 s	
(VI)	Nujol	2210 w, 2172 s, 2040 w	7.58; 2.10–2.80
	Chloroform	2210 w, 2175 s, 2147 w, 2040 w	
	Nitrobenzene	2210 w, 2175 s, 2150 sh, 2040 w	
	Acetone	2175 s, 2155 sh	
(VII)[c]	Chloroform	2212 w, sh, 2172 s, 2159 s, 2130 w	
CrL_6[d]	Nujol	2046 w, 1950+1880, overlap (200 br)	
	Chloroform	2062, 1972, 1934	

[a] Perkin–Elmer 621 or 457 instrument. [b] Perkin–Elmer R-10 instrument operating at 60.0 MHz; $CDCl_3$ solution; the area ratios were those required by the formula given. [c] Prepared according to ref. 3; *cf.* ref. 12. [d] Prepared according to ref. 9. [e] Pseudo quartet. [f] Integration supports the presence of the water signal in this complex absorption. [g] A shoulder is observed.

When the reaction between iron(II) perchlorate and isocyanide was carried out in methylene chloride, $[Fe(CNC_7H_7)_5(OClO_3)]ClO_4 \cdot H_2O$ (III) was obtained, even when the CNR/Fe ratio was 6/1. The formula given is valid only in the solid state, where the infrared spectrum showed the presence of perchlorate groups with both tetrahedral and C_{3v} symmetry[10] and hydrogen bonding of the water molecule. The conductivity value showed that compound (III) may be either a 1/1 or a 1/2 electrolyte, according to the nature of the solvent and to the concentration of the solute; in a good ionizing solvent, such as acetonitrile, it is a 1/2 electrolyte, while in nitrobenzene it is a 1/1 electrolyte at *ca.* 0.01 *M* concentration. The behaviour suggests an equilibrium as:

$$[FeL_5(OClO_3)]^+ + \text{Solvent} \rightleftarrows [FeL_5(\text{Solvent})]^{++} + ClO_4^-$$

Even in chloroform solution the cation $[FeL_5(OClO_3)]^{++}$ is absent as the infrared spectrum in this solvent showed only one strong and broad band at 1094 cm^{-1}, typical of tetrahedral perchlorate group.

The presence in the $CHCl_3$ solution of $[FeL_5(H_2O)]^{++}$ cation, obtained by rearrangement of the solute, can be excluded, as this cation was isolated by us in compound (IV), and found to have two CN stretching frequencies, instead of the one observed here. Compound (III) is fairly stable in the solid state, although attemped dehydration by heating *in vacuo*, gave compound (I), among other products.

Although a FeL_5X moiety requires three infrared active CN stretching frequencies $(2A_1+E)$, only one band, with a shoulder, was observed, in the solid state; accidental degeneracy and/or partial overlapping of bands are likely, and, indeed, the band is broad and asymmetric. Solution spectra are not helpful, as an asymmetric broad band was observed.

The reaction between iron(II) perchlorate and isocyanide was carried out also in acetone, from which only dark oils were obtained, and in methanol, from which two compounds were isolated. One was identified as $[FeL_6](ClO_4)_2$ (I) and the other as $[FeL_5(H_2O)](ClO_4)_2 \cdot H_2O$ (IV). The infrared spectrum of compound (IV) showed two broad CN stretching frequencies, in comparison with the three required by group theory for a molecule with C_{4v} symmetry. Because one of the two bands observed is rather low (2093 cm^{-1}), it is likely to be due to the A_1 type of vibration which takes place along the C_4 axis of the molecule, and, therefore, in a position *trans* to the H_2O ligand. Because H_2O has no π-accepting property, back-donation is stronger towards the isocyanide ligand placed on the C_4 axis.

Because the results obtained ruled out the possibility of obtaining $[FeL_4](ClO_4)_2$ by reaction of iron(II) perchlorate and the isocyanide ligand, another route was tried which did not involve the $[Fe(H_2O)_6]^{++}$ cation. By treating FeL_4Cl_2 with excess sodium perchlorate in refluxing acetone diamagnetic, hexa-coordinate $[Fe(CNC_7H_7)_5Cl]ClO_4$ was isolated: there was no evidence in favour of the presence of the $[FeL_4]^{++}$ cation derivatives.

It seems that the arrangement of five isocyanide ligands plus a different ligand around the iron atom yields rather stable compounds, at least in the solid state, although these are not as stable thermally as $[Fe(CNR)_6]^{++}$ derivatives.

Because no tetra-coordinate iron(II) derivative was obtained from the perchlorate, another possible example was investigated: the 1/1 adduct between FeL_4Cl_2 and $HgCl_2$ was prepared as described by Malatesta[3]. This adduct (VI) was found to be a 1/1 electrolyte in many solvents, so that a structure such as $[FeL_4Cl(Solvent)_n](HgCl_3)$ $(n=0,1)$ or $[FeL_4(Solvent)_n](HgCl_4)$ $(n=0, 1, 2\text{-}cis, 2\text{-}trans)$ is likely in solution. The conductivity values in acetonitrile solution are strongly concentration-dependent, suggesting a complicated behaviour, *e.g.* dissociation of the chloromercurate(II) anion.

The infrared spectrum in the CN stretching region is quite similar in nujol mull, in acetone, in nitrobenzene, and in chloroform, suggesting that the pattern of CNR ligand around the iron atom is always the same, both in solution and in the solid state. The IR spectrum (Nujol mull) did not show any low frequency band which could be assigned to $HgCl_4^{2-}$ or to "$HgCl_3^-$" ion (375 cm^{-1} in Bu_4NHgCl_3).

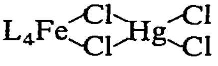
A structure such as $[cis\text{-}FeL_4(Solvent)_2](HgCl_4)$ or $[cis\text{-}FeL_4Cl(Solvent)]HgCl_3$ in solution, and such as  $\mathrm{L_4Fe}\genfrac{}{}{0pt}{}{\diagup\mathrm{Cl}\diagdown}{\diagdown\mathrm{Cl}\diagup}\mathrm{Hg}\genfrac{}{}{0pt}{}{\diagup\mathrm{Cl}}{\diagdown\mathrm{Cl}}$ in the solid state satisfies all the requirements.

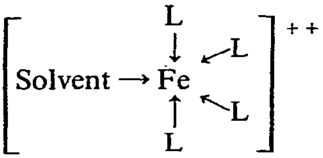
TABLE 3

CONDUCTIVITY DATA

	Compound	Solvent	Concn. ($\times 10^{-3}$)	Λ (ohm^{-1}·cm^{2}·mole^{-1})
(I)	$[FeL_6](ClO_4)_2$	Nitrobenzene	1.20	46.4
		Acetone	1.06	200
		Acetonitrile	1.09	250
(III)	$[FeL_5(OClO_3)]ClO_4$	Acetonitrile	1.0	267
		Nitrobenzene	9.88	19.3
			3.95	22.8
			1.98	27.1
			0.80	32.3
			0.31	32.9
(IV)	$[FeL_5(H_2O)](ClO_4)_2 \cdot H_2O$	Acetonitrile	0.28	286
		Nitromethane	0.28	195
(V)	$[FeL_5Cl]ClO_4$	Acetonitrile	0.47	126
		Nitromethane	0.48	96.3
(VI)	$FeL_4Cl_2 \cdot HgCl_2$	Acetone	0.85	95
		Nitrobenzene	1.04	23.8
		Acetonitrile	0.94	186.2
			0.47	205
			0.094	321
(VII)	*trans*-FeL_4Cl_2[a]	Acetone	1.17	40[b]
	cis-FeL_4Cl_2[a]	Acetone	1.11	49.8
		Nitrobenzene	0.98	3.8
(VIII)	$[Bu_4N]HgCl_3$	Nitrobenzene	2.04	30
		Acetonitrile	1.50	177

[a] Prepared according to ref. 3. [b] The value rose to 48.5 after 2 min and to 54 after 5 min. The solution afforded orange flakes after standing overnight.

A structure $L_4Fe(Cl)(HgCl_3)$, though similar to that of $SnCl_3$ derivatives, is rather unlikely, as Fe–Hg bonds are generally of the Fe–HgCl not of the Fe–$HgCl_3$ type, as in $C_5H_5Fe(CO)_2HgCl$, or in $Fe(CO)_4(HgCl)_2$. Since the number of CN stretching bands is higher than required, penta-coordinate structures can be discarded, except for a structure such as (A).



(A)

It is not possible, however, to write for the solid state a reasonable structure with the arrangement of isocyanide ligands around the iron atoms represented in the solution structure (A).

EXPERIMENTAL

Analytical, ν(CN), NMR and conductivity data are given in Tables 1–3. Additional IR and NMR data are reported under the appropriate compound. The melting points are somewhat dependent on the rate of heating, because decomposition often takes place during heating. All preparations (VIII excepted) were carried out at least twice.

Preparation of the starting materials

p-Tolyl isocyanide was prepared according to the procedure of Ugi[4]. Iron(II) perchlorate was prepared from aqueous perchloric acid and an excess of iron; the filtered aqueous solution was evaporated to dryness under reduced pressure; the compound used contained 14.3% iron, according to titration with potassium permanganate. *cis*-And *trans*-$Fe(CNC_7H_7)_4Cl_2$ were prepared according to Malatesta[3]; use of the additional product which can be isolated from the mother liquor should be avoided[11], although it might have the same infrared spectrum (4000–400 cm^{-1}) and the same decomposition range.

Hexakis(p-tolyl isocyanide)iron(II) perchlorate (I)

To solid, ice-cooled *p*-tolyl isocyanide (3.38 g) solid iron(II) perchlorate (2.87 g) was added. The isocyanide melted when the mixture was heated on a water bath at 20–25°, while stirring and scratching with a glass rod. The brown-black reaction mixture was taken up with methanol in portions (100 ml in all); the suspension was filtered, the dirty-yellow insoluble part was filtered off and washed with methanol thrice (10 ml in all). The crude compound (0.5 g), m.p. 245°, was washed with benzene, dissolved in chloroform (15 ml), and precipitated with diethyl ether (20 ml), to yield the analytical sample, ivory-white, m.p. 250°, soluble in polar chlorinated solvents, and insoluble in water, methanol, benzene, ether, and ethyl acetate. ν_{max} (nujol mull) at 1500s, 1213w, 1191w, 1171m, 1117sh, 1085s, br, 1017m, 822s, 719s, 695w, 644w, 615s, 586s, 521s, 513m, 501sh, 499s, 262w cm^{-1}; no remarkable change in the 4000–300 cm^{-1} region in a $CHCl_3$ solution. On adding diethyl ether to the mother liquor an additional compound, m.p. 245°, was obtained; filtration and evaporation under reduced pressure of the remaining solution afforded a dark oil.

The compound (I) does not react with picric acid, either in methanol or in ether, but reacts with Reinecke's salt, $NH_4[Cr(NH_3)_2(CNS)_4]\cdot\frac{2}{3}H_2O$, in methanol solution yielding pink crystals, m.p. 212°, ν(CN) 2195 cm^{-1}, no absorption due to ClO_4^- ion.

Hexakis(p-tolyl isocyanide)iron(II) tetraphenylborate (II)

Compound (I) (0.10 g) was suspended in methanol, excess sodium tetraphenylborate in methanol was added, and the suspension was stirred a few minutes. The white crystals (0.05 g) were filtered, and washed with methanol, m.p. 175° (dec.), there was no ClO_4^- absorption in the IR spectrum.

Perchloratopentakis(p-tolyl isocyanide)iron(II) perchlorate monohydrate (III)

Iron(II) perchlorate (0.624 g) was suspended in dichloromethane (30 ml), and *p*-tolyl isocyanide (0.91 g) in the same solvent (24 ml) was added dropwise, under stirring. After a few hours standing, a small residue was removed by filtration and the solution was concentrated under reduced pressure to *ca.* 20 ml. On adding diethyl ether (*ca.* 90 ml) a yellow crystalline precipitate (0.94 g) was obtained; additional precipitate (0.45 g) could be obtained by addition of diethyl ether to the mother liquor. The combined precipitates were crystallized from dichloromethane/ether (10 + 50 ml), yellow crystals, m.p. 198° with some decomposition at 145° (hot plate), or *ca.* 158° (capillary). ν_{max} (nujol mull) at 3200m, br, 1600w, 1499m, 1213w, 1193w, 1167m, 1127sh, 1124sh, 1108s, br, 1041s, br, 1016s, 939m, 924m, 827s, 812s, 719m, 692w, 643w, 624sh, 613s, 567sh, 560sh, 555s, 538sh, 516m, 503s, 496sh, 481sh, 427m, 413w, 270w cm^{-1}; additional data ($CHCl_3$) 3350m, br, 1596m, br, 1500 m, 1094s, br, (nitrobenzene) 3400m, br.

The same compound was obtained even when the isocyanide/iron ratio of the reagents was 6/1. The compound did not lose the molecule of water at 25° under vacuum (0.1 mm Hg); the loss began to take place very slowly at 64°, and occurred more quickly at 100° over P_4O_{10}, accompanied by some decomposition, as indicated by the brown colour and changes in the 3200 and 1100 cm^{-1} region of the infrared spectrum. The heated sample was taken up with excess methanol, and filtered. The ivory-white residue, m.p. 220°, and the ivory-white precipitate obtained by repeated crystallization from chloroform/ether of the residue left after evaporation of the methanol solution were identified as compound (I) by mixed m.p. and infrared spectrum.

Compound (III) reacted with Reinecke's salt in methanol affording perchlorate-free, pale orange crystals, m.p. 166, ν(CN) 2185 cm^{-1}. Compound (III) reacted with 2,2-bipyridine in acetone (1/1 and 1/3 mole ratio); after 3 h the solvent was removed *in vacuo*, the oily residue washed with benzene, and dissolved in acetone; on addition of benzene to the solution, red crystals, m.p. 275°, were obtained, identical with these obtained from 2,2-bipyridine and iron(II) perchlorate, according to IR spectrum, colour, and m.p.

Aquopentakis(p-tolyl isocyanide)iron(II) perchlorate hydrate (IV)

A methanol solution (30 ml) of iron perchlorate (3.46 g) was added slowly to a methanol solution (30 ml) of *p*-tolyl isocyanide (5.0 ml). The solution was allowed to stand for a few hours then concentrated to *ca.* 45 ml to give a yellow precipitate (0.194 g), which was filtered off; from the filtrate a second yellow precipitate (0.105 g) was obtained after slight concentration. Both precipitates melted at *ca.* 250° (dec.), and had the same infrared spectrum as compound (I). The solution was then evaporated to dryness, and the dense oil obtained was dissolved in acetone (35 ml); on slow addition of benzene (50 ml) to the solution a yellow precipitate was obtained (1.26 g), m.p. 132. The analytical sample, m.p. 132°, was obtained by crystallization from chloroform/ether (1/1). ν_{max} (nujol mull) at *ca.* 3500w, very broad, 3220w, br, 3146w, 1607w, 1594w, 1510m, 1501m, 1460s, 1409w, 1378s, 1312w, 1190w, 1166w, 1090s, br, 1015sh, 926w, 811s, 718m, 694w, 671w, 643w, 613w, 579m, 550w, 516w, 500w, 274m.

Pentakis(p-tolyl isocyanide)chloroiron(II) perchlorate (V)

An acetone solution (100 ml) of violet, *trans*-tetrakis(*p*-tolyl isocyanide)-dichloroiron(II) (0.8895 g) was mixed with an acetone solution (10 ml) of sodium perchlorate trihydrate (1.108 g). The solution was refluxed 3.5 h and evaporated to dryness *in vacuo*. The residue was extracted with methylene chloride (15 ml), and a yellow product, m.p. 173–179° (0.350 g), was precipitated by addition of diethyl ether; after crystallization from dichloromethane/ether (8+50 ml) the m.p. was raised to 186°, unchanged after an additional crystallization. ν_{max} (nujol mull) at 1501s, 1279w, 1198w, 1196w, 1167w, 1113w, sh, *ca.* 1080s, br, 1034w, 1014w, 952w, br, 821sh, 817s, 811sh, 718m, 696w, 615s, 560s, sh, 544s, 515m, 508m, 501s, 493m, 470w. This compound had the same properties as one reported previously[1] and prepared in the same way as here, for which slightly different, but incorrect, analytical results had been provided.

Tetrakis(p-tolyl isocyanide)dichloroiron(II) adduct with mercury chloride (VI)

Violet, *trans*-tetrakis(*p*-tolyl isocyanide)dichloroiron(II) (0.4 g) was dissolved in the minimum amount of chloroform, mercury(II) chloride (0.183 g) was added under stirring. On adding methanol (20 ml) to the solution compound (VI), m.p. 180°, was obtained, soluble in acetone, acetonitrile, nitrobenzene, dimethyl sulphoxide, dimethylformamide, and chlorinated solvents. The compound was obtained also starting from the *cis*-isomer. Similarly, yellow adducts were obtained[1] with $CdCl_2$, m.p. 110°, and with $SnCl_4$, hygroscopic. Compound (VI) has ν_{max} (nujol mull) at 3090vw, 3070w, 3035w, 1578w, 1502s, 1460s, 1413w, 1378m, 1368sh, w, 1310w, 1288w, 1210w, 1171m, 1117w, 1040w, 1020w, 945w, 840w, 813s, 732w, 721w, 700w, 646w, 576m, 560m, 549w, 508m, 480w, sh, 315m, 288vw, 264vw. The electronic spectrum showed absorption at 367 ($\varepsilon = 2730$), and 274 ($\varepsilon = 28{,}400$) nm in chloroform.

Tetra-n-butylammonium trichloromercurate(II) (VIII)

The white compound precipated on mixing aqueous tetra-*n*-butylammonium chloride and mercury(II) chloride. The low frequency IR spectrum showed strong absorption at 375 cm^{-1}.

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