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Iron(III) Trihalide Complexes of 4-Aminobenzophenone

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The following iron(III) trihalide complexes of 4-aminobenzophenone (L) have been prepared and studied by infrared, e.p.r. and electronic spectra and by conductometric and magnetochemical methods: $3FeCl_3 \cdot 2L$, $2FeCl_3 \cdot 3L$, $FeCl_3L_2$, $FeBr_3L$, $FeBr_3L_2$, $FeBr_3L_3$, $FeBr_3L_4$ *and* $FeBr_3L_6$. *The infrared spectra exclude a coordination of the ligand through the carbonylic oxygen atom and support a coordination through the aminic nitrogen atom with* $\nu(FeN)$ *bands in the 550–540 and 475–460* cm^{-1} *regions. The* $FeCl_3$ *complexes contain* $FeCl_4^-$ *ions.*

Introduction

As a donor ligand 4-aminobenzophenone (L) has two potentially coordinating sites. In previous investigations we have shown that it may be coordinated with non-transition metal ions through the aminic nitrogen or the carboxylic oxygen atoms. In some cases an interaction may also occur between a metal halide molecule and the π-electron system of the aromatic molecule [1–4]. Owing to the variable coordinating behaviour of this ligand we have now studied its complexes with the iron(III) trihalides.

Experimental

The ligand (Fluka) and all the reagents were of the best chemical grade. The complexes were prepared as follows.

$3FeCl_3 \cdot 2L$

By adding hexane to an EtOH solution saturated with $FeCl_3$ and containing L in a M:L = 3:1 ratio a brown viscous liquid separated. By washing repeatedly with petroleum ether a uniform microcrystalline product was obtained.

$2FeCl_3 \cdot 3L$

By adding hexane to an Et_2O solution of $FeCl_3$ and L in a M:L = 1:2 ratio a dark brown viscous liquid separated; by washing repeatedly with hexane a shining microcrystalline product was obtained.

$FeCl_3L_2$

The microcrystalline product precipitated from an Et_2O solution saturated with both $FeCl_3$ and L.

TABLE I. Analytical Data, found % (Calcd. %), and Colour of the Iron(III) Complexes of 4-Aminobenzophenone (L).

Complex	Colour	C	H	N
$3FeCl_3 \cdot 2L$	brown	35.20(35.41)	2.88(2.49)	3.21(3.18)
$2FeCl_3 \cdot 3L$	brown	51.05(51.08)	3.83(3.61)	4.39(4.58)
$FeCl_3L_2$	brown	56.47(56.04)	3.95(3.95)	5.24(5.02)
$FeBr_3L$	red brown	31.67(31.65)	2.77(2.23)	2.87(2.84)
$FeBr_3L_2$	brown	45.23(45.21)	3.62(3.18)	4.02(4.06)
$FeBr_3L_3$	brown	52.56(52.76)	3.91(3.72)	4.75(4.73)
$FeBr_3L_4$	brown	57.33(57.54)	4.35(4.06)	4.97(5.16)
$FeBr_3L_6$	yellow	63.56(63.28)	4.78(4.46)	5.88(5.68)

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TABLE II. Infrared Bands (cm^{-1}), Magnetic Moments μ_{eff} (B.M.) and Molar Conductivities Λ_M (Ω^{-1} mol^{-1} cm^2) in 10^{-3} *M* DMF Solution of the Iron(III) Complexes of 4-Aminobenzophenone (L).

	L	$3FeCl_3 2L$	$2FeCl_3 3L$	$FeCl_3 2L$	$FeBr_3L$	$FeBr_3 2L$	$FeBr_3 3L$	$FeBr_3 4L$	$FeBr_3 6L$
ν(CO)	1635vs	1650vs	1650sh	1640sh	1650vs	1648vs	1640sh	1640sh	1640sh
$\delta(NH_2)$	1625vs	1625vs	1628vs	1630vs	1633m	1627s	1630vs	1628vs	1630vs
		1603m	1603sh	1598sh	1610sm	1605w	1610w		
ν(FeN)		539s	540wb	539sm	551w	540mw	540sh	539w	
		473m	471ms	472w	461s	474mw	474w	476w	474mw
(FeX) vibr.		380vs	376vs	379vs	303s	287vs	279vs	280vs	
		330m	329sh	329sh	267s	240m	240vs	239vs	
		276mw	270mb	275m	143s				
		135s	132w	137s	106s				
μ_{eff}(B.M.)*		4.74	5.02	4.58	2.02	3.93	4.01	4.74	3.93
Λ_M		69.0	81.5	26.0	99.6	120.0	115.0	99.7	99.7

*Per ferric ion.

$FeBr_3L$

By adding hexane to an EtOH solution of $FeBr_3$ and L in a M:L = 1:1 ratio a brown viscous liquid separated; by washing repeatedly with petroleum ether a uniform microcrystalline product was obtained.

$FeBr_3L_2$, $FeBr_3L_3$ and $FeBr_3L_4$

These compounds crystallized from Et_2O solutions containing the reagents in M:L ratios of 1:2, 1:3 and 1:4, respectively.

$FeBr_3L_6$

By adding hexane to an EtOH solution saturated with both $FeBr_3$ and L a yellow-brown viscous liquid separated; by washing repeatedly with petroleum ether a microcrystalline product was obtained.

The compounds were washed with petroleum ether and dried *in vacuo* on P_2O_5; they are stable in air. Elemental microanalyses are reported in Table I. Molar conductivities were determined with a WTW conductivity bridge. Magnetic susceptibilities were determined at room temperature with the Gouy method and corrected for the Pascal constants. Electronic spectra were recorded on the solids as Nujol mulls on polythene with a Shimadzu MPS-50L spectrophotometer. Infrared spectra were recorded in KBr disks (4000–250 cm^{-1}) and as Nujol mulls on polythene (600–60 cm^{-1}) with a Perkin-Elmer 180 spectrophotometer (Table II).

Results and Discussion

The ν(NH) and $\delta(NH_2)$ bands of the ligand were identified from their shifts in the deuteriated compound [3]. Three very distinct bands are observed in the spectrum recorded on the solid ligand in KBr disks (3418ms, 3335s, 3220m cm^{-1}). These bands appear at about the same frequencies in most of the iron(III) halide complexes. For the $FeCl_3$ complexes their shape is only slightly distorted with respect to those of the ligand, while for the $FeBr_3$ complexes they are deeply distorted (1:1 and 1:2 complexes) or split (1:3 and 1:4 complexes). Moreover all the bromide complexes show a new broad band in the 2870–2890 cm^{-1} region.

The $\delta(NH_2)$ band at 1625 cm^{-1} shows a very slight increase in some complexes while a new band, mostly medium or weak, appears at 1600–1610 cm^{-1}. The ν(CO) band at 1635 cm^{-1} is shifted in the complexes to higher frequencies (1640–1650 cm^{-1}) excluding a coordination of the ligand through the carbonylic oxygen atom. It is therefore likely that the aminic nitrogen atom is the preferred coordination site in all the complexes.

Two new bands appearing in the spectra of the complexes at 540–550 and 460–475 cm^{-1} may be assigned to ν(FeN) modes in agreement with the frequencies observed for the SnX_4 [3] and BCl_3 and AlX_3 complexes [4] of this ligand and other literature values (480–470 cm^{-1}) for iron(III) complexes.

The $FeCl_3$ complexes show the same FeCl vibration bands. Those at 376–380, 329–330 and 132–137 cm^{-1} correspond to the ν_3, ν_1 and ν_4 bands, respectively, of the $FeCl_4^-$ ion [6]. The ν(FeCl) band at 270–276 cm^{-1} corresponds to the FeCl stretching frequency shown by other chromophores at about 265–280 cm^{-1} [7–9].

The molar conductivities of the $3FeCl_3 \cdot 2L$ and $2FeCl_3 \cdot 3L$ complexes (Λ_M = 69.0 and 81.5, respectively) are in the range given for 1:1 electrolytes in DMF (Λ_M = 65–90) [10]. An ionic constitution like $[Fe_2Cl_5L_2^+][FeCl_4^-]$ and $[FeCl_2L_3^+][FeCl_4^-]$ could account for these molar conductivities and for the presence of the $FeCl_4^-$ infrared bands. By assuming for the $FeCl_4^-$ ion a μ_{eff} = 6.0 [11] a residual magnetism of 2 × 4.11 and 4.04 B.M. calculated for the $[Fe_2Cl_5L_2^+]$ and $[FeCl_2L_3^+]$ ions, respectively, may correspond for the ferric ions of these complexes to a S = 3/2 ground state [6] probably due to a five coordination.

An ionic constitution like $[Fe_2Cl_5L_6^+][FeCl_4^-]$ may be proposed for the $FeCl_3L_2$ complex, thereby accounting for the presence of the $FeCl_4^-$ ion and in agreement with a 1:1 molar conductivity of Λ_M = 78 for the trinuclear complex.

Our measurements of the molar conductivities in DMF solution gave a Λ_M of 36 and 95 for $FeCl_3$ and $FeBr_3$, respectively. The molar conductivities of the $FeBr_3$ complexes are in the range observed for the free iron(III) bromide, indicating that a strong solvolysis occurs in DMF solution for all these compounds.

Only a few ν(FeBr) bands could safely be identified for some of these complexes. The $FeBr_3L$ complex shows two $\nu(FeBr)_t$ frequencies different from those of the other complexes and corresponding to those (306 and 273 cm^{-1}) given for the six coordinated $[FeBr_2(diars)_2]Br$ complex [6] and two strong bands assignable to $\nu(FeBr)_b$ or δ(FeBr) modes. The magnetic moment of this complex corresponds to one unpaired electron in an octahedral field $^2T_{2g}$ [6].

The $FeBr_3L_2$, $FeBr_3L_3$ and $FeBr_3L_4$ complexes show a very strong band at 287–279 cm^{-1} which, because of its high intensity, may be assigned to a $\nu(FeBr)_t$ mode, even if superimposed on or coupled with the medium–strong bands of the ligand at 288 and 282 cm^{-1}; also a new band is observed at 240 cm^{-1}. The multiplicity of ν(NH) bands observed for the $FeBr_3L_3$ and $FeBr_3L_4$ complexes could indicate the presence of uncoordinated ligand molecules. The $FeBr_3L_2$ and $FeBr_3L_3$ complexes may contain similar chromophores with a magnetic moment corresponding to a S = 3/2 ground state.

The $FeBr_3L_6$ complex shows a single ν(FeN) band and no detectable ν(FeBr) bands and has a magnetic moment corresponding to a S = 3/2 ground state.

Electron spin resonance was observed with polycrystalline samples of the three compounds

	$g_\perp$	$g_\parallel$
$FeBr_3L_2$	4.03	2.10
$FeBr_3L_3$	4.03	2.10
$FeBr_3L_6$	3.75	2.02

from which the above reported $g_\perp$ and $g_\parallel$ values can be deduced [12].

These values are similar to those ($g_\perp$ = 4.08 and $g_\parallel$ = 2.1) observed for the almost square-pyramidal $[Fe^{III}Cl(S_2CN(C_2H_5)_2]$ complex [13] and those ($g_\perp$ = 3.8 and $g_\parallel$ = 2) observed for the compound monochlorophthalocyaninatoiron(III) which almost certainly involves a similar square-pyramidal stereochemistry about the central iron atom [14].

The electronic spectra of the complexes show a very strong band in the 27–28 kK region, where the ligand shows a very strong band at 26.67 kK, and a very strong charge transfer band in the 23–20 kK region. No d–d bands could safely be identified in the 16–13 kK region.

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