

Reactions of Iron(III) Salts with 2-Pyridylamines. Synthesis and Physical Data, Including Mössbauer Spectra

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Complexes of iron(III) and iron(II) with various pyridylamines are reported (specifically di- and tri-(2-pyridyl)amine and 4- and 5-methyl-2-pyridyldi-(2-pyridyl)amine). The iron(III) complexes constitute three types which can be seen as stages in the base hydrolysis of the metal ion. Class A contains the anion $[Cl_3Fe \cdot O \cdot FeCl_3]^{2-}$; class B, which occurs only for the terdentate ligands, are monomers of the type $[(\text{ligand})FeX_3]$ ($X = \text{halogen}$). Most complex is class C, restricted to di-(2-pyridyl)amine, which are molecularly complex with two distinct iron sites, both spin 5/2 antiferromagnetically coupled. An aged specimen of one compound (4 years) shows considerable change in iron(III) environments and unusual temperature dependence of Mössbauer parameters.

Iron(II) thiocyanate derivatives are reported. They are generally straightforward and most are ionic containing either four co-ordinate $[Fe(NCS)_4]^{2-}$ or six co-ordinate $[Fe(\text{bidentate})(NCS)_4]^{2-}$ anions.

The compounds reported are characterised as far as possible by reference to their magnetic properties and spectroscopic, particularly ^{57}Fe Mössbauer, data.

Introduction

We have, over the past few years, published several papers describing the synthesis and physical properties of complexes of various pyridylamines [1]. They have proved to be versatile ligands with both non transition metals and transition metals, showing a variety of interesting behaviour. More detailed studies of individual compounds, or series of compounds, are hampered by lack of crystallographic data which, to date, are restricted to some complexes of copper(II) [2, 3] and one of iron(II) [4]. We now report data, including Mössbauer spectra, obtained for some iron complexes, which we have compiled into the last paper in the present series, until such times as the crystallographic situation should change.

Experimental

Di-(2-pyridyl)amine was a commercial specimen, tri-(2-pyridyl)amine was prepared by the method of

Wibaut and La Bastide [5] and 4- and 5-methyl-pyridyldi-(2-pyridyl)amine (4MPT and 5 MPT) were as previously reported [6].

Iron(III) Complexes

Bis(di-2-pyridylammonium)μ-oxo-hexachlorodiferate(II) monohydrate

Anhydrous iron(III) chloride (0.3 g) in dry ethanol (10 cc) was added dropwise to a cold solution of di-(2-pyridyl)amine (0.5 g) in ethanol (10 cc). A bright yellow product was formed immediately. This was filtered and washed with ethanol. Similar products were obtained with tri-(2-pyridyl)amine and with 4- and 5-methyl-2-pyridyl-di-(2-pyridyl)amines, in both cases only after refluxing. Di(2-pyridyl)amine however afforded a different product on refluxing the reactants (in ethanol or acetonitrile) for 30 min. A dark brown material with an iron:ligand ratio of 2:3 was obtained (Table I). The use of iron(III) bromide afforded a product in which the metal:ligand ratio was again 2:3 but which had a slightly different total composition (Table I).

Trichlorotri-(2-pyridyl)amineiron(III) and trichloro 4-methyl-2-pyridyl-di-(2-pyridyl)amineiron(III)

Iron(III) chloride (0.3 g) in ethanol (10 cc) was added dropwise to a solution of the pyridylamine base (0.5 g) in ethanol (10 ml). A bright yellow product separated out immediately which was filtered and washed with ethanol. In the case of the 4-methyl-substituted ligand, the same product was obtained on refluxing, but when the tri(2-pyridyl)amine preparation was refluxed, the product described above was formed.

Di-isothiocyanatobis di-(2-pyridyl)amineiron(III) tetrakisothiocyanatodi-(2-pyridyl)amineferrate(III)

Iron(III) chloride (0.3 g) in ethanol (10 cc) was added to potassium thiocyanate (1.0 g) in ethanol (10 cc) and filtered into a solution of di-(2-pyridyl)amine (0.5 g) in ethanol (10 cc). The dark red solution was refluxed for 20 min and, on setting aside, violet black crystals of the product separated.

TABLE I. Analytical Data.

No.	Compound	Colour	Analysis (Found)				Analysis (Calculated)					
			C	H	N	Halogen	Fe	C	H	N	Halogen	Fe
1	(Dipyam H ⁺) ₂ [(Cl ₃ Fe) ₂ O] ²⁻	Yellow	34.4	2.70	11.5	29.3	16.4	35.0	2.94	12.3	31.1	16.3
2	(Tripyam H ⁺) ₂ [(Cl ₃ Fe) ₂ O] ²⁻	Yellow	43.5	3.30	14.0	25.2	14.0	42.9	3.00	13.3	25.4	13.3
3	(SMPTH ⁺) ₂ [(Cl ₃ Fe) ₂ O] ²⁻	Yellow	44.4	3.70	13.1	24.9	13.3	44.3	3.50	12.9	24.6	12.9
4	Fe ₂ (dipyam) ₃ Cl ₄ O·5H ₂ O	Brown	41.0	3.60	14.0	16.0	13.3	40.1	4.20	14.0	16.9	13.3
5	Fe ₂ (dipyam) ₃ Br ₃ (OH)O	Brown	38.7	3.30	13.1	25.6	12.6	40.1	3.12	14.0	26.7	12.4
6	(Tripyam) FeCl ₃	Yellow	44.4	3.10	13.6	25.7	14.1	43.9	3.00	13.6	25.8	13.6
7	(4MPT) FeCl ₃	Yellow	44.9	3.60	13.1	24.9	13.2	45.2	3.30	13.2	25.2	13.1
8	[Fe(dipyam) ₂ (NCS) ₂] [Fe(dipyam)(NCS) ₄]	Violet-black	44.9	3.40	23.2	-	12.1	44.4	3.40	23.6	-	11.6
9	[Fe(tripyam) ₂ (NCS) ₂] [Fe(tripyam)(NCS) ₄]	Deep violet	50.4	3.20	21.4	-	10.0	50.8	3.00	21.0	-	9.5
10	[Fe(tripyam) ₂] [Fe(NCS) ₄]	Red-brown	48.2	2.80	20.0	-	13.0	48.6	2.80	20.0	-	13.4
11	[Fe(4MPT) ₂ (NCS) ₂] H ₂ O	Brown	57.1	4.00	19.5	-	8.2	57.1	4.20	19.6	-	7.8
12	[Fe(4MPT) ₂] [Fe(NCS) ₄]	Orange-brown	48.4	3.80	18.9	-	13.0	49.8	3.25	19.4	-	12.9
13	[Fe(3MPT) ₂] [Fe(NCS) ₄]	Red-brown	50.2	3.30	19.5	-	12.5	49.8	3.25	19.4	-	12.9

A similar procedure afforded the tri-(2-pyridyl)amine product.

Iron(II) Complexes

Some reactions were carried out with iron(II) for comparative purposes.

Bistri-(2-pyridyl)amineiron(II) tetrakisothiocyanatoferrate(II) (and related compounds)

All reactions were carried out in an atmosphere of nitrogen. Iron(II) chloride (0.25 g) in ethanol (10 cc) was added to potassium thiocyanate (0.7 g) in ethanol (10 cc) and filtered into a solution of tri-(2-pyridyl)amine (0.5 g) in ethanol (10 cc) and refluxed for 10 min. On setting aside a reddish brown material separated out. The same method afforded [Fe(5-MPT)₂] [Fe(NCS)₄]. When 4-methyl-2-pyridyldi-(2-pyridyl)amine was used, two products were obtained: the dark brown [Fe(4MPT)₂(NCS)₂]·H₂O which, on warming converted to the reddish brown [Fe(4MPT)₂] [Fe(NCS)₄]·H₂O.

Physical Measurements

Mössbauer spectra were recorded as previously described [7] for powdered samples, data were computed using a curve fitting programme developed by Coulard and modified by Gillespie. Spectra were recorded for all specimens at room temperature and, for some complexes, were duplicated at liquid nitrogen temperature. Magnetic susceptibility determinations were by the Gouy method and conductivity data were obtained using a Henelec bridge. Infra-red spectra were obtained for nujol mulls in caesium iodide supports with Perkin Elmer 457 and 225 grating spectrophotometers. Electronic spectra were recorded with a Unicam SP700 instrument incorporating the SP735 reflectance attachment.

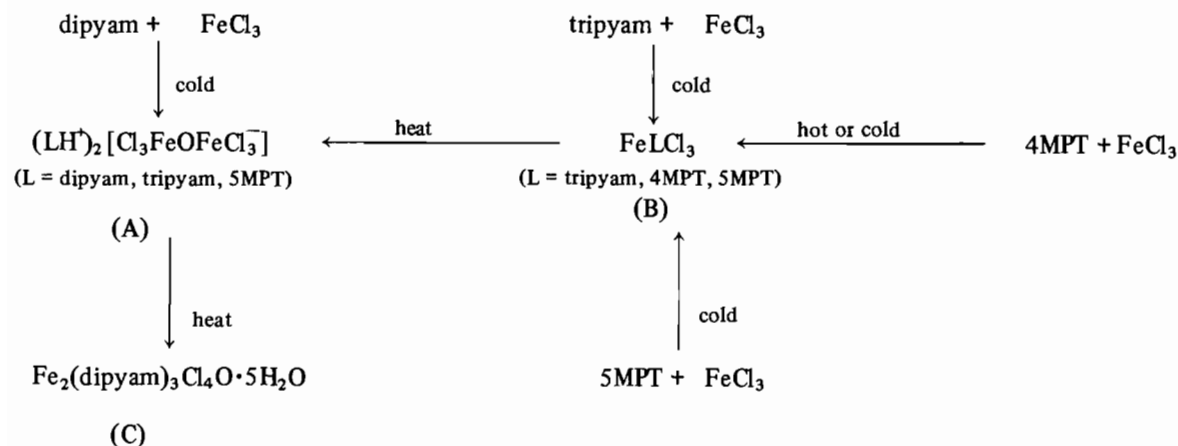
Carbon, hydrogen and nitrogen analyses were obtained by standard micro-analytical techniques within the department. Iron was analysed by atomic absorption spectroscopy and halogen was determined gravimetrically after decomposition of the complex by fusion with sodium carbonate. Ion exchange studies were carried out using Deacidite FF as the anion exchange resin and Zeocarb 225 as the cation exchange resin.

Results

Analytical data are gathered into Table (I), physical data are gathered into Table (II) (conductivity, magnetic and infra-red data) and Table III (Mössbauer data).

Iron(III) Complexes

The reaction between iron(III) chloride and various pyridylamines in ethanol may be conveniently summarised in the following scheme:



Scheme

dipyam = di-(2-pyridyl)amine; tripyam = tri-(2-pyridyl)amine; 4MPT, 5MPT = 4- and 5-methyl-2-pyridyl-di-(2-pyridyl)amine)

Thus, up to a point, the compounds may be regarded as stages in the base hydrolysis of the iron(III); the extent of the reaction depending upon the particular pyridylamine, e.g. 4-methyl-2-pyridyl-di-(2-pyridyl)amine affords only (4MPT)FeCl₃. It is now convenient to discuss the three types of iron(III) complex A (1, 2, 3, Table I), B (6, 7, Table I) and C (4, 5, Table I).

The compounds of type A are characterised by the appearance of NH stretching frequencies in the infra-red spectra; indeed the bands arising from the di-(2-pyridyl)amine entity in complex 1 (Table II) are virtually identical with those of (dipyamH)[Fe-

Cl₄], which was prepared for comparison [7], and different from the spectra of metal complexes in which the amine is co-ordinated. Also the complexes 1, 2 and 3 (Table I) have conductivities in

dilute DMF or nitromethane which are close to values expected for 2:1 electrolytes. Thus an ionic formulation involving pyridylammonium cations is implied. A band between 800 and 890 cm⁻¹ is noted in the i.r. spectra of the complexes which is characteristic of ν(FeOFe) for an oxo-bridged complex [9]; this observation, together with the assignment of two iron-chlorine stretching vibrations, is consistent with the presence of an anion [Cl₃Fe-O-FeCl₃]²⁻. The effective magnetic moment at room temperature is low, but Mössbauer chemical isomer shift data (Table III) indicate a 5/2 spin state for the iron(III) [10]; thus the two iron(III) centres are antiferromagnetical-

TABLE II. Physical Data.

No. ^a	μ _{eff} (B.M.) ^b	M(DMF) ^c	Significant Infra-Red Bands (cm ⁻¹ with assignment)
1	2.3	100	3320 (νNH); 890 (Fe-O-Fe); 375, 323 (νFeCl)
2	2.0	155 ^d	890 (Fe-O-Fe); 360, 317 (νFeCl)
3	2.2	100	863 (Fe-O-Fe); 360, 318 (νFeCl)
4	2.2	35	3530 (νOH); 845 (Fe-O-Fe); 360, 355sh., 343 (νFeCl)
5	2.1	200	3530 (νOH); 800 (Fe-O-Fe); 286, 250 (νFeBr)
6	5.69	25 ^d	354, 310, 292 sh (νFeCl)
7	5.8	35 ^d	360, 310, 295 sh (νFeCl)
8	5.7	94	2070, 2035, 2013, 1995sh (νCN); 840 (νCS); 490 (δNCS); 295 (complex) (νFe-CNS)
9	5.8	95	2065, 2050, 2030 (νCN);
10	3.8	100 ^d	2068sh, 2060 (νCN); 485 (δNCS)
11	5.5	30 ^d	2068 (νCN); 3490 (H ₂ O)
12	5.34	100 ^d	2085sh, 2057 (νCN); 834 (νCS); 496 (δNCS); 300 (νFe-NCS)
13	5.34	90 ^d	2090sh, 2058 (νCN); 836 (νCS); 482 (δNCS); 309 (νFe-NCS)

^aSee Table (I) for key. ^bAmbient temperature. ^c10⁻³ M solutions. ^dNitromethane solution.

TABLE III. Mössbauer Data.

No ^a	Ambient Temp.		80K	
	δ mm sec ⁻¹ ^b	δ mm sec ⁻¹ ^b	Δ mm sec ⁻¹ ^c	Δ mm sec ⁻¹ ^c
1	0.23	1.20	0.34	1.31
2	0.20	1.19	—	—
3	0.23	1.31	0.34	1.31
4 ^d	0.14	0.81	0.18	1.12
	0.44	0.73	0.33	1.42
4 ^e	0.25	1.28	0.33	1.33
	0.41	0.75	0.43	0.54
5	0.43	0.86	—	—
	0.42	0.53	—	—
6	0.30	0.00	0.44	0.00 ($t_{1/2} = 0.92$)
7	0.35	0.20	—	—
8	0.37	0.62	—	—
9	0.35	0.66	—	—
10	0.37	0.00	—	—
11	1.10	1.17	—	—
12	0.37	0.20	—	—
13	0.35	0.20	0.41	0.00
			1.10	2.93

^aSee Table I for key. ^b ± 0.01 mm sec⁻¹. ^c ± 0.01 mm sec⁻¹. ^dSample 4 years old. ^eSample freshly prepared.

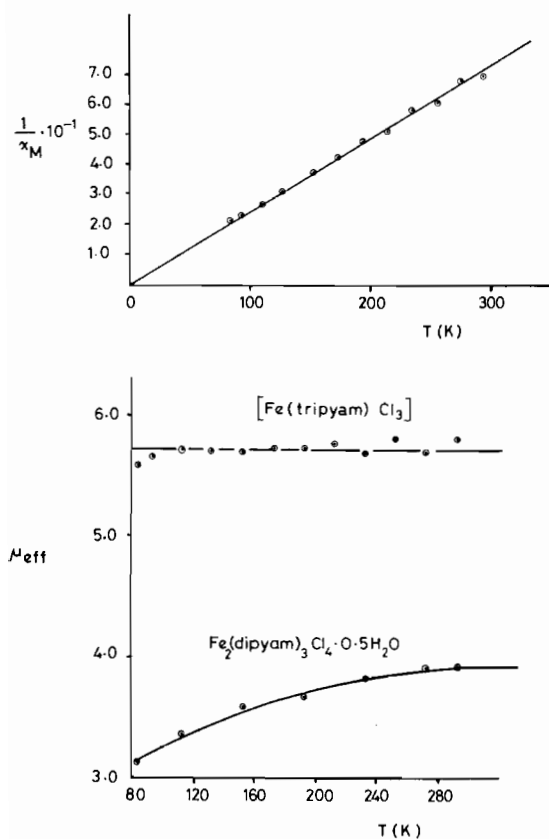


Figure 1. (a). Plot of $1/\chi_M$ against T (K) for $[\text{Fe}(\text{triptyam})\text{Cl}_3]$. (b). Plot of μ_{eff} against temperature for $[\text{Fe}(\text{triptyam})\text{Cl}_3]$ and for an aged specimen of $\text{Fe}_2(\text{dipyam})_3\text{Cl}_4 \cdot 0.5\text{H}_2\text{O}$.

ly coupled. Furthermore, the Mössbauer data support a tetrahedral configuration [11], the quadrupole splitting indicating a local symmetry less than cubic, this being entirely consistent with the proposed formulation as $(\text{LH}^+)_2[\text{Cl}_3\text{Fe}-\text{O}-\text{FeCl}_3]^{2-}$ (L = dipyam, 4MPT, 5MPT).

The compounds of type B have stoichiometry FeLCl_3 (where L = triptyam or 4 MPT). The infrared spectra [7] show quite clearly that the pyridylamines are terdentate [12, 13], thus a simple monomeric structure is apparently indicated. Conductivities in nitromethane are not negligible, but are too low to be consistent with any plausible ionic structure, hence some degree of solvolysis is implied. The effective magnetic moments and Mössbauer parameters at ambient temperatures support assignment of a $5/2$ spin state for the iron(III). However, the Mössbauer data at 80K for $[\text{Fe}(\text{triptyam})\text{Cl}_3]$ (Table III) show a very significant broadening of the resonance. This led us to examine the magnetic properties over a range of temperatures (300–80K), but the compound proved to be well behaved over this temperature range. Thus μ_{eff} was constant (even if marginally lower than expected for $S = 5/2$) and the Curie–Weiss law was obeyed with a Weiss constant tending to zero (Fig. 1 (a), (b)). It is not feasible to attribute the broadening of the Mössbauer line to incipient magnetic ordering at 80K (unlikely anyway). A more probable explanation is that a small quadrupole splitting is present the higher energy component of which is broadened to the extent of being undetectable at room temperature. Such behaviour is not uncommon in iron(III)

complexes and is often attributed to fast electronic relaxation involving the lower Kramer's doublet $M_s = \pm \frac{1}{2}$ arising from zero field splitting with positive D [14, 15]. The origin of the quadrupole splitting is probably distortion from ideal C_{3v} symmetry in the crystal lattice, a suggestion which could also explain the origin of three infra-red active iron-chlorine stretching vibrations (Table II). Thus, within the limitations of our measurements (80K limit) the data available generally support the simple monomeric formulation.

The type C compounds are the most complex of those reported. Extensive analytical data (Table I) indicate a stoichiometry of $Fe_2Cl_4O(dipyam)_3 \cdot 5H_2O$ for the chloride and of $Fe_2Br_3O(OH)(dipyam)_3$ for the bromide. However it must be pointed out that a range of compositions give an "analytical fit", the stoichiometrically most simple forms are given in Table I. The chloro- and bromo- compounds are not stoichiometrically related, they have greatly differing conductivities in DMF (Table II), but both may be reproducibly prepared. The infra-red spectra of both compounds confirm the presence of $-OH$ groups, show bands characteristic of $\nu(FeOFe)$ and indicate the presence of terminal halide ligands. The room temperature magnetic moments are low. The Mössbauer data show the presence of two iron sites (Table III) both of which correspond to spin 5/2 as judged from the isomer shift data. One site ($\Delta \sim 0.75$ mm sec^{-1}) has parameters consistent with a distorted six co-ordinate environment, but the other has a remarkably large quadrupole splitting ($\Delta = 1.28$ mm sec^{-1}). Since it is not really plausible to invoke some intermediate spin state for this iron site, an alternative suggestion that the co-ordination number may be greater than six might be made. For example, seven co-ordinate high spin iron(III) in a mixed nitrogen-oxygen environment is seen in $NH_4HFeDTPAH_2O$ ($\Delta = 1.095$ mm sec^{-1}) ($H_5DTPA =$ diethylenetriaminepentacetic acid) [16]. The bromide (compound 5, Tables I and III) also has two iron sites one of which is considerably more distorted than the other.

We remeasured the Mössbauer parameters of a sample of compound 4 which was some four years old. The results in Table III indicate that considerable change has occurred to the iron environments over that period of time, although the elemental analysis had not altered. The major change has affected the site of large Δ in the freshly prepared sample. On cooling to 80K even more strange effects are observed in that both sites now show very large quadrupole splitting. We have examined the magnetic susceptibility of this specimen to 80K but observe no discontinuities. The Curie-Weiss law is obeyed, but with a Weiss constant in excess of 100° (Fig. 2); μ_{eff} shows temperature dependence but the variation is smooth (Fig. 1(b)). The situation is clearly complex and a phase change on cooling would seem

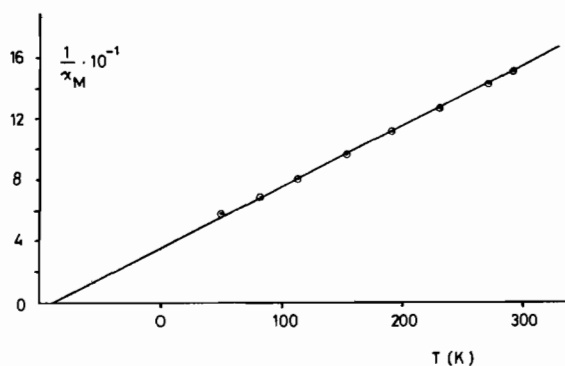


Figure 2. Plot of $1/\chi_M$ against T (K) for an aged specimen of $Fe_2(dipyam)_3Cl_4O \cdot 5H_2O$.

at present to be the least unlikely explanation. This might conceivably produce extra distortion at the iron site and increase Δ without actually producing a discontinuity in the magnetic behaviour between 298 and 80K. The systems are clearly complex in behaviour and are of considerable molecular complexity; further speculation as to structure is not justified but it is interesting to speculate how common the ageing phenomenon observed here is for other polynuclear iron systems.

Iron(III) Thiocyanate Complexes

Compounds 8 and 9 (Table I) are intensely coloured solids of stoichiometry $FeL_{1.5}(NCS)_3$ ($L =$ dipyam or tripyam), hence the molecular formula is probably $Fe_2L_3(NCS)_6$. The infra-red spectrum below 600 cm^{-1} of the tri-(2-pyridyl)amine complex is typical of bidentate tri(2-pyridyl)amine [12], thus formulations $[FeL_2(NCS)_2][FeL(NCS)_4]$, $[FeL_3][Fe(NCS)_6]$ and $[L_2Fe(NCS)_2FeL_2](NCS)_2$ are all possible in view of the fact that DMF solutions conduct electricity (Table II). The $\nu(CN)$ region of the infra-red spectrum is fairly complex, but is indicative of isothiocyanato-groups. No clear evidence for bridging groups is seen. The diffuse reflectance spectra of both compounds are characterised by a strong charge transfer band between 17 and 18 kK and a weaker feature at 9 kK. The similarity of spectra may be taken to imply similar iron(III) environments for each compound.

Cation and anion exchange experiments with aqueous ethanolic solutions of the complexes, followed by isolation of residues for spectroscopic examination revealed that the pyridylamine and thiocyanate groups were present in both anion and cation, a conclusion compatible only with the formulation $[FeL_2(NCS)_2][FeL(NCS)_4]$ given in Table I. The cation may exist in *cis*- or *trans*- forms. This *cis*- isomer is the more probable on steric grounds but the *trans*- isomer is not impossible. It may reasonably be assumed that $\nu(CN)$ for the anion will lie at lower frequency than for the cation, thus for compound 8

the bands between 2035 and 1995 cm^{-1} may arise from $[\text{FeL}(\text{NCS})_4]^-$, thus leaving the single band at 2070 cm^{-1} to imply a *trans*- geometry for the cation. However, for 9, which has an almost identical electronic spectrum with 8, the broad band at 2030 cm^{-1} is assignable to the anion leaving two bands to be assigned to the cation. Clearly the infra-red spectra do not provide a reliable guide to stereochemistry for those materials.

The magnetic data are typical for high spin iron(III) (Table II) as are the Mössbauer parameters in Table III. One quadrupole doublet is seen but the width of the resonance is such as to suggest the presence of two doublets of very similar δ and Δ .

Iron(II) Complexes

Compounds 10–13 in Table I are reasonably straightforward materials. Both tripyam and 5MPT afford directly compounds which are formulated as $[\text{FeL}_2][\text{Fe}(\text{NCS})_4]$. Whereas 4MPT forms an intermediate $[\text{Fe}(4\text{MPT})_2(\text{NCS})_2]\text{H}_2\text{O}$ which, on heating, converts to $[\text{Fe}(4\text{MPT})_2][\text{Fe}(\text{NCS})_4]$. The evidence for the formulations $[\text{FeL}_2][\text{Fe}(\text{NCS})_4]$ may be briefly summarised. The conductivities in nitromethane (Table II) are quite consistent with a 1:1 electrolyte, and the effective magnetic moment indicates the presence of one high spin iron(II) centre. The Mössbauer data show the presence of a low spin iron(II) site and the parameters in Table II are in good agreement with those previously reported for FeL_2^{2+} (L = tripyam [17], or 4 and 5MPT [13]). It is not unusual for tetrahedral species to give weak signals at room temperature, but on cooling $[\text{Fe}(5\text{MPT})_2][\text{Fe}(\text{NCS})_4]$ a doublet ($\delta = 1.10$, $\Delta = 2.93 \text{ mm sec}^{-1}$) characteristic of high spin iron(II) and in good agreement with parameters previously reported for $[\text{Fe}(\text{NCS})_4]^-$ is seen. Finally, the infra-red data in the $\nu(\text{CN})$ region and the diffuse reflectance spectra, which are similar to those of $[\text{FeL}_2](\text{ClO}_4)_2$ [13, 17], fully support the formulation.

Compound 11 is of rather more interest. The 4MPT ligand is bidentate [19], the compound is essentially a non-electrolyte although some solvolysis might occur in solution, and the infra-red spectrum indicates isothiocyanato-groups. We do not attempt to deduce stereochemistry from the multiplicity of $\nu(\text{CN})$. The iron(II) is in the high spin state, a fact confirmed by both μ_{eff} and the Mössbauer chemical isomer shift. The quadrupole splitting is however rather smaller than that observed for similar systems, e.g. $[\text{Fe}(2,2'\text{-bipyridyl})_2$ -

$(\text{NCS})_2]$, $\Delta \sim 2.2 \text{ mm [20] sec}^{-1}$, but is within the range reported for iron(II) with $S = 2$ generally [10].

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