

Spectral Studies of some Octahedral Iron(II) Complexes with Nitrogen Donors

C. D. Burbridge and D. M. L. Goodgame

Received November 29, 1969

The preparations and Mössbauer, electronic, and infrared spectra of the compounds $Fe(\text{imidazole})_6X_2$ ($X = \text{Cl}, \text{Br}, \text{I}, \text{or } \text{ClO}_4$) are reported. These complexes contain the hexakis-imidazoleiron(II) cation, but similar studies on the compounds $Fe(\text{pyridine})_6X_2$ ($X = \text{Br}, \text{I}, \text{or } \text{NCO}$) show that these are of the type $[Fe\text{py}_6X_2] \cdot 2\text{py}$. The magnetic moments and Mössbauer and electronic spectra of the compounds $FeL_4(\text{NCO})_2$ ($L = \text{pyridine}, 4\text{-methylpyridine}, \text{or } \text{isoquinoline}$) show that these differ from their isothiocyanate and isoselenocyanate analogues in having the 5B_g level as the ground state.

Introduction

Imidazole (= Im) forms a well-defined series of complexes of stoichiometry $M(\text{Im})_6X_2$ with divalent first row transition metal ions.^{1,2} This contrasts with the behaviour of the more sterically hindered heterocycle pyridine, which forms few solid 6 : 1 complexes with these metal ions and, of these, only $[Fe\text{py}_6] \cdot [Fe_4(\text{CO})_{13}]$ is known³ to contain a discrete Mpy_6^{2+} cation. However, low frequency vibrational spectral studies² on a range of $M(\text{Im})_6X_2$ compounds indicated distortion from O_h symmetry in the $M(\text{Im})_6^{2+}$ cations. In the case of high-spin iron(II) Mössbauer spectroscopy provides an alternative way of examining such ligand distortions for a related series of compounds. We report here the synthesis of several salts containing the $Fe(\text{Im})_6^{2+}$ cation and their Mössbauer, electronic, and low frequency infrared (i.r.) spectra. Results are also given for some $FeL_4(\text{NCA})_2$ compounds where $L = \text{a heterocyclic amine}$ and $A = \text{O}, \text{S}, \text{or } \text{Se}$, and for some complexes of stoichiometry $Fe\text{py}_6X_2$.

Experimental Section

Preparation of Compounds. All solvents were dried and were deoxygenated by passing oxygen-free nitrogen through them before use. A nitrogen atmosphere was maintained during the preparations.

$Fe(\text{imidazole})_6X_2$ ($X = \text{Cl}, \text{Br}, \text{I}, \text{or } \text{ClO}_4$). A solution of the appropriate iron(II) salt (0.001 mole)

in 2.5 ml of a 1:1 mixture of ethanol and 2,2-dimethoxypropane was added to one of imidazole (0.008 mole) in 5-10 ml of the same solvent. A further quantity (ca. 5 ml) of 2,2-dimethoxypropane was added to the mixture, and, after 1 hr. at ca. 10°, the practically colourless or pale cream ($X = \text{I}$) crystals which had formed were filtered off, washed with ether and dried in vacuum. Individual details: *Chloride*: 70% yield. *Anal.* Found: Cl, 13.35; Fe, 10.25. *Calcd.*: Cl, 13.25; Fe, 10.4. Soluble in ethanol. *Bromide*: 65% yield. *Anal.* Found: Br, 25.6; Fe, 9.15. *Calcd.* Br, 25.6; Fe, 8.95. *Iodide*: 40% yield. *Anal.* Found: I, 35.4. *Calcd.* I, 35.3. Compound unchanged after several weeks storage in a closed tube. *Perchlorate*: 75% yield. *Anal.* Found: C, 32.4; H, 3.8; Fe, 8.4. *Calcd.* C, 32.6; H, 3.65; Fe, 8.4%. $\Lambda_M = 42 \text{ ohm}^{-1} \text{ cm}^2$ ($25^\circ, 10^{-3} M$ in PhNO_2).

$Fe(\text{isoquinoline})_4(\text{NCSe})_2$. A solution of iron(II) sulphate heptahydrate (1.4 g) in water (10 ml) and methanol (10 ml) was added to one of potassium selenocyanate (1.4 g) in water (10 ml) and methanol (20 ml) containing isoquinoline (10 ml). A yellow solid was immediately formed, which was filtered off, washed with ethanol, dried *in vacuo*, and then recrystallised from isoquinoline under nitrogen. *Anal.* Found: C, 58.7; H, 3.45; NCSe, 26.7. *Calcd.* C, 58.3; H, 3.6; NCSe, 26.8.

$Fe(\text{isoquinoline})_4(\text{NCO})_2$. Red-orange deliquescent crystals were obtained as above but using potassium cyanate (0.8 g). *Anal.* Found: C, 69.25; H, 4.5; N, 12.45. *Calcd.* C, 69.5; H, 4.3; N, 12.8.

$Fe(4\text{-methylpyridine})_n(\text{NCS})_2$ ($n = 4.5 \text{ and } 5$). Recrystallisation of $Fe(4\text{-methylpyridine})_4(\text{NCS})_2$ ⁴ from 4-methylpyridine at 60-70° gave fine yellow needles of stoichiometry $Fe(4\text{-methylpyridine})_{4.5}(\text{NCS})_2$. *Anal.* Found: C, 59.1; H, 5.45; NCS, 19.7. *Calcd.* C, 58.9; H, 5.4; NCS, 19.65. Slow crystallisation of the 4:1 complex from 4-methylpyridine at ca. 0° gave large, yellow, octahedral crystals of stoichiometry $Fe(4\text{-methylpyridine})_5(\text{NCS})_2$. *Anal.* Found: NCS, 18.2. *Calcd.* NCS, 18.2. Recrystallisation carried out near room temperature gave a mixture of crystal types. Both forms showed considerably increased stability towards aerial oxida-

(1) W. J. Eilbeck, F. Holmes, and A. E. Underhill, *J. Chem. Soc. (A)*, 757 (1967).

(2) D. M. L. Goodgame, M. Goodgame, P. J. Hayward, and G. W. Rayner Canham, *Inorg. Chem.*, 7, 2447, (1968).

(3) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, 88, 4847 (1966).

(4) C. D. Burbridge, D. M. L. Goodgame, and M. Goodgame, *J. Chem. Soc. (A)*, 349 (1967).

tion compared with the 4:1 compound.⁴ If the crystals were crushed, 4-methylpyridine was lost and the compound reddened over several hours. Conversion to the 4:1 compound could be achieved by shaking the powdered compounds with ether.

$Fe(4\text{-methylpyridine})_n(NCSe)_2$ ($n = 4, 4.5$ and 5). A method similar to that used for $Fe(\text{isoquinoline})_4(NCSe)_2$ gave a yellow solid. Recrystallisation of this from 4-methylpyridine at $0\text{-}10^\circ$ gave yellow needles of stoichiometry $Fe(4\text{-methylpyridine})_{4.5}(NCSe)_2$. *Anal.* Found: NCSe, 30.55; Calcd. NCSe, 30.7. Recrystallisation near 70° gave large, yellow, octahedral crystals of $Fe(4\text{-methylpyridine})_5(NCSe)_2$. *Anal.* Found: C, 52.8; H, 4.5; NCSe, 28.8. Calcd. C, 52.5; H, 4.8; NCSe, 28.7. The 4:1 complex could be prepared from either the 4.5:1 or 5:1 compound by shaking the powdered complex with several portions of ether and drying the product *in vacuo*. *Anal.* Found: NCSe, 32.85. Calcd. NCSe, 32.9.

$Fe(4\text{-methylpyridine})_4(NCO)_2$. Yellow needles were obtained as for the isoquinoline analogue. *Anal.* Found: C, 60.7; H, 5.6; N, 16.05. Calcd. C, 60.9; H, 5.5; N, 16.4.

$Fepy_4(NCSe)_2$. Pale yellow needles were prepared as for the isoquinoline analogue but without the use of methanol. *Anal.* Found: NCSe, 36.2. Calcd. NCSe, 36.1.

$Fepy_n(NCO)_2$. The procedure used for the isoselenocyanate gave a yellow solid. Recrystallisation of this from pyridine gave the 6:1 compound. *Anal.* Found: C, 62.3; H, 5.05; N, 17.9. Calcd. C, 62.5; H, 4.9; N, 18.2. Recrystallisation from methanol afforded the 4:1 compound. *Anal.* Found: C, 57.8; H, 4.5; N, 18.0. Calcd. C, 57.9; H, 4.4; N, 18.4. The yellow crystals of the 4:1 complex oxidize in air, turning brown in a few hours.

$Fepy_6X_2$ ($X = Br$ and I). The corresponding 4:1 complexes were recrystallised from pyridine at $0\text{-}10^\circ$. Slow crystallisation below room temperature was found necessary, particularly for the bromide, to avoid formation of the 4:1 compound. The yellow crystals were collected under nitrogen, washed with a little ice-cold pyridine and stored under nitrogen in a refrigerator. Under these conditions and if slightly damp with pyridine they could be kept for long periods. Before use the samples were placed under vacuum until dry, and analysed. *Bromide.* *Anal.* Found: Br, 23.25; Fe, 8.0. Calcd. Br, 23.2; Fe, 8.1. In air or after a long time *in vacuo* the crystals crumble to a powder with loss of pyridine. *Iodide.* *Anal.* Found: C, 45.9; H, 3.9; I, 32.4. Calcd. C, 46.15; H, 4.05; I, 32.4. The compound darkens rapidly in air.

Physical Measurements. These were carried out as described previously.^{2,4}

Results and Discussion

Imidazole Complexes. Complexes of stoichiometry $Fe(\text{Im})_6X_2$ ($X = Cl, Br, I, \text{ or } ClO_4$) were readily

obtained from dry, deoxygenated ethanol: 2,2-dimethoxypropane solutions of the iron(II) salt and an excess of imidazole. Evidence for the presence of the hexakisimidazoleiron(II) cation in the halide complexes is provided by their electronic spectra and by X-ray isomorphism studies. X-ray powder photographs show that isomorphism occurs within the following groups of complexes: $M(\text{Im})_6Cl_2$ ($M = Mn$ and Fe), $M(\text{Im})_6Br_2$ ($Me = Fe, Co, \text{ and } Ni$), $M(\text{Im})_6I_2$ ($M = Mn, Fe, Co, \text{ and } Ni$). The manganese, cobalt, and nickel compounds are considered to contain $M(\text{Im})_6^{2+}$ ions from spectral evidence.^{1,2}

The electronic spectra of the solid $Fe(\text{Im})_6X_2$ compounds (Table I) in the near infrared region are typical of high-spin iron(II) with nearly octahedral coordination, with the ${}^5T_{2g} \rightarrow {}^5E_g$ (in O_h) transition near $11,000\text{ cm}^{-1}$. The 5E_g level is split by $1500\text{-}2000\text{ cm}^{-1}$ but the virtual constancy of band position on changing the anion and the relatively small band splitting for the bromide and iodide compared with those of compounds such as $Fe(\text{isoquinoline})_4X_2$ ($X = Br$ or I)⁵ are not consistent with a formulation $[Fe(\text{Im})_4X_2] \cdot 2\text{Im}$.

The low frequency ($100\text{-}400\text{ cm}^{-1}$) i.r. spectra of the $Fe(\text{Im})_6X_2$ compounds (Table I) are quite similar to those of their manganese, cobalt, nickel, and zinc analogues² and the band assignments follow those made previously.²

The Mössbauer spectra of the compounds at room temperature each consist of a pair of bands, with the large quadrupole splitting (ΔE_q) usually found for distorted octahedral high spin iron(II) systems. The quadrupole splitting values observed here (Table I) would, on the basis of a tetragonal distortion, be consistent with a splitting of the t_{2g} orbital set of *ca.* 300 cm^{-1} . The extent of the ligand field distortion depends on the identity of the anion, as the ΔE_q values of the iodide and, particularly, the perchlorate are smaller than those of the chloride and bromide. This influence of the anion may simply be one of anion size, with concomitant crystal packing changes, but an additional factor could involve changes in imidazole-anion hydrogen bonding.

Pyridine, 4-methylpyridine, and isoquinoline complexes, FeL_nX_2 ($n > 4$). In contrast to imidazole, pyridine and its derivatives are reluctant to form complexes of the type FeL_6X_2 . Although solids of stoichiometry $Fepy_6X_2$ ($X = Br, I, \text{ or } NCO$) can be obtained by recrystallising the corresponding $Fepy_4X_2$ compounds from pyridine, their physical properties show that they are correctly formulated as $[Fepy_4X_2] \cdot 2py$. Their electronic spectra (Table II) are virtually identical to those of the corresponding $Fepy_4X_2$ compounds, with a very marked change on altering X. Also their i.r. spectra (relevant results are given in Table II) show bands at 604 and 402 cm^{-1} due to non-coordinated pyridine as well as the corresponding bands at $621\text{-}631$ and $421\text{-}424\text{ cm}^{-1}$ respectively due to complexed pyridine. The compound of stoichiometry $Fepy_6(NCO)_2$ has a $\nu(\text{Fe-NCO})$ band at 310 cm^{-1} corresponding to that in the analogous 4:1 complex. The i.r. spectra of the halide complexes

(5) D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *Inorg. Chem.*, **5**, 635 (1966).

Table I. Physical properties of some Fe(imidazole)_x compounds

X	Electronic Mössbauer parameters ^a			I.R. bands (cm ⁻¹)
	bands (cm ⁻¹)	ΔE _q	δ	
Cl	11,750, 9800	2.04	1.31	224 s, 197 s, 169 m, br, 158 m, ~132 m, br, 112 m
Br	11,750, 10,200	2.03	1.31	230 s, 186 s, 161 ms, ~110 m, br
I	11,700, 10,200	1.90	1.32	230 s, 185 s, 165 m, 156 m, ~100 m, br
ClO ₄	11,550, 10,100	1.20	1.35	230 s, ^b

^a mm/sec at room temperature; relative to sodium nitroprusside. ^b Not measured below 200 cm⁻¹

Table II. Electronic spectra and infrared spectra (220-640 cm⁻¹) of some iron(II) complexes with pyridine (L) and 4-methylpyridine (L')

Compound	Electronic bands (cm ⁻¹)	Infrared bands (cm ⁻¹) ^a				
		6a	16 b	16a	ν(M-NCX)	
L	—	—	603 m	—, 404 s	(375) ^b	—
FeL ₂ Br ₂	10,650, 7750	624 m	—	423 s, —	393 w, 386 w	—
[FeL ₂ Br ₂] ₂ L	10,600, 7000	624 m	604 w	422 s, 402 m	392 w, 386 w	—
FeL ₂ I ₂	11,350, 5800	628 m	—	421 s, —	390 w, 385 w	—
[FeL ₂ I ₂] ₂ L	11,350, 5150	631 m, 624 m,	604 mw	422 s, 402 mw	—, 386 w	—
FeL ₂ (NCO) ₂	12,650, 9200	622 m	—	423 s, —	—, —	309 s
[FeL ₂ (NCO) ₂] ₂ L	12,700, 9500	621 m	604 w	424 s, 402 w	—, —	310 s
		6a	11	15		ν(M-NCX)
L'	—	—	515 m	484 s	(341) ^b	—
FeL' ₂ (NCS) ₂	11,500, 9700 sh	535 m	—	488 s, br	349 w	261 s
[FeL' ₂ (NCS) ₂] ₂ L'	11,500, 9700 sh	534 m	517 w	486 s, br	349 w	259 s
FeL' ₂ (NCSe) ₂	11,450, 9700 sh	534 m	—	490 s, —	350 w	247 s ^c
[FeL' ₂ (NCSe) ₂] ₂ L'	11,500, 9650 sh	538 sh, 533 m	518 w	491 s, 484 sh	349 w	245 s ^d

^a Amine mode notation as in: J. H. S. Green, W. Kynaston, and H. M. Paisley, *Spectrochim. Acta*, 19, 549 (1963). ^b Raman active, infrared inactive in free ligand. ^c Also δ(NCSe) at 430 and 440 cm⁻¹. ^d Also δ(NCSe) at 430 and 435 cm⁻¹.

Table III. Physical properties of some iron(II) pseudohalide complexes

Compound ^a	Electronic bands (cm ⁻¹)	Mössbauer Parameters ^b		μ _{eff} (B.M.) (±0.04)	°K
		ΔE _q	δ		
Fepy ₂ (NCO) ₂	12,650, 9200	2.46	1.30	5.49	293
Fepy ₂ (NCS) ₂	11,250, 9900 sh	1.56	1.34	5.41	293
Fepy ₂ (NCSe) ₂	11,200, 9900 sh	0.71	1.30	5.58	295
Fe(4-Mepy) ₂ (NCO) ₂	12,500, 9550	2.45 ^c	1.31 ^c	5.46	293
Fe(4-Mepy) ₂ (NCS) ₂	11,500, 9700 sh	1.67	1.34	5.35	298
Fe(4-Mepy) ₂ (NCSe) ₂	11,450, 9700 sh	—	—	—	—
Fe(IQ) ₂ (NCO) ₂	13,000, 9750	2.47	1.29	5.47	294
Fe(IQ) ₂ (NCS) ₂	11,500, 9700 sh	1.50	1.36	5.44	298
Fe(IQ) ₂ (NCSe) ₂	11,600, 9800 sh	1.41	1.30	5.46	2.94

^a IQ = isoquinoline. ^b mm/sec (±0.04) at room temperature; relative to sodium nitroprusside. ^c ±0.1 mm/sec.

were also examined in the region 70-220 cm⁻¹ and the results for each pair of 6:1 and 4:1 complexes were the same.

The iron(II) pseudohalide complexes Fe(4-methylpyridine)₂(NCA)₂ (A = S or Se) also form crystalline solids of type [FeL₂(NCA)₂]_nL in which non-coordinated amine molecules are held in the crystal lattice. In each case by control of the temperature at which the crystallisation is carried out compounds with n = 1/2 or 1 can be isolated and these have different crystal habits. Their spectral properties (Table II) leave no doubt that the formulation [FeL₂(NCA)₂]_nL (n = 1/2 or 1) is the correct one.

Orbital Splittings in FeL₂(NCA)₂ (A = O, S, or Se). Earlier work⁴ correlating the Mössbauer spectra and (L = pyridine, 4-methylpyridine, or iso-quinoline) suggest magnetic properties of the compounds FeL₂(NCS)₂

gested that the splitting of the t_{2g} orbital set in the tetragonal ligand field was such as to leave the orbital doublet d_{xz}, d_{yz} lowest. Extension of this work to the corresponding selenocyanates and cyanates has shown a difference between the orbital splitting patterns of the cyanates and those of the other pseudohalide complexes.

Mössbauer, magnetic, and electronic spectral results for the selenocyanates and cyanates are given in Table III, which also includes previously published data^{4,5} for the thiocyanates for comparison. The results for the selenocyanate complexes of pyridine and isoquinoline suggest that these resemble their thiocyanate analogues in that the ground state splitting is such that ⁵E_g is below ⁵B_{2g}. The magnetic moments and Mössbauer quadrupole splitting values observed for the isocyanates, however, show that for these compounds the ground state splitting order is

reversed, with ${}^5B_{2g}$ lowest, and there is a good correlation with previous calculations⁴ for this ground state. This reversal on passing from NCS and NCSe to NCO implies that the isocyanate group is a weaker π -acceptor in these compounds than the other two pseudohalide ions.

The electronic spectra of each pair of thiocyanate and selenocyanate complexes are virtually identical, but those of the corresponding cyanates show significant differences. In each case, replacement of NCS or NCSe by NCO results in a marked hypsochromic shift of the higher energy component of the ${}^5T_{2g} \rightarrow {}^5E_g$

transition, with an accompanying increase in the splitting of the 5E_g level. The latter observation suggests that, if the σ -donor capacity of the heterocyclic ligands remains unchanged on altering the anion, then that of the isocyanate group differs appreciably from those of the NCS and NCSe groups. However, there is no certainty that the in-plane field is constant for all three pseudohalide complexes.

Acknowledgments. We thank the S.R.C. for a research studentship (to C.D.B.) and Dr. L. V. C. Rees for the use of Mössbauer apparatus.