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The Preparation and Properties of Iron(II) Xanthates

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The new iron(II) complex $Fe(Chxn)_2$, where Chxn is cyclohexylxanthate, has been found to be antiferromagnetic. Mössbauer parameters show that it contains two iron(II) sites, presumably in a polymeric (dimeric) system. It spontaneously decomposed in a few days even in tubes sealed in vacuum, but many stable species, i.e. *the base adducts,* trans-*$Fe(Chxn)_2L_2$, where L = MeOH, EtOH, various substituted pyridines, or isoquinoline; the* cis-*adduct, $Fe(Chxn)_2$(1,10-phenanthroline); and the tris-chelates, $R_4N[Fe(Chxn)_3]$ (R = Me, Et, and Bu^n), have been isolated. These have been characterised as octahedral, high-spin iron(II) complexes from Mössbauer, magnetic, and reflectance measurements. The complex $Fe(Chxn)_2$(3,5-dimethylpyridine)$_2$ was obtained in two forms, one of which contains two iron sites ascribed tentatively to the presence of* cis- *and* trans-*complexes. The methyl- and ethyl-xanthate complexes $Fe(Mexn)_2$ and $Fe(Etxn)_2$ were also unstable, and were isolated as bis(pyridine) adducts.*

Introduction

Bis(N,N-dialkyldithiocarbamato)iron(II) complexes $[Fe(R_2NCS_2)_2]$ have been found [1] to fall

TABLE I. Analyses of Xanthato-iron(II) Complexes.

Compound	Calculated (%)				Found (%)[a]			
	C	H	N	Fe	C	H	N	Fe
(1) $Fe(Chxn)_2$	41.35	5.41		13.76	41.07	5.59		13.81
(2) $Fe(Chxn)_2(EtOH)_2$	43.34	6.82		11.22	43.26	7.09		11.33
(3) $Fe(Chxn)_2(MeOH)_2$	40.86	6.38		11.88	40.34	6.45		11.65
(4) $Fe(Chxn)_2(py)_2$	51.02	5.67	4.96	9.90	50.87	5.80	4.66	9.90
(5) $Fe(Chxn)_2(3\text{-Me-py})_2$	52.66	6.08	4.73	9.43	52.25	6.12	4.62	9.31
(6) $Fe(Chxn)_2(4\text{-Me-py})_2$	52.66	6.08	4.73	9.43	52.47	6.21	4.52	9.27
(7a) $Fe(Chxn)_2(3,5\text{-Me-py})_2$	54.15	6.45	4.51	9.01	54.96	6.60	4.86	8.85
(7b) $Fe(Chxn)_2(3,5\text{-Me-py})_2$[b]	54.15	6.45	4.51	9.01	52.79	6.89	4.49	9.11
(8) $Fe(Chxn)_2(3,5\text{-Cl-py})_2$	41.01	3.99	3.99	7.96	40.41	3.99	3.97	8.02
(9) $Fe(Chxn)_2(quin)_2$	57.80	5.42	4.21	8.41	56.73	5.56	3.99	8.42
(10) $Fe(Me\text{-chxn})_2(4Ph\text{-py})_2$	61.27	5.95	3.76	17.22[c]	61.33	5.79	4.08	17.40[c]
(11) $Fe(Chxn)_2(phen)$	53.32	5.16	4.78	21.90[c]	52.13	5.10	5.19	22.28[c]
(12) $Me_4N[Fe(Chxn)_3]$	45.78	6.91	2.14		44.70	6.78	2.12	
(13) $Et_4N[Fe(Chxn)_3]$	48.91	7.45	1.97	7.86	48.62	7.64	1.70	7.77
(14) $Bu^n_4N[Fe(Chxn)_3]$	53.92	8.38	1.70	6.79	54.03	8.65	1.58	6.76
(15) $Fe(Me\text{-chxn})_2 \cdot H_2O$	42.45	6.19		12.36	42.68	5.97		12.51
(16) $Fe(Etxn)_2(py)_2$	42.08	4.38	6.13	12.25	42.19	4.35	5.90	12.18
(17) $Fe(Mexn)_2(py)_2$	39.22	3.74	6.54	13.05	38.94	3.61	6.44	13.13

[a] Analysed for iron by combustion to Fe_2O_3; analyses for C, H and N carried out by the University of Surrey Microanalytical Section. [b] Isolated from 70% ethanol by the addition of K(Chxn) to the suspension obtained by the addition of 3,5-dimethylpyridine to iron(II) chloride. [c] Sulphur analyses.

into two classes: dimers containing square pyramidal iron (R = Et, Pr^n, or Bu^n), or apparently six-coordinate polymers (R = Me or $R_2 = C_4H_8$), and the former exhibited uncommonly large quadrupole splittings [1, 2] in their Mössbauer spectra. This Paper reports preparative, magnetic, and Mössbauer investigations of new iron(II) complexes (Table I) of the xanthate anion $RO{-}CS_2$. These behave rather differently from the iron(II) dithiocarbamates in spite of the presence of identical donor atoms.

Experimental

Reagents

Potassium cyclohexylxanthate was prepared by the reaction [3] between carbon disulphide and cyclohexanol containing potassium hydroxide and was recrystallised from absolute ethanol. The other xanthates were similarly prepared. The substituted pyridines and all solvents were of reagent grade or better and were de-oxygenated before use. Aqueous or aqueous–ethanolic solutions of iron(II) chloride tetrahydrate were stood over iron wire in a nitrogen atmosphere if traces of iron(III) appeared to be present.

Preparation of the Complexes

All operations were carried out under nitrogen or in a vacuum. The following abbreviations will be used: $CH_3OCS_2^-$ = Mexn; $C_2H_5OCS_2^-$ = Etxn; $C_6H_{11}OCS_2^-$ = Chxn; 2-methylcyclohexylxanthate = Me-Chxn; pyridine = py; methylpyridine = Mepy; 4-phenylpyridine = 4Ph-py; 3,5-dichloropyridine = 3,5-Cl-py; 1,10-phenanthroline = phen; isoquinoline = quin.

Fe(Rxn)₂

Aqueous ethanol was used in the earlier attempts to prepare bis(cyclohexylxanthato)iron(II) and the products contained varying amounts of a bis(ethanolate) (see below) according to the composition of the solvent. The unsolvated compound was prepared by adding aqueous iron(II) chloride tetrahydrate to aqueous potassium cyclohexyl-xanthate in 1:2 molar ratio. The sticky brown precipitate obtained was recrystallised from an acetone-water mixture, filtered off, washed with water, and dried by continuous pumping for 10 hr. The product, $[Fe(Chxn)_2]$ was preserved from oxidation in Pyrex tubes sealed in vacuum but even so it decomposed over a few days.

The compound, bis(2-methylcyclohexylxanthato)-iron(II) separated from similar aqueous solutions as a monohydrate. The presence of water was shown by the analysis and the i.r. spectrum.

Attempts to investigate bis-chelates of methyl- and ethylxanthates were unsuccessful. Brown solids, presumably $[Fe(Mexn)_2]$ and $[Fe(Etxn)_2]$ or hydrates of these, were isolated from the reaction of the potassium xanthates and iron(II) chloride in aqueous solution. Unfortunately, the solids soon decomposed, turning black in a few hours even in sealed tubes and were not investigated further. Holah and Murphy [4] reported the same behaviour.

[Fe(Chxn)₂(ROH)₂]

The adduct with R = Et separated slowly when iron(II) chloride and K(Chxn), dissolved in 80% ethanol, were mixed in 1:2 molar ratio. The brown compound was filtered off, washed with 80% ethanol and absolute ethanol and dried. The green adduct with R = Me was similarly prepared from 60% methanol. These adducts and those reported below were stable in nitrogen or under vacuum.

No solid separated, even on concentration, when ethanol was replaced by tetrahydrofuran.

Adducts of Heterocyclic Bases

In general, the brown bis(ethanol) adduct of $[Fe(Chxn)_2]$ was first prepared from aqueous ethanol, filtered off and washed with 50% ethanol. Then, a solution of an excess of the heterocyclic base in ethanol was added to the adduct on the filter. The solid soon became yellow or yellow-green and the mixture was allowed to stand for two hours. The product was then filtered off, washed with absolute ethanol, and dried by continuous pumping for several hours. This did not lead to any detectable loss of base.

The adduct obtained with 3,5-lutidine by this procedure contained, as deduced from an inspection of the Mössbauer parameters (Table IV), iron(II) in two different sites (product 7a). By the reaction of potassium cyclohexylxanthate in 70% ethanol with the suspension obtained from the addition of the lutidine in excess to iron(II) chloride also in 70% ethanol, product 7b, of the same formula but with one iron(II) site only was obtained.

The addition of pyridine to the bis(ethanol) adduct as above gave a yellow product which was shown to contain iron(II) from its Mössbauer and magnetic properties, but from analyses contained variable (about 3 molecules) amounts of pyridine. The pure bis(pyridine) adduct was, however, obtained by adding an excess of pyridine in methanol to the bis(methanol) adduct.

As only small quantities of 3,5-dichloropyridine were available, this adduct was prepared by the addition of K(Chxn) in 70% ethanol to the dark green solution obtained from the mixing of solutions, also in 70% ethanol of iron(II) chloride and the pyridine in 1:2 molar ratio.

When the brown solids thought to be $[Fe(Mexn)_2]$ and $[Fe(Etxn)_2]$ were treated with pyridine the yellow air-sensitive complexes $[Fe(Mexn)_2(py)_2]$ and $[Fe(Etxn)_2](py)_2]$ were obtained.

TABLE II. Magnetic Data.

Compound	μ_e (B.M.) 295K	μ_e (B.M.) 90K	θ(°)	Diamagnetic Corrn. (c.g.s. × 10^6)
(1) $Fe(Chxn)_2$	4.90	4.16	51	218
(2) $Fe(Chxn)_2(EtOH)_2$	5.15	5.09	0	286
(3) $Fe(Chxn)_2(MeOH)_2$	4.95	4.90	0	262
(4) $Fe(Chxn)_2(py)_2$	5.32	5.32	0	316
(5) $Fe(Chxn)_2$(3-Me-py)$_2$	5.22	5.13	0	340
(6) $Fe(Chxn)_2$(4-Me-py)$_2$	5.16	5.23	0	340
(7a) $Fe(Chxn)_2$(3,5-Me-py)$_2$	5.05	5.07	0	364
(8) $Fe(Chxn)_2$(3,5-Cl-py)$_2$	5.26	5.25	0	387
(9) $Fe(Chxn)_2(quin)_2$	5.07	5.06	0	376
(13) $Et_4N[Fe(Chxn)_3]$	5.46	5.48	0	439
(14) $Bu^n_4N[Fe(Chxn)_3]$	5.36	5.37	0	534
(15) Fe(Me-chxn)$_2$·H_2O	4.12	3.60	44	252
(16) $Fe(Etxn)_2(py)_2$	5.10	5.16	0	233
(17) $Fe(Mexn)_2(py)_2$	5.19	5.18	0	209

(NEt$_4$)[Fe(Chxn)$_3$] and (NBu$^n_4$)[Fe(Chxn)$_3$]

These brown salts precipitated when an aqueous solution of K(Chxn) was added to an aqueous solution containing iron(II) chloride and the tetra-alkylammonium chloride, the reactants being in the molar ratio required by the formulae. The salts were filtered off, washed with distilled water and ethanol, and dried in vacuum.

Diffuse Reflectance Spectra

These were measured at room and liquid nitrogen temperatures on a Unicam S.P. 700C spectrophotometer with an S.P. 735 reflectance attachment. The samples were enclosed in a sealed silica cell.

Magnetic Measurements

The magnetic measurements were carried out down to liquid nitrogen temperatures by the Gouy method on the solids in sealed Pyrex tubes. Measurements at several field strengths showed that there was no field dependence. The diamagnetic connections were calculated from Pascal's Constants.

Mössbauer Spectra

These were measured using a constant acceleration spectrometer incorporating a 400 channel Intertechnique SA41 multichannel analyser operating in the multiscaling mode. A source of ^{57}Co in a rhodium matrix (Radiochemical Centre, Amersham, Bucks, England) was used and the samples were held in sealed plastic containers which were loaded under an inert atmosphere. A liquid nitrogen cryostat of the bath type was used for the low-temperature measurements. Inspection of the Mössbauer spectrum of iron(II) fluoride, FeF_2, revealed that the absorber temperature in this cryostat was close to 77K. The velocity scale was calibrated using the known peak positions in the spectrum of natural iron foil. Spectra were fitted using a standard least squares fitting programme assuming Lorentzian line-shapes.

Results

Magnetic Measurements

Only the magnetic moments, μ_{eff}, of $[Fe(Chxn)_2]$ and $[Fe(Me\text{-}Chxn)_2H_2O]$ decreased significantly over the available temperature range (Table II). The reciprocal molar susceptibilities of these compounds obeyed the Curie–Weiss law with Weiss constants of 51° and 44° respectively. The magnetic moments of the other compounds were within the range 4.9–5.4 B.M. and their reciprocal susceptibilities followed the Curie law ($\theta \sim 0°$). The magnetic moments of the pyridine adducts $[Fe(Mexn)_2Py_2]$ and $[Fe(Etxn)_2Py_2]$ are very close to the values reported [5] for solutions believed to contain these species (4.92 and 4.90 B.M. respectively at 36 °C). The only reported [4] magnetic moments of iron(II) xanthates are values at room temperature of 4.4 B.M. for $[Fe(Etxn)_2]$ and 5.5 B.M. for $(Et_4N)[Fe(Etxn)_3]$.

Mössbauer Spectra

The chemical isomer shifts of all compounds relative to natural iron were (Table IV) approximately 1.0 mm s^{-1} as expected for high-spin iron (II). The quadrupole splittings of the monodentate base adducts (compounds 2–10) were approximately 3 mm s^{-1}. However the general preparative method gave samples of compound 7a [Fe(Chxn)$_2$(3,5-Me-

TABLE III. Reflectance Spectra.[a]

Compound	Colour	$^5T_{2g} \rightarrow {}^5E_g$ (cm^{-1})	
(1) $\mathrm{Fe(Chxn)_2}$	brown		7,200 vb
(2) $\mathrm{Fe(Chxn)_2(EtOH)_2}$	brown	10,000w	8,600sh
(3) $\mathrm{Fe(Chxn)_2(MeOH)_2}$	green	10,400 w	8,600 sh
(4) $\mathrm{Fe(Chxn)_2(py)_2}$	yellow	11,000 w	9,400 sh
(5) $\mathrm{Fe(Chxn)_2(3\text{-}Me\text{-}py)_2}$	yellow-green	11,000 w	9,000 sh
(6) $\mathrm{Fe(Chxn)_2(4\text{-}Me\text{-}py)_2}$	yellow-green	10,000 w	8,000 w
(7a) $\mathrm{Fe(Chxn)_2(3,5\text{-}Me\text{-}py)_2}$	yellow	9,800 w v b	8,700 sh
(8) $\mathrm{Fe(Chxn)_2(3,5\text{-}Cl\text{-}py)_2}$	yellow	10,000 w v b	
(9) $\mathrm{Fe(Chxn)_2(quin)_2}$	yellow	very broad absorption	
(13) $\mathrm{Et_4N[Fe(Chxn)_3]}$	brown	8,400	7,300 sh
(14) $\mathrm{Bu^n_4N[Fe(Chxn)_3]}$	brown	8,200 w v b	
(15) $\mathrm{Fe(Me\text{-}chxn)_2 \cdot H_2O}$	brown	10,000 sh v b	
(16) $\mathrm{Fe(Etxn)_2(py)_2}$	yellow	11,500 w	8,400 w
(17) $\mathrm{Fe(Mexn)_2(py)_2}$	yellow	11,200 w	8,700 sh

[a] Abbreviations used; v b = very broad, sh = shoulder, w = weak.

TABLE IV. Mössbauer Parameters.[a]

Compound	T/K	δ/mm s^{-1}	ΔE/mm s^{-1}
(1) $\mathrm{Fe(Chxn)_2}$	300	0.864, 0.861	2.199, 1.750
	77	0.999, 0.986	2.686, 1.837
(2) $\mathrm{Fe(Chxn)_2(EtOH)_2}$	300	0.966	3.603
	77	1.080	3.625
(3) $\mathrm{Fe(Chxn)_2(MeOH)_2}$	300	0.965	3.620
	77	1.086	3.572
(4) $\mathrm{Fe(Chxn)_2(py)_2}$	300	0.895	3.114
	77	1.012	3.110
((5) $\mathrm{Fe(Chxn)_2(3\text{-}Me\text{-}py)_2}$	300	0.916	3.123
	77	1.014	3.105
(6) $\mathrm{Fe(Chxn)_2(4\text{-}Me\text{-}py)_2}$	300	0.922	2.734
	77	1.034	2.731
(7a) $\mathrm{Fe(Chxn)_2(3,5\text{-}Me\text{-}py)_2}$	300	0.884, 0.897	3.191, 1.447
	77	1.149, 1.022	3.217, 1.822
(7b) $\mathrm{Fe(Chxn)_2(3,5\text{-}Me\text{-}py)_2}$	300	0.911	3.078
	77	0.991	3.075
(8) $\mathrm{Fe(Chxn)_2(3,5\text{-}Cl\text{-}py)_2}$	300	0.885	3.636
	77	1.017	3.633
(9) $\mathrm{Fe(Chxn)_2(quin)_2}$	300	0.896	3.125
	77	1.015	3.109
(10) $\mathrm{Fe(Me\text{-}chxn)_2(4Ph\text{-}py)_2}$	300		
	77	1.019	2.974
(11) $\mathrm{Fe(Chxn)_2(phen)}$	300		
	77	1.015	2.651
(12) $\mathrm{Me_4N[Fe(Chxn)_3]}$	300	0.804	0.992
	77	1.016	1.467

(continued on facing page)

TABLE IV. *(continued)*

Compound	T/K	δ/mm s^{-1}	ΔE/mm s^{-1}
(13) $Et_4N[Fe(Chxn)_3]$	300		
	77	1.028	1.974
(14) $Bu^n_4N[Fe(Chxn)_3]$	300	0.894	1.501
	77	1.022	1.907
(16) $Fe(Etxn)_2(py)_2$	300	0.908	2.932
	77	–	–
(17) $Fe(Mexn)_2(py)_2$	300	0.901	3.008

[a] The chemical shift, δ, is relative to the centre of the natural iron spectrum.

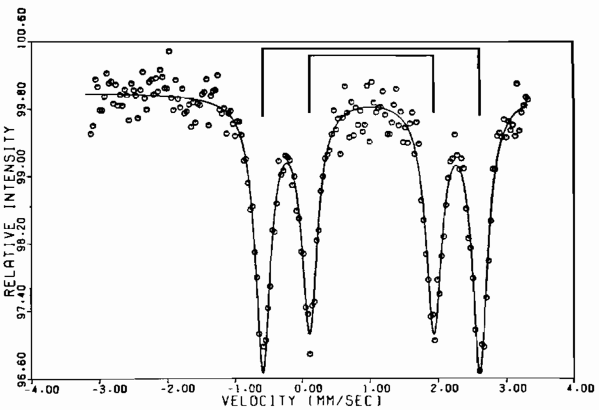

Figure. Mössbauer spectrum of $Fe(Chxn)_2(3,5\text{-}Me\text{-}Py)_2$.

$py)_2]$ whose spectra showed an additional inner doublet with a much reduced splitting (Figure). A different preparative procedure gave a product with the same analyses (compound 7b) but with a spectrum exhibiting the outer pair of lines only. No iron (III) absorption could be seen in any of the spectra indicating that negligible oxidation had occurred either during the actual preparation or during the subsequent transfer to the spectrometer.

The Mössbauer parameters for $[Fe(Mexn)_2(Py)_2]$ and $[Fe(Etxn)_2(Py)_2]$ are very similar to those reported [5] for pyridine pastes of $[Fe(Mexn)_3]$, $\delta = 0.94$ mm s^{-1}, $\Delta = 2.98$ mm s^{-1} and those of $[Fe(Etxn)_3]$, $\delta = 0.93$ mm s^{-1}, $\Delta = 2.97$ mm s^{-1}.

The tris(xanthato) complexes exhibited considerably smaller quadrupole splittings than the base adducts as might be expected from the symmetry difference between the near octahedral nature of the tris complexes as opposed to the tetragonal or lower symmetry of the base adducts.

Diffuse Reflectance Spectra

Reflectance spectra were measured over the range 40,000 cm^{-1} to 5000 cm^{-1} at room and liquid nitrogen temperatures. Most spectra contained two bands or one very broad band in the region of 10,000 cm^{-1} although with $[Fe(Chxn)_2]$, $(Et_4N)[Fe(Chxn)_3]$, $(Bu^n_4N)[Fe(Chxn)_3]$ the bands were at considerably lower frequencies. The absorptions in this region were weak and sometimes poorly resolved and for $Fe(Chxn)_2(quin)_2$ no peaks or shoulders could be detected although the absorption decreased continuously to lower frequencies. Cooling had little effect so only room-temperature spectra are presented in Table III. Each compound exhibited intense bands, presumably charge-transfer and ligand absorptions to high frequencies. The reflectance spectra of $[Fe(Mexn)_2(Py)_2]$ and $[Fe(Etxn)_2(Py)_2]$ are very similar to the spectra reported by Saleh and Straub [5] for solutions of tris(xanthato)iron(III) species dissolved in pyridine although these authors refer to peaks at 453 nm (22,100 cm^{-1}) and 407 nm (24,600 cm^{-1}) whereas their spectra and ours show only broad shoulders on a higher frequency band in this region.

Discussion

The chemical isomer shifts (Table IV) of the xanthato complexes establish that they are high-spin iron(II) complexes for which values of approximately 1 mm s^{-1} are commonly obtained [6]. Octahedral high-spin d^6 complexes are expected [7] to have effective magnetic moments of *ca.* 5.4 B.M. at room temperature but increasing electron delocalisation and distortion from cubic symmetry can cause the magnetic moments to be closer to the spin-only value. Marked temperature variation of the moment down to liquid nitrogen temperature is not expected. This behaviour is generally followed by the xanthato-complexes and confirm the high-spin iron(II) assignment from the Mössbauer results.

The empirical formulae, except for $[Fe(Chxn)_2]$, immediately suggest octahedral structures. The complex $Fe(Chxn)_2$ derivative is unusual in that no other ligands are present in the formula unit and it exhibited a four-peak Mössbauer spectrum which suggests that two iron sites are present. Thus, it is different from the only other known example of this kind, the n-butyl complex which has been reported [2b] to give just a two peak Mössbauer spectrum. It might be that our cyclohexylxanthato compound consists of a mixture of dimers and octahedral polymers as the former are known to give appreciable quadrupole splittings and the latter to give lower quadrupole splittings, but a dimer structure containing non-equivalent iron sites has been established [8] for (Fe(II)acetylacetonate$_2$)$_2$ and such a structure would be expected to give a four-peak spectrum. Indeed, the magnetic susceptibility data (Table II) are in harmony with such a formulation: the moment falls with temperature and in this regard it is quite different from the base adducts all of which have near zero values of θ in their Curie–Weiss plots. For dimeric structures, the moment is expected to behave in this way but it is noteworthy that interaction is observed here smaller than in the dimeric bisdithiocarbamato compounds which have however a different structure [1]. A further example of a compound exhibiting multiple-peak Mössbauer spectra is provided by the 3,5-dimethylpyridine adducts. These were obtained in two different forms (see experimental section) and one of these gave rise to a four-peak Mössbauer spectrum. Here the peak multiplicity is most likely due to the presence of *cis* and *trans* forms. With high-spin iron compounds there will not be in general a simple relationship between the quadrupole splittings for such isomeric forms but it is reasonable to suppose that the *trans* compound will show a greater quadrupole splitting than its *cis* isomer or analogue. A perusal of the quadrupole splitting data in Table IV for appropriate pairs of compounds serves to underline this point.

Octahedral, high-spin iron(II) complexes are expected to exhibit one weak transition, $^5T_{2g} \rightarrow {}^5E_g$, in the near i.r. region, but distortion from octahedral symmetry frequently causes two bands, or one very broad and asymmetric band, to be present. The spectral data (Table III) therefore suggest distorted octahedral structures for the iron(II) xanthates, the distortion being greater in the base adducts as these generally show two distinct absorptions near to 10,000 cm^{-1}. The absorptions are at lower frequency in the spectra of the tris(xanthates) as would be expected if S replaces O- or N-donor atoms of bases. The presence of one broad band at 7200 cm^{-1} in the spectrum of Fe(Chxn)$_2$ indicates that this is a S-bridged complex.

Recently, Saleh and Straub found [5] that the golden yellow 1:3 adducts of the iron(III)-xanthates, Fe(Mexn)$_3$ and Fe(Etxn)$_3$, with pyridine, earlier reported by Dubsky, *et al.* [9] were "most likely" complexes of iron(II) formed by oxidation of one third of the ligand to the disulphide by iron(III) in the presence of pyridine. The stoichiometry of the solids was not established by analysis, but it was assumed that the most likely formula was Fe(Rxn)$_2$-(py)$_2$. The complexes were investigated as pastes with pyridine, or in solution. However, it was deduced, very reasonably, from the magnetic and Mössbauer results, that iron(II) species were present. When we became aware of these results the present work with the cyclohexylxanthate ligand was almost complete and seemed to confirm Saleh and Straub's deductions because it showed that bis(pyridine) adducts (and many others) can be prepared directly from the iron(II) xanthate, Fe(Chxn)$_2$. We have now further confirmed their deductions by the direct preparation from iron(II) salts of Fe(Mexn)$_2$(py)$_2$ and Fe(Etxn)$_2$(py)$_2$ not only with closely similar magnetic and Mössbauer parameters as the pastes, but also with satisfactory elemental analyses and diffuse reflectance spectra similar to the solution [5] spectra.

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