Inorganica Chimica Acta, 106 (1985) 109–114

The Preparation and Characterisation of Some Complexes of Iron(II) with Amino Acids

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Received September 11, 1984

Abstract

The following complexes of iron(II) with the amino acids glycine, alanine, phenylglycine, phenylalanine, leucine, serine, aspartic acid, glutamic acid, glutamine, tryptophan, histidine, methionine, S-methylcysteine, cystine, and glycylglycine have been isolated: $Fe(Gly)_2$, $Fe(Ala)_2$, $Fe(Phegly)_2$, $Fe(Phe)_2 \cdot 2H_2O$, $Fe(Leu)_2 \cdot 2H_2O$, $Fe(Ser)_2$, $Fe(Asp) \cdot 2H_2O$, $Fe(Glu) \cdot 2H_2O$, $Fe(Gln)_2$, $Fe(Trp)_2$, $Fe(His)_2 \cdot H_2O$ and $2H_2O$, $Fe(Met)_2$, $Fe(MeCys)_2$, Fe(CysCys) and $Fe(GlyGly)_2$. Their magnetic behaviour, reflectance spectra, and Mössbauer parameters are consistent with high spin, hexacoordinate iron(II), and imply extended structures involving carboxylate bridges.

Introduction

Metal–amino acid complexes have long been of interest as models for metal–ligand systems and interactions which may occur in nature, and complexes of bivalent metals such as cobalt(II), nickel(II), and copper(II) have been well characterised [1]. In contrast, complexes of iron(II), except with some sulphur-containing amino acids [2, 3], are scarce and poorly characterised. This is presumably because iron(II) complexes as solids or in aqueous solution often oxidise rapidly in air. In this paper the preparation and properties of a number of iron(II)–amino acid complexes are described. Some results have been reported in a preliminary form [4].

Results and Discussion

Preparations of Iron(II)–Amino Acid Complexes

Several methods were used in the preparation (Experimental) of the iron(II)–amino acid complexes (Table I)**, the most successful involving the addition of a solution of the lithium salt [5] of the amino acid (prepared from the amino acid and lithium hydroxide) to hydrated iron(II) chloride in ethanol or methanol. Lithium chloride is soluble in the resulting aqueous alcoholic mixture, and the complexes separate readily. Attempts to crystallise complexes by the concentration of aqueous solutions containing iron(II) and the sodium salt of the amino acid were generally unsuccessful because of high solubility, difficulties in preventing aerial oxidation, and the separation of variably hydrated products. One complex, $Fe(His)_2 \cdot H_2O$, was prepared from iron(II) hydroxide and the amino acid, but the hydroxide is difficult to obtain pure and tends to block filters. The glutamato-, aspartato-, and cystinato-iron(II) complexes contain amino acid and metal ion in 1:1 ratio; the remainder are 2:1 complexes (Table I).

Bis(Amino Acidato)iron(II) Complexes

No iron(II) complexes of the simple monoamino, monocarboxylic amino acids have been isolated hitherto, although the crystal structure of one glycine complex containing the cation *trans*-$[Fe(OH_2)_4(O_2CCH_2NH_3)_2]^{2+}$ has been reported [6]. The complex was obtained from sulphuric acid, and the zwitterionic glycine is monodentate via the carboxylate group.

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**Gly = $NH_2CH_2CO_2^-$, Ala = $CH_3CH(NH_2)CO_2^-$, Phegly = $C_6H_5CH(NH_2)CO_2^-$, Phe = $C_6H_5CH_2CH(NH_2)CO_2^-$, Leu = $(CH_3)_2CHCH_2CH(NH_2)CO_2^-$, Ser = $HOCH_2CH(NH_2)CO_2^-$, Asp = $^-O_2CCH_2CH(NH_2)CO_2^-$, Glu = $^-O_2CCH_2CH_2CH(NH_2)CO_2^-$, Gln = $H_2NCOCH_2CH_2CH(NH_2)CO_2^-$, Trp = $C_8H_6NCH_2CH(NH_2)CO_2^-$, His = $C_3H_3N_2CH_2CH(NH_2)CO_2^-$, Met = $CH_3SCH_2CH_2CH(NH_2)CO_2^-$, MeCys = $CH_3SCH_2CH(NH_2)CO_2^-$, CysCys = $^-O_2CCH(NH_2)CH_2SSCH_2CH(NH_2)CO_2^-$.

0020-1693/85/$3.30

TABLE I. Analyses.

Compound	Colour	Analyses[a] (%)			
		Fe	C	H	N
$Fe(Gly)_2$	off-white	26.7(27.6)	23.3(23.5)	3.8(3.9)	13.5(13.7)
$Fe(Ala)_2$	off-white	23.2(24.1)	30.4(31.0)	5.3(5.2)	12.1(12.1)
$Fe(Phegly)_2$	grey-blue	15.4(15.7)	53.2(53.9)	4.4(4.5)	7.7(7.9)
$Fe(Phe)_2 \cdot 2H_2O$	pale blue	13.5(13.3)	51.6(51.4)	5.9(5.7)	6.6(6.7)
$Fe(Leu)_2 \cdot 2H_2O$	pale blue	16.1(15.9)	40.2(40.9)	8.1(8.0)	7.8(8.0)
$Fe(Ser)_2$	grey-blue	20.7(21.2)	26.8(27.3)	4.5(3.5)	10.3(10.6)
$Fe(Asp) \cdot 2H_2O$	off-white	24.8(25.1)	21.2(21.5)	3.4(4.0)	6.0(6.3)
$Fe(Glu) \cdot 2H_2O$	pale blue	23.3(23.6)	24.6(25.3)	4.6(4.6)	5.9(5.9)
$Fe(Gln)_2$	pale blue	15.8(16.2)	34.1(34.7)	5.2(5.2)	15.7(16.2)
$Fe(Trp)_2$	grey-blue	12.0(12.1)	56.9(57.1)	4.6(4.8)	12.2(12.1)
$Fe(His)_2 \cdot H_2O$	off-white	13.9(14.5)	37.8(37.5)	4.7(4.7)	21.2(21.9)
$Fe(His)_2 \cdot 2H_2O$	orange	14.0(13.9)	34.4(35.8)	4.6(5.0)	20.6(20.9)
$Fe(Met)_2$	grey-green	15.8(15.8)	33.9(33.8)	5.6(5.8)	7.9(7.7)
$Fe(MeCys)_2$	grey-blue	17.9(17.2)	29.0(29.6)	4.9(4.9)	8.4(8.6)
Fe(CysCys)	pale yellow	19.1(19.0)	23.8(24.5)	3.5(3.4)	9.0(9.5)
$Fe(GlyGly)_2$	white	17.4(17.6)	29.9(30.2)	4.5(4.4)	17.3(17.6)

[a]Calculated values in parentheses.

TABLE II. Magnetic, Mössbauer and Reflectance Data.

Compound	Magnetic data[a]				Reflectance data[b]	Mössbauer data[c]	
	T/K	μ_{eff}/B.M.	θ/°	$10^6 \times$ Diamagnetic correction/c.g.s. units	$\bar{\nu}$/cm^{-1}	δ/mm s^{-1}	ΔE mm s^{-1}
$Fe(Gly)_2$	295	5.28	−5	−74	10800 sh	1.225	2.82
	90	5.39			8500 s		
$Fe(Ala)_2$	295	5.13	0	−86	10000 wsh	–	–
	90	5.09			9400 vwsh		
					8000 ms		
$Fe(Phegly)_2$	295	5.28	0	−93	11800 m	1.19	2.90
	90	5.30			7300 m		
$Fe(Phe)_2 \cdot 2H_2O$[d]	295	5.69	+5	−114	11800 m	1.19	2.55
	90	5.61			9400 w		
$Fe(Ser)_2$	295	5.29	0	−90	12200 m	1.31	2.42
	90	5.34			8300 w		
$Fe(Asp) \cdot 2H_2O$	295	5.22	+13	−90	11400 m	–	–
	90	4.98			10300 s		
					5800 m		
$Fe(Glu) \cdot 2H_2O$	295	4.52	0	−89	11400m	1.49	3.28
	90	4.52			10400s		
					6200m		
$Fe(Gln)_2$	295	5.58	−8	−137	14200 m	1.10	2.28
	90	5.73			11000 w		
					8500 wsh		
$Fe(Trp)_2$	–	–			10700 wsh	1.07	2.99
					8000 m		
$Fe(His)_2 \cdot 2H_2O$	295	4.99	+8	−195	11700 m	1.38	2.65
	90	4.77			10000 w		

(continued on facing page)

TABLE II. *(continued)*

Compound	Magnetic data[a]				Reflectance data[b]	Mössbauer data[c]	
	T/K	μ_{eff}/B.M.	θ/°	10^6 × Diamagnetic correction c.g.s. units	$\bar{\nu}$/cm^{-1}	δ/mm s^{-1}	ΔE mm s^{-1}
$Fe(Met)_2$	295	5.76	+5	−180	12300 s	1.21	2.58
	90	5.65			8300 m		
$Fe(MeCys)_2$	295	5.96	+31	−129	15000 sh	1.21	2.72
	90	5.38			11800 m		
					8400 sh		
Fe(CysCys)	295	5.44	+23	−234	11800 m	1.45	2.82
	90	5.04			9600 sh		
$Fe(GlyGly)_2$	295	5.38	+13	−69	9600 s	1.36	2.96
	90	5.19			8400 ms		

[a]Calculated from $\mu_{eff} = 2.828\ (\chi_a T)^{1/2}$ and Curie–Weiss law, $\chi_a^{-1} \propto (T + \theta)$. [b]Recorded at room temperature, there was little change on cooling to liquid nitrogen temperature. [c]Recorded at liquid nitrogen temperature; isomer shifts with respect to natural iron. [d]For $Fe(Leu)_2 \cdot 2H_2O$, $\mu_{eff} = 5.65$ and 5.62 B.M. at 295 and 90 K, $\theta = 5°$.

The effective magnetic moments, μ_{eff}, of the complexes of glycine, alanine, phenylglycine, phenylalanine and leucine (Table II) are higher than the spin-only value for high-spin iron(II) complexes (4.90 B.M.), but they are of the magnitude and show the type of temperature variation that might be expected for hexaco-ordinate, high-spin iron(II) complexes with varying degrees of electron delocalisation and distortion from octahedral symmetry [7]. Except possibly for $Fe(Phe)_2 \cdot 2H_2O$ and $Fe(Leu)_2 \cdot 2H_2O$, in which the water molecules may be coordinated, polymerisation through interaction with carboxylate groups bound to adjacent metal ions is necessary to produce hexacoordinate structures. As the magnetic moments show little temperature variation this does not lead to antiferromagnetic interaction. The chemical isomer shifts are typical [8] of high spin, iron(II) compounds in confirmation of the magnetic data. The values of ΔE, the quadrupole splitting, are also suggestive of hexaco-ordination as are the weak broad bands in the diffuse reflectance spectra near 11000 cm^{-1} which can be assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition split through distortion from regular octahedral symmetry.

There are potential donor groups in the side chains of the anhydrous complexes $Fe(Trp)_2$, $Fe(Ser)_2$ and $Fe(Gln)_2$, but the nitrogen atom of the indole ring of tryptophan does not participate in metal ion binding [9]; and, although there is some evidence for weak chelation of the OH group of serine and the $-CONH_2$ group of glutamine in solution, there is no evidence of alcohol coordination from the few crystal structures of serinato complexes which have been reported [9]. It is therefore likely that six coordination is completed by interaction between carboxylate groups {and perhaps $-CONH_2$ groups in $Fe(Gln)_2$} bound to adjacent units.

Metal–histidine complexes are well known, and where crystal structures have been carried out, *e.g.* on bis(histidinato)cobalt(II), the amino acid is tridentate [10]. It has been reported [11] that the iron(II)–histidine complex in aqueous solution is oxidised irreversibly by air unlike the cobalt(II) complex which combines reversibly with dioxygen. No solid iron–histidine complex was isolated [11], but bis(histidinato)iron(II) can be obtained as the monohydrate from iron(II) hydroxide and histidine, and the dihydrate from lithium histidinate and iron(II) chloride (Experimental). The magnetic and Mössbauer properties and diffuse reflectance spectrum (Table II) are of a typical hexaco-ordinate, high spin iron(II) complex.

The magnetic and Mössbauer properties, and the reflectance spectra of $Fe(Met)_2$ and $Fe(MeCys)_2$ are similarly characteristic of hexaco-ordinate iron(II) complexes. However, the thioether group has not been found to bind to hard or borderline metal ions in solution or in the solid state [9]. Thus extended structures [12] involving carboxylate bridges to adjacent units are again likely. The colour change during the preparations (Experimental) may indicate temporary coordination of the thioether group. The hydrates, $Fe(Met)_2 \cdot H_2O$ and $Fe(MeCys)_2 \cdot 0.5H_2O$, have been reported earlier [3]. It was proposed that the SMe groups were coordinated, but polymeric structures as suggested here were not excluded.

Mono(Amino Acidato)iron(II) Complexes

Single crystal X-ray investigations [13] have shown that in $M(Asp)(H_2O)_2 \cdot H_2O$, where M = Zn or Co, the amino and α-carboxylate groups are coordinated, and the distorted octahedral stereochemistry of the metal ions is completed with bonds to water molecules, and to the carboxylate side

chain of aspartate bonded to an adjacent metal ion. In $Zn(Glu)\cdot 2H_2O$, glutamate is similarly bound to one zinc ion by its glycinate ring and to other zinc ions by the side chain carboxylate group. The magnetic and spectroscopic properties of $Fe(Asp)\cdot 2H_2O$ and $Fe(Glu)\cdot 2H_2O$ indicate that they have similar extended structures.

The isolation of an impure iron(II) complex of cystine has been reported [14]. Provided air is excluded, Fe(CysCys) can be obtained in a satisfactory state of purity. Its properties (Table II) again suggest that the cystinate ligands participate in an extended structure to produce hexaco-ordinate iron(II). The infrared spectrum resembles those [15] of the corresponding copper(II), nickel(II) and zinc(II) complexes.

Infrared Spectra

The IR spectra of amino acids contain a broad, strong $-NH_3^+$ stretching band in the region of 3100 cm^{-1} which was replaced by several sharp bands some of which were to higher frequency in the spectra of the iron(II) complexes. This indicates deprotonation and coordination of the $-NH_2$ groups. Combination and overtone bands in the 2100 cm^{-1} region characteristic of $-NH_3^+$ groups were absent from the spectra of the complexes. There were differences in the positions of the asymmetric and symmetric-CO_2 stretching vibrations of the acids and the complexes consistent with the coordination of the carboxyl groups, but no clear patterns emerged presumably because of the complicated coordination of the carboxyl groups in the extended structures.

Experimental

Preparation of Iron(II)–Amino Acid Complexes

In general, the iron(II) complex separated in good yield when the lithium salt of the amino acid in water or methanol (or the sodium salt in water) was added to hydrated iron(II) chloride in methanol or ethanol, or to aqueous iron(II) sulphate. Since the amino acid complexes are air sensitive, they were prepared and handled under nitrogen in modifications of previously described apparatus. They were dried by continuous pumping for several hours and preserved in sealed glass tubes.

Solvents were de-gassed before use. AnalaR iron(II) salts and the amino acids were obtained commercially.

Bis(glycinato)iron(II)

A mixture of lithium hydroxide monohydrate (2.0 g), glycine (4.5 g), and methanol (200 cm^3) was heated on a steam bath for half an hour and then left to cool. The solution was filtered, and a solution of iron(II) chloride tetrahydrate (5.0 g) in methanol (60 cm^3) added to the filtrate. The cream precipitate obtained was filtered off, washed with methanol and dried.

Bis(alaninato)iron(II)

An aqueous solution of lithium hydroxide monohydrate (1.8 g) was added to an aqueous solution of DL-α-alanine (4.0 g) and the mixture heated on a steam bath for two hours. The solution was evaporated under vacuum to near-dryness and the gummy product shaken with ethanol (100 cm^3). Any alanine which did not dissolve was filtered off, and the filtrate added slowly to a solution of iron(II) chloride tetrahydrate (4.3 g) in ethanol (50 cm^3), with shaking and cooling. The off-white precipitate which appeared was filtered off, washed with ethanol and dried for 14 hours.

Bis(phenylglycinato)iron(II)

An aqueous solution of sodium phenylglycinate was prepared by dissolving sodium hydroxide (1.0 g) and DL-phenylglycine (4.0 g) in water (170 cm^3). The mixture was heated on a steam bath for half an hour, cooled, and the excess of phenylglycine filtered off. The filtrate was slowly added to a solution of iron(II) sulphate heptahydrate (3.0 g) in water (50 cm^3) with shaking. The light greyish-blue precipitate which formed was filtered off, washed with water and acetone, and dried.

Bis(phenylalaninato)iron(II) dihydrate

An aqueous solution of sodium phenylalaninate was prepared by adding sodium hydroxide (0.9 g) to a suspension of a slight excess of DL-α-phenylalanine (6.7 g) in water (130 cm^3). The mixture was heated on a steam bath for 40 minutes, cooled, and the excess of phenylalanine filtered off. The filtrate was added to an aqueous solution of iron(II) sulphate heptahydrate (4.0 g) in water (40 cm^3). The pale blue sticky precipitate was washed by decantation with water, and then shaken with acetone, filtered off and dried.

Bis(leucinato)iron(II) dihydrate

An aqueous solution of sodium leucinate was prepared by heating sodium hydroxide (1.2 g) in water (100 cm^3) with DL-leucine (4.0 g) on a steam bath for one hour. The suspension was cooled and filtered to remove the excess leucine, and the filtrate added to a solution of iron(II) sulphate heptahydrate (4.2 g) in water (100 cm^3). The blue-white precipitate formed was washed by decantation with a large excess of water, filtered off, washed with ethanol, and dried. This compound is very air sensitive, turning orange-brown immediately on exposure to air.

Bis(serinato)iron(II)

A solution of lithium serinate was prepared by dissolving lithium hydroxide monohydrate (1.6 g) and DL-serine (4.0 g) in methanol (200 cm^3) by heating the mixture on a steam bath for 30 minutes. After cooling the remaining solid was filtered off, and the filtrate added slowly to a solution of iron(II) chloride tetrahydrate (3.8 g) in methanol (70 cm^3). The pale grey-blue precipitate was filtered off, washed with methanol and dried.

Aspartatoiron(II) dihydrate

A solution of dilithium aspartate was prepared by dissolving lithium hydroxide monohydrate (1.9 g) and L-aspartic acid (3.0 g) in water (30 cm^3). This was slowly added, with shaking, to a solution of iron(II) chloride tetrahydrate (4.5 g) in methanol (130 cm^3). The white precipitate was filtered off, washed with methanol and dried. The solid soon turned green and then brown in air.

Glutamatoiron(II) dihydrate

A solution of dilithium glutamate was prepared by dissolving lithium hydroxide monohydrate (3.4 g) and L-glutamic acid (5.8 g) in water (100 cm^3). This was added to a solution of iron(II) chloride tetrahydrate (4.0 g) in ethanol (30 cm^3). A pale blue precipitate formed which was filtered off, washed with water and ethanol, and dried. The dry compound turned green immediately on exposure to the air.

Bis(glutaminato)iron(II)

A saturated methanolic solution of lithium glutaminate was prepared by heating a suspension of lithium hydroxide monohydrate (1.3 g) and L-glutamine (4.4 g) in methanol (100 cm^3) on a steam bath for 20 minutes. After cooling the solution was filtered and the filtrate added to a solution of iron(II) chloride tetrahydrate (3.0 g) in methanol (35 cm^3). The precipitate, which was white at first but became light blue and lumpy on standing, was shaken with additional methanol (120 cm^3), filtered off, washed with methanol and dried. It became yellow-brown immediately on exposure to air.

Bis(tryptophanato)iron(II)

A saturated aqueous solution of sodium tryptophanate was prepared by heating a suspension of DL-tryptophan (4.2 g) with aqueous sodium hydroxide (0.9 g NaOH, 200 cm^3 water) for 40 minutes on a steam bath. After cooling, the solution was filtered, and the filtrate slowly added to a solution of iron(II) sulphate heptahydrate (3.0 g) in water (60 cm^3) with shaking. The grey-blue precipitate was filtered off, washed with much water, then acetone, and dried.

Bis(histidinato)iron(II) monohydrate

A pale blue-green suspension of iron(II) hydroxide was prepared by mixing aqueous solutions of ethylenediammoniumiron(II) sulphate (13.0 g in 50 cm^3 of water) and sodium hydroxide (2.7 g in 50 cm^3 of water). The iron(II) hydroxide was filtered off, washed with water and then treated with an aqueous solution of histidine (8.5 g in 100 cm^3 of water). Excess hydroxide was filtered off, and the filtrate evaporated to half volume. No precipitate appeared. The addition of acetone produced a white precipitate of histidine, but the addition of ethanol (100 cm^3) gave a cream precipitate of the complex which was filtered off, washed with ethanol and dried.

Bis(histidinato)iron(II) dihydrate

An aqueous solution of lithium histidinate was prepared by dissolving lithium hydroxide monohydrate (2.4 g) and L-histidine (9.2 g) in water (50 cm^3). This was slowly added, with shaking, to a solution of iron(II) chloride tetrahydrate (6.0 g) in ethanol (60 cm^3). A creamy precipitate formed initially, but it dissolved as more lithium histidinate solution was added to give an orange solution. On standing overnight, pale orange crystals formed. These were filtered off, washed with ethanol and dried.

Bis(methioninato)iron(II)

Lithium hydroxide monohydrate (2.5 g) and L-methionine (8.9 g) in 50% aqueous ethanol (50 cm^3) were heated on a steam bath for 30 minutes, the excess methionine filtered off, and the filtrate added to a solution of iron(II) chloride tetrahydrate (6.0 g) in absolute alcohol (60 cm^3). The black precipitate which came down rapidly changed to dark green in about five minutes. It was left for two days, until no further colour change was observed, filtered off, washed with absolute ethanol, and dried. The pale grey green solid became brown immediately on exposure to the air. A grey blue product analysing approximately as a monohydrate was also obtained. A solution of L-methionine (8.5 g) in water (25 cm^3) was added to a solution of iron(II) ammonium sulphate (10 g) in water (60 cm^3). A grey-blue precipitate came down immediately. This was filtered off, washed with water and absolute ethanol, and dried. It became brown immediately on exposure to the atmosphere.

Bis(S-methylcysteinato)iron(II)

A solution of lithium S-methylcysteinate was prepared from lithium hydroxide monohydrate (2.4 g) and L-S-methylcysteine (8.0 g) and water (30 cm^3). The mixture was heated on a steam bath for 30 minutes, allowed to cool, filtered, and the filtrate added to a solution of iron(II) chloride tetrahydrate

(6.0 g) in absolute ethanol (60 cm^3). A black precipitate came down which, as with the methionine complex, soon lightened in colour. After several hours, when no further change in colour was noted, the fine pale blue precipitate was filtered off, washed with ethanol and dried. The compound was extremely air-sensitive, becoming grey-brown immediately on exposure to the atmosphere.

Cystinatoiron(II)

A solution of lithium cystinate was prepared by dissolving lithium hydroxide monohydrate (2.4 g) and L-cystine (7.0 g) in water (25 cm^3). The solution was warmed on a steam bath for an hour and any undissolved cysteine filtered off. The warm filtrate was added to a solution of iron(II) chloride tetrahydrate (6 g) in absolute ethanol (60 cm^3). A pale yellow-brown precipitate came down immediately. The fine precipitate was filtered off with difficulty, washed with water and absolute ethanol, and dried. The pale yellow solid became grey-brown rapidly on exposure to the atmosphere.

Bis(glycylglycinato)iron(II)

A solution of lithium glycylglycinate was prepared by heating a mixture of glycylglycine (3.5 g) and lithium hydroxide monohydrate (0.6 g) suspended in aqueous methanol (300 cm^3 MeOH, 20 cm^3 water). The remaining solid was filtered off and the filtrate slowly added to a solution of iron(II) chloride tetrahydrate (1.5 g) in methanol (50 cm^3) with shaking. The white precipitate was filtered off, washed with methanol and dried.

Attempts to prepare iron(II) complexes of proline, hydroxyproline, tyrosine, β-alanine, 4-aminobutyric acid, glutathione, and ascorbic acid gave air-sensitive materials which could not be characterised.

Physical Measurements

Magnetic measurements were carried out down to liquid nitrogen temperature by the Gouy method on samples sealed *in vacuo* in Pyrex tubes. Measurements at several field strengths were used to ensure that ferromagnetic impurities were absent. The apparatus was supplied by Newport Instruments, Newport Pagnell, Bucks. The field was calibrated with $Hg[Co(NCS)_4]$. Diffuse reflectance spectra of samples in sealed cells were recorded on a Unicam SP 700C spectrophotometer. Mössbauer data were obtained at liquid nitrogen temperature. The iron content of the complexes was determined by direct combustion to Fe_2O_3, or as the oxinate.

Acknowledgement

We thank the Ministry of Agriculture, Fisheries and Food for a research grant.

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