Transition Metal–Schiff Base Complexes. Part VI.[1] Mössbauer and Magnetic Investigations of Some Iron(II) and Iron(III) Systems

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Iron(II) complexes of the quadridentate Schiff base *NN'*-ethylenebis(salicylideneimine) and related ligands are high-spin with Mössbauer parameters typical of iron(II). Failure to realise the air-sensitivity of these compounds has caused others to report unusually low isomer shifts and quadrupole splittings. Reaction of the appropriate amine and the bis(salicylaldehydato)iron(II) complex has some preparative advantages over direct reaction of the Schiff base with an iron(II) salt. Magnetic and Mössbauer results for distorted octahedral base adducts of bis-(salicylaldehydato)iron(II) are also reported, and from like investigations some iron(III) chloro-complexes with Schiff bases are assigned monomeric five-co-ordinate structures.

THE iron(II) complex (I; R = H, X = $[CH_2]_2$) of the quadridentate Schiff base salen, *NN'*-ethylenebis(salicylideneimine), the complexes of several ring-substituted analogues of salen, and of the related bidentate ligands, *N*-phenyl- and *N*-methyl-salicylideneimine, have been found [2] from magnetic investigations down to liquid nitrogen temperature, to be high-spin. (Salen)-iron(II) was also found [3] to have an isomer shift, δ = 1·20 mm s^{-1} relative to sodium nitroprusside, and a quadrupole splitting, ΔE = 2·15 mm s^{-1}, in keeping [4a] with its formulation as a high-spin, iron(II) compound. It was therefore surprising to find in a recent book [4b] on Mössbauer spectroscopy that (salen)iron(II) is reported to have the very different δ and ΔE values of 0·49 and 0·97 mm s^{-1} respectively, *i.e.*, values which could be considered [4a] typical of high-spin iron(III) compounds. Several independent groups of workers have reported unusual Mössbauer parameters [4b-6] for (salen)iron(II) and various related complexes and explained them in terms of π-bonding, *etc.* In our magnetic investigations it was found essential [2] to handle this type of iron(II) compound with very careful exclusion of air since oxidation produced oxo-bridged iron(III) compounds which could not readily be distinguished by analysis alone from the iron(II) compounds. Traces of oxidation also led to field-dependent susceptibilities. It was also found [3] that oxidised (salen)iron(II), *i.e.* $[Fe(salen)]_2O$, had δ = 0·61 mm s^{-1} and ΔE = 0·73 mm s^{-1}, so it seemed to us that the Mössbauer parameters for the so-called (salen)iron(II) had been obtained on oxidised samples. To confirm this, to decide whether compounds (I) have planar structures, and to compare their Mössbauer behaviour with that of their nitrosyl adducts,[1,7] some (salen)iron(II) complexes have been investigated. Several other high-spin iron(II) compounds, which had been assigned unusual Mössbauer parameters, have been studied as have some related iron(III) chloro-complexes (Table).

During the course of our work, de Vriess, Trooster, and de Boer have reported [8] Mössbauer results for several of these iron(II) compounds in close agreement with ours. They too conclude that oxidation caused the anomalous results.

RESULTS AND DISCUSSION

Iron(II) *Complexes.*—Magnetic investigations showed that all the iron(II) compounds were high-spin ($t^4_{2g}e^2_g$ configuration) with magnetic moments of *ca.* 5·0 B.M. at 295 K. Minor differences, 0·2 B.M. or less, were observed between preparations in this work [I; X = $(CH_2)_2$: R = H, 5·01 B.M.; R = 5-Me, 5·11 B.M.; R = 5-NO_2, 4·81 B.M.], and those of the same compound obtained earlier,[2] and these are probably due to difficulties in handling these air-sensitive compounds. However, unlike others,[6,8] we consider that this reproducibility shows that it is possible to distinguish magnetochemically between iron(II) and iron(III) complexes, provided adequate precautions are taken to exclude air from the former. New magnetic data are presented in the Table. The samples for which magnetic results are reported showed negligible field-dependence of susceptibility. Even brief exposure led to traces of ferromagnetic impurity. Preparations of bis(salicylaldehydato)bis-(piperidine)iron(II) with reasonable analyses still had field-dependent susceptibilities so no magnetic data have been reported. The ferromagnetic impurities were not apparent from the Mössbauer spectrum. Otherwise, Mössbauer spectra were recorded for those samples

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[7] B. W. Fitzsimmons, L. F. Larkworthy, and K. A. Rogers, unpublished work.

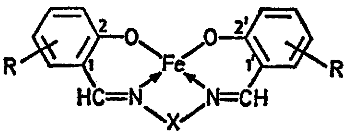
[8] J. L. K. F. de Vriess, J. M. Trooster, and E. de Boer, *Chem. Comm.*, 1970, 604.

which showed no field dependence. Typical Mössbauer spectra are shown in Figures 1 and 2. The isomer shifts (Table) are approximately 1·2 mm s^{-1}, typical of iron(II) in agreement with the magnetic results. It is certain that some workers[4b-6] were unwittingly investigating the Mössbauer properties of iron(III) compounds; no other explanation is necessary for the unexpected Mössbauer parameters obtained.

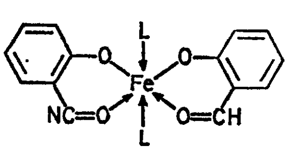
Magnetic moments near the spin-only value which are almost temperature independent indicate[9] considerable distortion from regular octahedral symmetry, but do not distinguish between a planar monomeric structure, and five- or six-co-ordination through oxygen bridges. The quadrupole splittings of compounds (I) and their small variation with temperature, though indicative of considerable distortion, do not seem large enough for planar molecules. The mineral gillespite[10] contains high-spin iron(II) in a planar environment but has an unusually small quadrupole splitting. The five-co-ordinate compound Fe(terpyridyl)Br$_2$, has[11] a larger quadrupole splitting (2·76 mm s^{-1}) than compounds (I). The quadrupole splittings of compounds of types (I) and (II) are of similar magnitude, and in the latter the base would be expected to be co-ordinated as shown crystallographically for bis(salicylaldehydato)bis(aquo)nickel-(II)[12] giving a distorted octahedral configuration. Thus

Compound	Colour	Analytical data % [a]				Mössbauer data			Magnetic data [b] $\mu_{eff.}$/B.M.		Diamagnetic correction/
		C	H	N	Fe	Temp./K	δ/mm s^{-1}	ΔE/mm s^{-1}	295 K	90 K	c.g.s.u. × 10^6
(I), X = $(CH_2)_2$											
(1) R = H	Brown	59·5	5·0	8·7	17·3	300 *c*	1·23	2·23			
		(59·7)	(4·4)	(8·7)	(17·3) *c*	80	1·32	2·35			
							(1·24) *d*	(2·50) *d*			
						300 *e*	1·23	2·22			
		59·5	4·6	8·7	16·9 *e*	80	1·27	2·28			
(2) R = 5-Me	Red-brown	61·4	5·1	7·9		80	1·33	2·22			
		(61·7)	(5·2)	(8·0) *c,f*							
(3) R = 3-MeO	Red-brown	54·0	5·0	6·9	13·8	300	1·20	2·36	5·14	5·07	217
		(54·0)	(5·05)	(7·0)	(13·95) *c,g*	80	1·29	2·54			
(4) R = 5-NO_2	Brown	46·85	4·1	13·75		80	1·38	2·38			
		(46·6)	(2·9)	(13·6) *e*							
	Brown	44·4	3·2	16·0	13·0	300	1·28	1·99			
		(44·7)	(3·3)	(13·0)	(13·0) *e,h*	80	1·43	2·22			
(I), X = (o-C_6H_4)											
(5) R = H	Olive	61·9	4·5	7·3	14·3	300 *c*	1·15	2·40	5·04 *c*	5·01	182
		(61·9)	4·2)	(7·2)	(14·4) *c,i*	80	(0·59) *j*	(0·78)			
							1·30	2·46	5·17 *e*		
							(1·20) *d*	(2·42) *d*			
						300 *e*	1·16	2·38	4·90 *c,k*	4·91	170
		60·7	4·3	6·4	14·8 *e*	80	1·27	2·43			
	Black	64·6	4·25	7·4		300 *l*	1·20	2·30			
		(64·9)	(3·8)	(7·6) *l*		80	1·31	2·30			
(II)											
(6) L = H_2O	Grey-brown	50·05	4·5		16·3	300	1·40	2·48	5·00	5·04	148
		(50·3)	(4·2)		(16·7)	80	1·52	2·53			
							(1·43) *d*	(2·51) *d*			
(7) L = piperidine	Dark green	59·7	6·8	5·9	12·35	300	1·32	2·22			
		(61·5)	(6·9)	(6·0)	(11·9) *m*	80	1·42	2·30			
(8) L = pyridine	Purple-black				12·1	300	1·31	2·38	5·19		220
					(12·2)	80	1·40	2·55			
(9) L = β-picoline	Dark green	62·3	5·0	5·6	11·9	300	1·33	2·34	5·14 *p*	5·09	247
		(64·5)	(5·0)	(5·8)	(11·5) *n*	80	1·41	2·34			
(10) L = γ-picoline	Purple-black	64·4	5·1	6·0	11·3	300	1·34	2·16	4·97	4·96	247
		(64·5)	(5·0)	(5·8)	(11·5)	80	1·40	2·24			
(11) L = 3,5-lutidine	Black	65·1	5·5	5·5	11·0	300	1·28	2·15			
		(65·6)	(5·5)	(5·5)	(10·9)	80	1·43	2·15	5·07 *q*	5·04	270
(III)											
(12)	Black	59·1	3·6	6·7	14·0	300	0·62	1·04	5·64	5·65	193
		(59·2)	(3·5)	(6·9)	(13·8) *r*	80	0·63	1·06			
						4·2	0·72	1·10			
(IV)											
(13) $R^1 = R^2$ = Me	Purple-black	45·9	5·9	8·9		300	0·58	0·97			
		(45·9)	(5·9)	(8·9) *r*		80	0·68	1·08			
						4·2	0·74	1·18			
(14) R^1 = Ph, R^2 = Me	Purple-black	60·4	5·1	6·4		300	0·57	1·00	5·86	5·85	206
		(60·3)	(5·0)	(6·4) *r*		80	0·70	1·16			
						4·2	0·87	1·20			

[a] Calculated values in parentheses. [b] Curie–Weiss law taken as $\chi_A^{-1} \propto (T + \theta)$; $\theta = 0$ except where shown otherwise. [c] From iron(II) acetate and Schiff base. [d] Ref. 8 [e] From salicylaldehydatoiron(II) complex. [f] Oxidised very rapidly on exposure to air; other compounds were moderately stable. [g] Monohydrate: requires 4·5% weight loss; found 3·8% at 170°. [h] One preparation gave a monohydrate. [i] Monohydrate: requires 4·6% weight loss; found 4·5% at 170°. [j] Oxidised. [k] Anhydrous compound. [l] Anhydrous compound; prepared from methanolic iron(II) acetate and Schiff base in dimethylformamide. [m] On washing with water the purple bis(aquo)-complex formed. [n] The β-picoline was readily lost from this compound. [p] $\theta = 2°$. [q] $\theta = 1°$. [r] Chloride analyses, calculated values in parentheses, compounds (12): 8·6 (8·75); (13): 11·4 (11·3); (14): 8·1 (8·1)%.



(I)



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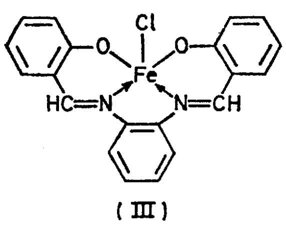
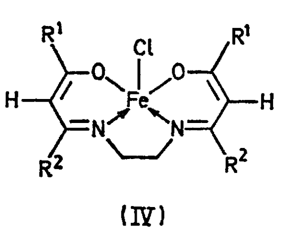


(III)



(IV)

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[10] R. G. Burns, M. G. Clark, and A. J. Stone, *Inorg. Chem.*, 1966, **5**, 1268.

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[12] J. M. Stewart, E. C. Lingafelter, and J. D. Breazeale, *Acta Cryst.*, 1961, **14**, 888.

compounds (I) are not planar, but are polymers of higher co-ordination number. Five-co-ordination is common in Schiff base complexes, either through the formation of oxygen bridges [13,14] or co-ordination of a water molecule,[15] but only crystallographic investigations can distinguish between this and six-co-ordination in the iron(II) compounds. Compounds (I) do not exhibit antiferromagnetism unlike (salen)manganese(II) [2] and (salen)iron(III) chloride,[16] but this does not preclude polymeric structures since the (salen)copper(II) dimer is magnetically normal because of the large Cu–O bond distance between monomer units. It does not now seem likely that the reactivity towards oxygen of the ' active ' form of (salen)cobalt(II), or (salen)iron(II), implies a planar structure since the ' inactive ' form of (salen)cobalt(II) is dimeric [14a,b] with five-co-ordinate cobalt, and ' active ' (salen)cobalt(II) is believed [14c] to have similar dimers in a more open crystal structure.

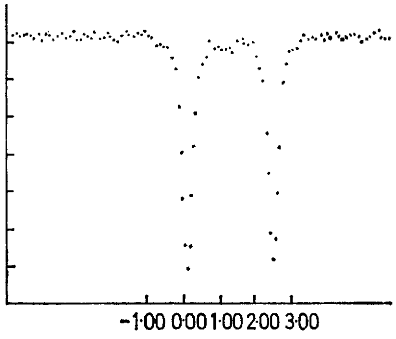

FIGURE 1 Mössbauer spectrum of compound (5) at 80 K

The isomer shift and the quadrupole splitting of the bisaquo-compound of type (II) are somewhat larger than the corresponding parameters of the bis(amine) adducts which show little differences among themselves. Ligands with nitrogen donor atoms are higher in the nephelauxetic series than those with oxygen donor atoms. Thus, this result is some confirmation of the recognised correlation that isomer shift decreases with greater nephelauxetic effect.

Iron(III) *Chloro-complexes*.—A number of quadridentate Schiff base chloro-complexes of iron(III) have been studied in the past, especially the intramolecular antiferromagnetic dimers [Fe(salen)X]$_2$, which are axially bridged species in which the ferric ions couple together reasonably strongly. Their Mössbauer spectra were first elucidated by Okamura *et al.*[17]

In the present study, compounds of type (III) [Table, no. 12)] and (IV) [nos. (13) and (14)] were investigated. They are here formulated as five-co-ordinate monomers in contrast to [Fe(salen)Cl]$_2$ and we advance evidence in support of this structure here.

These compounds were prepared by methods analogous to those used for [Fe(salen)Cl]$_2$. Compound (12) can be regarded as being derived from compound (5) by oxidative addition of chlorine. Paramagnetic susceptibility measurements over a temperature range on compounds (12) and (14), are summarised in the Table. The magnetic moments of these compounds remain constant down to the lowest temperature attained and the actual values are not too far from the 5·92 B.M. expected for a $^6A_1$ ground state. The moment of compound (13) was found to be 5·73 B.M. at room temperature. Whilst this value is somewhat low, we believe that all these compounds are simple paramagnets. Further information on this point can be extracted from the Mössbauer spectra. Figure 3 shows the spectra of compounds (12), (13), and (14) at 80 K. The high-temperature spectra like those of many high-spin ferric compounds, show evidence of asymmetric peak broadening arising from slow electronic relaxation. The parameters for these spectra at all temperatures studied are given in the Table. These isomer shifts and quadrupole splittings tell nothing about the degree of interaction between adjacent ferric ions whilst being quite characteristic of high-spin iron(III) generally. They can be compared with $\Delta E = 0·980$ mm s^{-1} and $\delta = 0·730$ mm s^{-1} found for chlorobis(pentan-2,4-dionato)iron(III) which is known [18] to be square pyramidal. Information relevant to the question of the amount of spin–spin interaction was obtained by measuring the Mössbauer spectra at low temperatures and in applied magnetic fields.

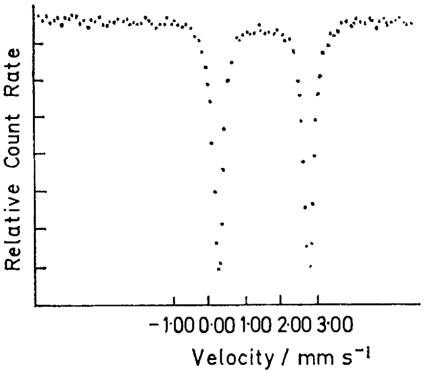

FIGURE 2 Mössbauer spectrum of compound (6) at 80 K

At 4·2 K, compounds (12), (13), and (14) show quadrupole doublets of approximately equal height in contrast to the marked broadening of the high energy peak observed at high temperature. This behaviour is more readily understood after measuring the Mössbauer spectra

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[13] D. Hall and T. N. Waters, *J. Chem. Soc.* (*A*), 1960, 2644.

[14] (*a*) S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, 1969, **B25**, 1671; (*b*) R. DeIasi, S. L. Holt, and B. Post, *Inorg. Chem.*, 1971, **10**, 1498; (*c*) M. Calligaris, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc.* (*A*), 1970, 1069.

[15] D. Hall and F. H. Moore, *J. Chem. Soc.* (*A*), 1966, 1827; G. E. Batley and D. P. Graddon, *Austral. J. Chem.*, 1967, **20**, 885; F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, 1960, 2639.

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[17] M. Y. Okamura, I. M. Klotz, C. E. Johnson, M. R. C. Winter, and R. J. P. Williams, *Biochemistry*, 1969, **8**, 1951.

[18] M. Cox, B. W. Fitzsimmons, L. F. Larkworthy, K. A. Rogers, and A. W. Smith, *J. Chem. Soc.* (*A*), 1971, 2158.

in applied magnetic fields because these compounds exhibit substantial hyperfine fields, indicating that they are monomeric. Had any of these compounds been dimeric, they would have had diamagnetic ground states and shown just simple quadrupole doublets in zero applied field. Small splitting into a doublet and a triplet would have been observed in applied fields with high temperature behaviour similar to that described here.

We conclude that the broadening apparent in the high temperature spectra arises from zero field splitting into three Kramers doublets, with the zero field splitting parameter D, being positive for these, such that the fastest relaxing Kramers doublet, $M_s = \pm\frac{1}{2}$, lies lowest in energy.

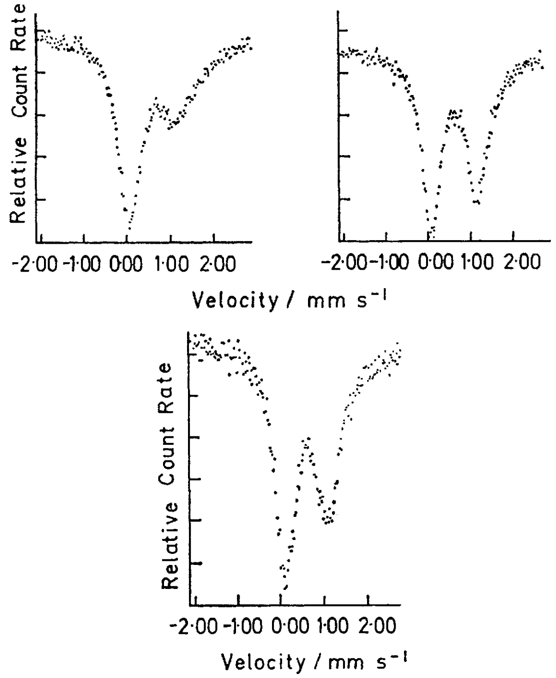

FIGURE 3 Mössbauer spectra of compounds (12)—(14) at 80 K

Information on the sign of the principal component of the electric field gradient can be obtained from these magnetic spectra. The magnetic hyperfine quadrupole splitting is given by $\Delta E = \frac{1}{2}e^2Qq_\theta = \frac{1}{2}(E_3 - E_1)$ where E_3 is the separation between lines 5 and 6 and E, that between 1 and 2 (the lines are numbered in the order of increasing Doppler velocity). Here, Q is the electric quadrupole moment of the $I = \frac{3}{2}$ level of ^{57}Fe and eq_θ is the component of the electric field gradient in the direction of H_n.

Consider first the behaviour of compound (12). Figure 4 shows its Mössbauer spectrum at 4·2 K in zero field and in applied external fields of 1·5 and 3·0 T. The large hyperfine field confirms that this compound has a paramagnetic ground state at 4·2 K. The intensity ratio of lines in the magnetic spectra corresponds to the expected 3 : 4 : 1 : 1 : 4 : 3 but some extra peaks can be discerned as the centre of the spectrum and these are probably due to the $M_s = \pm\frac{3}{2}$ Kramers doublet being populated. V_{pp} in the direction of the effective field is negative and the apparent quadrupole splitting is $\frac{1}{2}e^2q_0Q = -0{\cdot}2$ mm s^{-1}. Since $\Delta E = 1{\cdot}10$ mm s^{-1}, the hyperfine field is not polarized along the Z axis and θ *ca.* 62°. V_{zz} is positive. This means that the hyperfine field is fluctuating along the Z axis in zero applied field.

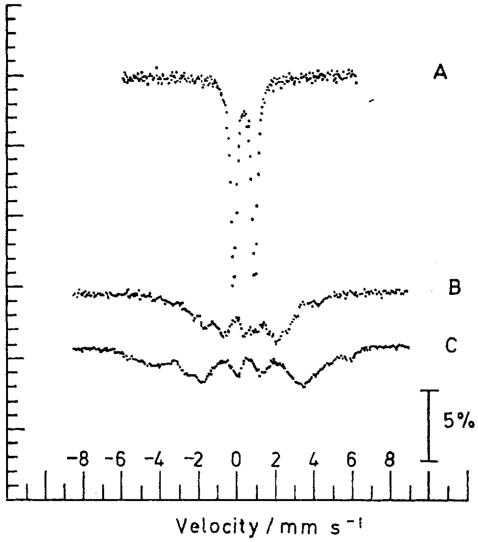

FIGURE 4 Mössbauer spectra of compound (12) at 4·2 K in (A) zero field, (B) applied magnetic field of strength 1·5 T, and (C) 3·0 T

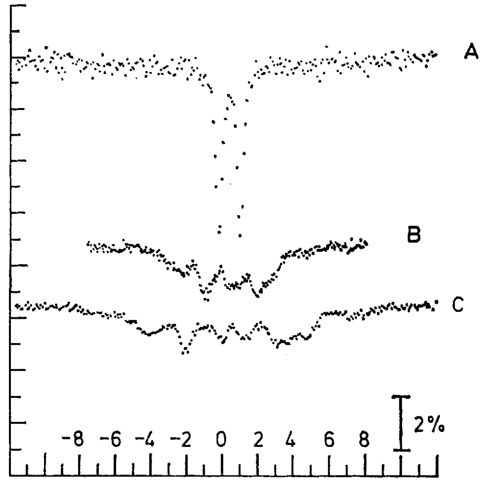

FIGURE 5 Mössbauer spectra of compound (13) at 4·2 K in (A) zero field, (B) 1·5 T, and (C) 3·0 T

Compounds (13) and (14) behave in an analogous way (see Figures 5 and 6) except that some peak asymmetry persists in compound (14) at 4·2 K. As the magnetic spectrum is so similar to those of compounds (12) and (13), we consider that this is a relatively unimportant facet of its behaviour.

EXPERIMENTAL

Preparation of Iron(II) *Compounds*.—The iron(II)–Schiff base complexes were prepared as before [2] by reaction (1) of the preformed ligand, in ethanol or dimethylformamide containing some sodium or potassium hydroxide, with freshly prepared aqueous iron(II) acetate, or (2) by reaction of the appropriate primary amine with the salicylaldehydatoiron(II) compound prepared as below. Method (2) does not seem to have been used previously for iron(II) compounds. It has some advantages in that the salicylaldehydatoiron(II) complex can be more soluble in organic solvents than the acetate, the iron(II) is already complexed, and the addition of hydroxide during the formation of the Schiff base complex is unnecessary. To prepare compound (6), a methanolic solution of freshly distilled salicylaldehyde containing a deficiency of potassium hydroxide was added to aqueous iron(II) acetate. The purple solid which precipitated was filtered off, washed, and dried. To prepare compound (1), the solid was boiled for 30 min in ethanol with an equivalent amount of ethylenediamine. Compound (5) was similarly prepared from *o*-phenylenediamine, and compound (4) from 5-nitrosalicylaldehyde. Compounds (7)—(11) were prepared by the addition of a solution of salicylaldehyde in the liquid base to an aqueous solution of iron(II) sulphate. The pyridine, β-picoline, and piperidine adducts lose base readily. Attempts to prepare an α-picoline adduct were unsuccessful.

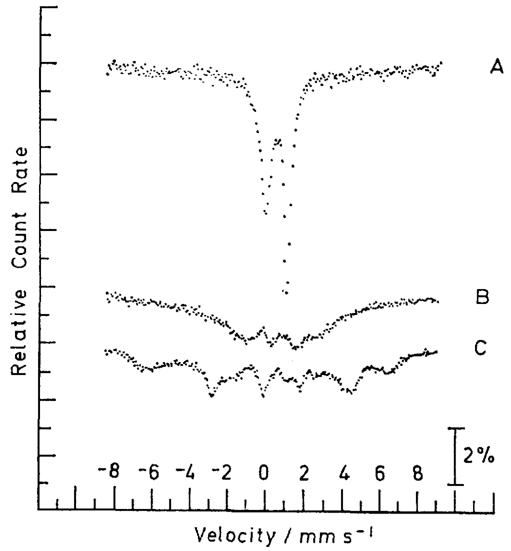

FIGURE 6 Mössbauer spectra of compound (14) at 4·2 K in (A) zero field, (B) 1·5 T, and (C) 3·0 T

Other workers [8] have prepared the iron(II) chelates by mixing solutions of aqueous iron(II) sulphate and alcoholic ligand, and then distilling off all the solvent. No microanalyses were reported. Although sulphate can be used successfully, sometimes it contaminates the product. Our samples were prepared, filtered off, washed, and dried under nitrogen or *in vacuo*. All operations were carried out in the absence of air, and all solvents were deoxygenated before use. There is reasonable agreement between our Mössbauer parameters for compounds (1), (5), and (6), and those recently reported.[8] However, it is not clear from ref. 8 that compound (6) is a dihydrate as normally obtained, and the green colour found for compound (5) would suggest from our results that it is a monohydrate.

Preparation of Iron(III) *Compounds*.—Compound (12) was prepared by refluxing anhydrous iron(III) chloride with the Schiff base in ethanol for several hours. It crystallised on cooling. Compounds (13) and (14) were similarly obtained from dry benzene through which ammonia gas was passed. On cooling a mixture of the product and ammonium chloride was deposited. The crystalline compound was dissolved in benzene, filtered hot from the ammonium chloride, and crystallised by the addition of light petroleum.

Magnetic and Mössbauer Data.—Magnetic measurements were made down to liquid nitrogen temperatures by the Gouy method. Air sensitive samples were sealed in Pyrex tubes. Measurements at four field strengths were used to ensure that there were negligible ferromagnetic impurities. Mössbauer data were obtained at room and liquid nitrogen temperatures using counting equipment described by Fitzsimmons.[19] A Centronic Mössbauer effect analyser (20th Century Electronics) drive unit and Intertechnic SA 41 400 channel analyser were used to complete the Mössbauer effect apparatus. Spectra at 4·2 K in zero and applied perpendicular magnetic fields were measured at the P.C.M.U., Harwell. All Mössbauer data reported are with respect to sodium nitroprusside.

Analyses.—Iron was estimated either by ignition of the complex to the oxide Fe_2O_3, or gravimetrically, as the oxinate.

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