Iron Complexes of *N*-Substituted Thiosalicylideneimines. Part 2.[1] Magnetic and Mössbauer Spectral Studies † of Iron(II) Complexes

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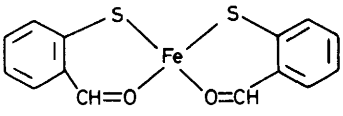
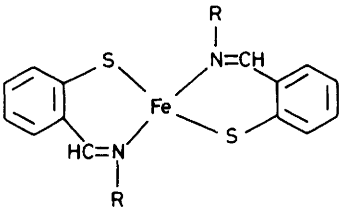
A detailed variable-temperature study has been made of the magnetic susceptibilities and Mössbauer spectra of bis(thiosalicylaldehydato)iron(II), [Fe(tsal)$_2$], *NN'*-ethylenebis(thiosalicylideneiminato)iron(II), [Fe(tsalen)], *NN'*-propane-1,3-diylbis(thiosalicylideneiminato)iron(II), [Fe(tsalpd)], and bis[*N*-(*p*-methoxyphenyl)thiosalicylideneiminato]iron(II), [Fe(mptsaln)$_2$]. A variety of spin states and magnetic exchange effects are observed: [Fe(tsal)$_2$], high spin $S = 2$, binuclear species with antiferromagnetic coupling; [Fe(tsalen)], intermediate spin $S = 1$, antiferromagnetic coupling, polymeric species; [Fe(tsalpd)], high spin $S = 2$, binuclear species with antiferromagnetic coupling; [Fe(mptsaln)$_2$], high spin $S = 2$, with zero-field splitting.

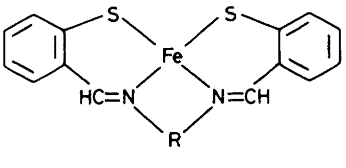
Iron(II) complexes of thiosalicylaldehyde and related thiosalicylideneimines have been prepared and their reactions with CO and O_2 studied.[1] This paper reports detailed studies of the magnetic and Mössbauer spectral properties of some representative compounds: namely, bis(thiosalicylaldehydato)iron(II), [Fe(tsal)$_2$] (1); the bidentate complex bis[*N*-(*p*-methoxyphenyl)thiosalicylideneiminato]iron(II), [Fe(mptsaln)]$_2$ (2); and the tetradentate complexes *NN'*-ethylenebis(thiosalicylideneiminato)iron(II), [Fe(tsalen)] (3a), and *NN'*-propane-1,3-diylbis(thiosalicylideneiminato)iron(II), [Fe(tsalpd)] (3b).



[Fe(tsal)$_2$] (1)



[Fe(mptsaln)$_2$] (2; R = p-MeOC$_6$H$_4$)



[Fe(tsalen)] (3a; R = CH$_2$CH$_2$)
[Fe(tsalpd)] (3b; R = CH$_2$CH$_2$CH$_2$)

A variety of spin states and magnetic exchange effects is observed in these compounds which enables comparisons to be made with the related *N_2O_2*-bonded salicylideneimines of the [Fe(salen)] [H$_2$salen = *NN'*-ethylenebis(salicylideneimine)] type. There are few sulphur-oxygen or sulphur-nitrogen chelates of Fe^{II} whose detailed electronic structures are known and the present study should help to delineate these co-ordination environments.

Experimental

The complexes were prepared and purified as described previously.[1] Room temperature magnetic moments were measured by the Faraday method, using Hg[Co(NCS)$_4$] and [Ni(en)$_3$][S$_2$O$_3$] (en = ethylenediamine) as calibrants. Field strengths between 5 and 6.5 kG were used to check for the presence of field-dependent impurities and all samples were found to give susceptibilities independent of the applied field. Diamagnetic corrections were calculated by the use of Pascal's tables.

Variable-temperature magnetic susceptibilities over the temperature range 4.2—300 K were measured on a modified Oxford Instruments Faraday magnetometer[2] with main fields of 10 kG and/or 40 kG and a gradient field of 1 000 G cm^{-1}. Samples of between 10 and 40 mg were placed in a gold bucket and suspended from a Sartorius electronic microbalance by a fine quartz fibre. Measurements in the range 4.2—20 K were made manually and automatic data-logging equipment was then used for measurements at higher temperatures. The calibration of the instrument was checked using AnalaR grade samples of CuSO$_4$·5H$_2$O.

Detailed tabulations of susceptibility and moment as functions of temperature for the complexes [Fe(tsal)$_2$], [Fe(tsalen)], [Fe(tsalpd)], and [Fe(mptsaln)$_2$] can be obtained on request to the authors.

Mössbauer spectra were recorded on an instrument which has previously been described.[3] The applied-field spectra shown in Figures 3(*b*) and 5(*b*) were fitted by use of the program LANG ‡ assuming a $S = 0$ ground state.

Results and Discussion

The pertinent magnetic parameters for the complexes are shown in the Table. Detailed discussions for each system are given below.

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† *Non-S.I. units employed:* G = 10^{-4} T; B.M. = 0.927×10^{-23} A m^2; Oe = 1 000/4π A m^{-1}; $\chi_{c.g.s.} = 4\pi \times 10^{-6}$ S.I. unit.

‡ This program has been described by G. Lang and B. W. Dale, *Nucl. Instrum. Methods*, 1974, **116**, 567.

Table. Magnetic susceptibilities and Mössbauer spectral parameters for some Fe^{II} thiosalicylideneimines

		Mössbauer spectra at 4.2 K		Proposed Fe^{II} spin state
Compound	μ_{Fe} ^{a}/B.M.	δ ^{b}/ mm s^{-1}	ΔE/ mm s^{-1}	
[Fe(tsal)$_2$]	5.01	1.08	2.49	2
[Fe(mptsaln)$_2$]	5.16	0.70	2.23	2
[Fe(tsalen)]	1.90	0.44	2.20	1
[Fe(tsalpd)]	4.11	0.87	3.32	2

^{a} At 295 K. ^{b} Relative to iron metal.

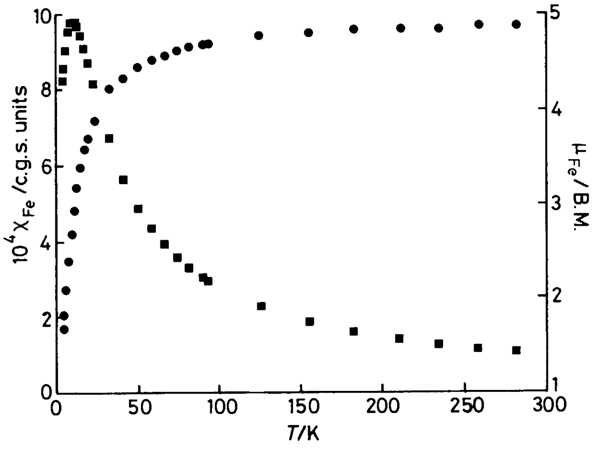

Figure 1. Temperature dependence of magnetic susceptibility, χ_{Fe} (■), and magnetic moment, μ_{Fe} (●), for [Fe(tsal)$_2$]

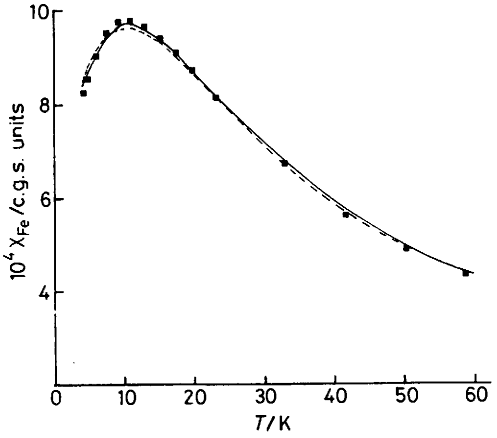

Figure 2. The variation of χ_{Fe} with temperature for [Fe(tsal)$_2$]: (■) experimental; (- - - -) calculated from a $-2J\ S_1S_2$ analysis with $g = 2.03$ and $J = -1.7$ cm^{-1}; (——) calculated using equation (i) with $g = 2.02$, $J = -1.6$ cm^{-1}, and $D = 1.3$ cm^{-1}

[Fe(tsal)$_2$].—The room temperature magnetic moment of the complex is 5.01 B.M. at 295 K. A plot of μ_{Fe} *versus* T is shown in Figure 1. The moment is essentially independent of temperature between 300 and *ca.* 70 K but decreases rapidly at low temperatures reaching 1.8 B.M. at 4.2 K. The corresponding χ_{Fe} *versus* T plot shows a maximum in susceptibility at *ca.* 10 K which is characteristic of weak antiferromagnetic coupling between neighbouring Fe^{II} centres.

The results could be fitted to the equation derived from a simple spin Hamiltonian of the type $-2J\ S_1S_2$, which assumes that the high-spin $S = 2$ Fe^{II} centres are orbitally nondegenerate. The parameters derived from the best least-squares fit are $g = 2.03$ and $J = -1.7$ cm^{-1} (Figure 2). Confirmation of the $S = 2$ spin state is afforded by the Mössbauer spectral parameters for [Fe(tsal)$_2$] given in the Table which are typical of high-spin Fe^{II}. A 25 kOe applied-field spectrum at 4.2 K shows no increase in the effective magnetic field at the iron nucleus which is compatible with an $S' = 0$ ground state resulting from antiferromagnetic coupling of two $S = 2$ atoms. The quality of the fit of the χ_{Fe} data, especially at very low temperatures, can be improved by including a single-ion zero-field splitting parameter, D, in the Hamiltonian given by equation (i). The best-fit parameters then become $g = 2.02 \pm 0.01$, $J = -1.6 \pm 0.1$ cm^{-1}, and $D = 1.3 \pm 0.1$ cm^{-1} (Figure 2).

$$\mathscr{H} = -2J\ S_1S_2 + D[S_{1z}^2 + S_{2z}^2 - 2S(S+1)/3] + g\beta H(S_1 + S_2) \quad \text{(i)}$$

While the magnetic properties of the related complex bis(salicylaldehydato)iron(II), [Fe(sal)$_2$], are not known, those of the diaqua-derivative, [Fe(sal)$_2$(H$_2$O)$_2$], show high-spin behaviour with Mössbauer parameters [4,5] similar to those obtained here for the thiosalicylaldehyde complex. Substitution of *O*-donor by *S*-donor atoms in the aldehyde complex does not therefore markedly change the spin state of the Fe^{II}. Binuclear ligand-bridged structures of the kind needed to explain the present magnetism are known for other bidentate chelates of Fe^{II} with ligands such as β-diketones,[6,7] *o*-aminobenzenethiol,[8] dithiolates,[9] and dithiocarbamates,[10,11] all of which display weak antiferromagnetism. Recent studies of some homobinuclear Fe^{II} macrocycles by Hendrickson and co-workers [12] also have similar g and J values to those displayed by [Fe(tsal)$_2$].

[Fe(tsalen)] *and* [Fe(tsalpd)].—The tetradentate complexes, [Fe(tsalen], [Fe(tsalpn)],* and [Fe(tsalphen)] * show somewhat anomalous magnetic moments at room temperature, *viz.* 1.9 B.M. per Fe atom. These values lie outside the normal ranges expected for low-, intermediate-, or high-spin Fe^{II} complexes and are immediately indicative of either spin equilibrium or magnetic exchange effects. The zero-field Mössbauer spectrum of [Fe(tsalen)] at 4.2 K (Figure 3) shows only one sharp quadrupole doublet with a δ value of 0.44 mm s^{-1}, which is not symptomatic of a spin equilibrium model since one might expect to see two doublets or a low-spin signal at this temperature. The δ value is in fact compatible with an $S = 1$ ground state, as has been observed for the Fe^{II} complexes with phthalocyanin [13] and α,β,γ,δ-tetraphenylporphyrin [14] ligands. A spin exchange model is therefore favoured over a spin equilibrium and this choice is further supported by the small hyperfine magnetic field generated in a 25 kOe applied-field Mössbauer spectrum which is indicative of a diamagnetic $S' = 0$ ground state brought about by antiferromagnetic coupling of neighbouring $S = 1$ Fe^{II} atoms.[15] The solid line shown in Figure 3(*b*) is the calculated spectrum using the program LANG assuming a diamagnetic ($S = 0$) spin state. The field at the nucleus was calculated to be *ca.* 85% of the applied field. A similar effect was observed [15] in the antiferromagnetically-coupled com-

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* *NN'*-propane-1,2-diylbis(thiosalicylideneiminato)iron(II), [Fe(tsalpn)] [see (3), R = CH$_2$CHMe] and *NN'*-*o*-phenylenebis(thiosalicylideneiminato)iron(II), [Fe(tsalphen)] [see (3), R = *o*-C$_6$H$_4$].

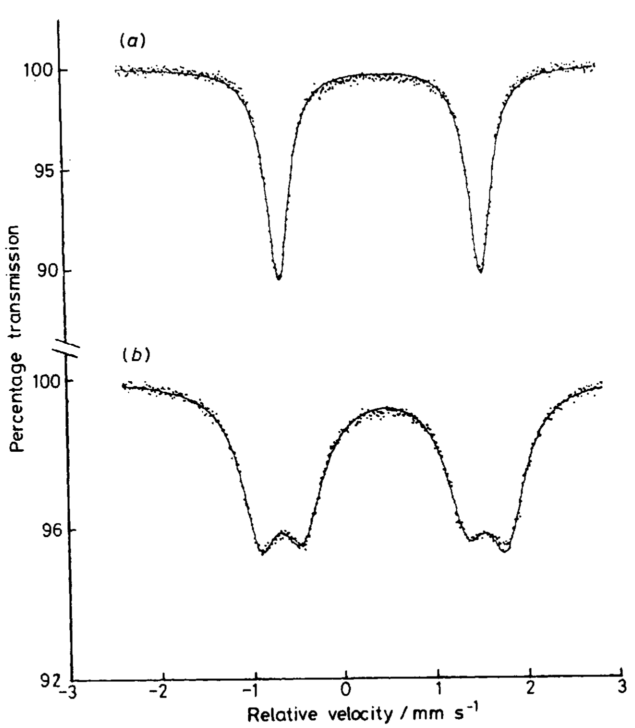


Figure 3. Zero-field (*a*) and applied field (*b*) Mössbauer spectra of [Fe(tsalen)] at 4.2 K. The solid line in (*b*) is the best-fit curve using LANG with $H_{eff.}$ = 21.4 kOe, δ = 0.44 mm s^{-1}, ΔE = 2.18 mm s^{-1}, V_{zz} positive, and η = 0.07

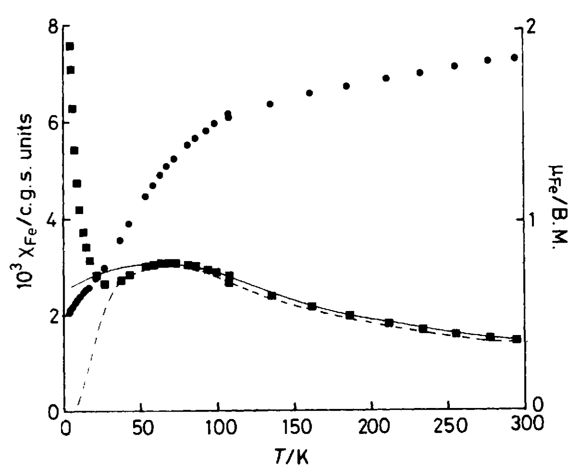


Figure 4. The magnetic behaviour of [Fe(tsalen)]: (■) χ_{Fe} experimental; (●) μ_{Fe} experimental; (——) calculated from equation (ii) (Heisenberg chain) with g = 1.49 and J = −19.0 cm^{-1}; (– – – –) calculated from equation (iii) (dimer) with g = 1.39 and J = −21.8 cm^{-1}

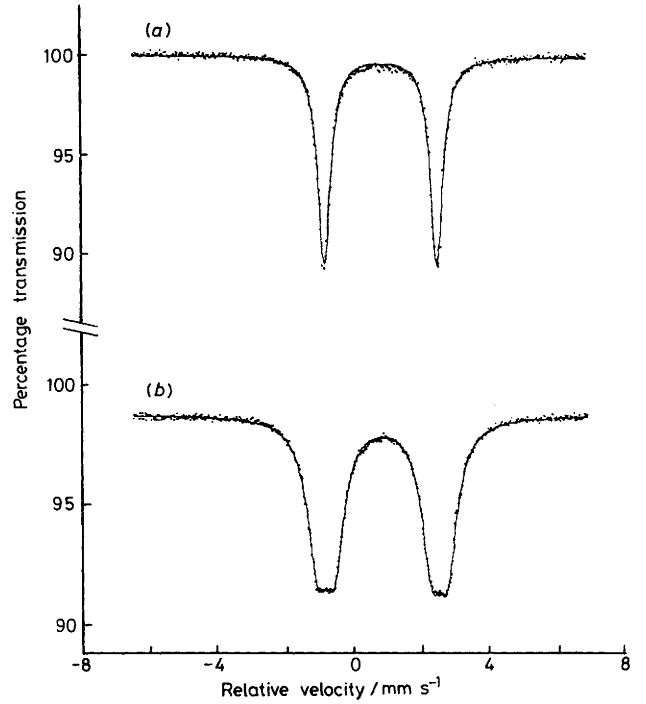


Figure 5. Zero-field (*a*) and applied field (*b*) Mössbauer spectra of [Fe(tsalpd)] at 4.2 K. The solid line in (*b*) is the best-fit curve using the program LANG with $H_{eff.}$ = 23.7 kOe, δ = 0.87 mm s^{-1}, ΔE = 3.32 mm s^{-1}, V_{zz} positive, and η = 0.09

pound [{Fe(salen)Cl}$_2$] and is probably due to a small induced negative hyperfine field arising from admixture, into the ground state, of high-lying crystal-field split levels.

The 25 kOe applied field does not completely remove the degeneracy associated with the $I = \frac{1}{2}, \frac{3}{2}$ levels of the ^{57}Fe nucleus [Figure 3(*b*)] and although the splitting is not well resolved, the applied-field spectrum suggests that V_{zz}, the principal component of the electric field gradient tensor is positive. The quadrupole splitting is similar to that of [Fe(tsal)$_2$] and indicates a general similarity of the co-ordination spheres in the two species.

The compound [Fe(tsalen)] exhibits a highly temperature-dependent magnetic moment (Figure 4), decreasing from 1.8 B.M. at 294 K to 0.51 B.M. at 4.3 K. The corresponding χ_{Fe} *versus* T plot is rather unusual and, as shown in Figure 4, it displays a very broad maximum at *ca.* 68 K and a sharp increase at very low temperatures. The latter seems likely to be due to a magnetic impurity, possibly monomeric [Fe(tsalen)], since three separate preparations showed the same increase at low temperatures, but with a 10% variation in χ_{Fe} at 4.3 K. The remainder of the data above 40 K were reproducible from sample to sample. Since the magnetic impurity was not detectable in the Mössbauer spectrum, we estimate its concentration at less than 2%.

The general shape of the χ_{Fe} *versus* T curve above 40 K for [Fe(tsalen)] is reminiscent of antiferromagnetic coupling occurring between Fe^{II} atoms within some kind of polymeric structure. The data were fitted to both binuclear $S = 1$ [equation (ii)] and Heisenberg linear-chain [equation (iii)] models using a least-squares fitting program. The best fits

$$\chi_{Fe} = \frac{N\beta^2 g^2}{3kT}\,\frac{[15 + 3\exp(-4J/kT)]}{[5 + 3\exp(-4J/kT) + \exp(-6J/kT)]} \qquad \text{(ii)}$$

$$\chi_{Fe} = \frac{2N\beta^2 g^2}{3kT}\,\frac{[1 + \coth(-4J/kT) - (-J/4kT)]}{[1 - \coth(-4J/kT) + (-J/4kT)]} \qquad \text{(iii)}$$

are shown in Figure 5, that for the linear chain giving better overall agreement. The appropriate parameters are: $S = 1$ dimer, $g = 1.39 \pm 0.02$, $J = -21.8 \pm 0.2$ cm^{-1}; $S = 1$ linear chain, $g = 1.49 \pm 0.02$, $J = -19.0 \pm 0.2$ cm^{-1}. The low g values must be, in part, a natural consequence of using these models to explain the low $\mu_{eff.}$ values observed. There are

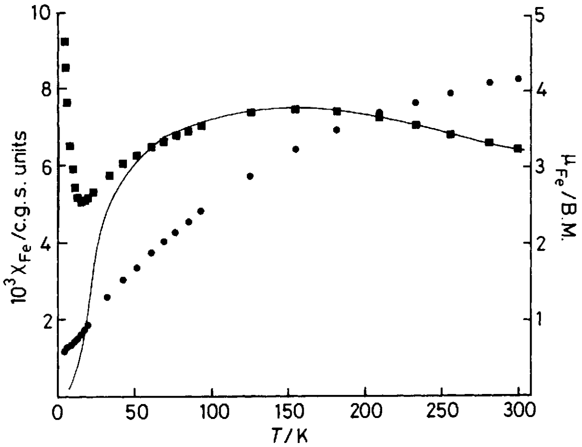


Figure 6. The magnetic behaviour of [Fe(tsalpd)]; (■) χ_{Fe} experimental; (●) μ_{Fe} experimental; (——) calculated from a $-2JS_1S_2$ analysis with $g = 2.21$ and $J = -23.8$ cm^{-1}

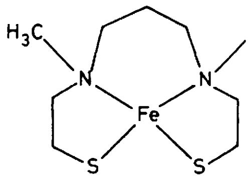
few examples of $S = 1$ $\mathrm{Fe^{II}}$ systems and they are, as indicated above, generally restricted to monomeric square planar $\mathrm{Fe^{II}}$ macrocycles such as the $\mathrm{Fe^{II}}$ complexes of α,β,γ,δ-tetraphenylporphyrin [16] and phthalocyanin [17] for which spin-Hamiltonian analysis has yielded g values of 2.94 and 2.74, respectively. Clearly the magnetic properties of [Fe(tsalen)] are quite different to those of the other square planar species and do not appear to have any counterpart amongst $\mathrm{Fe^{II}}$ chelate complexes so far reported.

An *X*-ray crystallographic study of [Fe(tsalen)] has not yet been carried out, but by analogy with [Co(tsalen)] [18] it is thought most likely that intermolecular bridging *via* sulphur–iron bonds will be involved. Tetragonally distorted six-co-ordinate geometry around Fe is probable in view of the similarity of the quadrupole splitting to that of six-co-ordinate adducts of [Fe(salen)].[5] The tsalen ligand has been shown capable of square planar co-ordination to $\mathrm{Fe^{II}}$ in the low-spin carbonyl adduct [Fe(py)(tsalen)(CO)] (py = pyridine).[1,19]

The general behaviour of [Fe(tsalpd)] in many ways parallels that of [Fe(tsalen)], although there are some pertinent differences. The Mössbauer spectrum at 4.2 K (Figure 5) shows a sharp quadrupole doublet with parameters different to those of [Fe(tsalen)] and compatible with the presence of high-spin $S = 2$, $\mathrm{Fe^{II}}$. In an applied field of 25 kOe the lines broaden and show only partial splitting, which, as in the case of [Fe(tsalen)], indicates a positive V_{zz} and $S' = 0$ ground state. This difference in Mössbauer spectral behaviour between [Fe(tsalen)] and [Fe(tsalpd)] contrasts with the report [4] of similar Mössbauer parameters being found for [Fe(salen)] and [Fe(salpn)].

The magnetic moment is 4.11 B.M. at room temperature and decreases gradually to 0.59 B.M. at 4.2 K (Figure 6). The corresponding χ_{Fe} *versus* T curve (Figure 6) shows a broad maximum in the susceptibility with a sharp rise at very low temperatures, the latter being most likely due to monomeric impurity as in the case of [Fe(tsalen)] and other reported polynuclear $\mathrm{Fe^{II}}$ systems.[12] The χ_{Fe} data in the range 40—300 K gave good agreement with the simple Heisenberg equation for $S_1 = S_2 = 2$ dimers using the parameters $g = 2.21$, $J = -23.8$ cm^{-1}, and temperature-independent paramagnetism $N\alpha = 0$ c.g.s. units.

The magnetic data for [Fe(tsalpd)] are similar in most details to those reported by Lippard and co-workers [20,21] for the $\mathrm{Fe^{II}}$ complex (4), which exists in the solid state as a dimer with Fe–S bridges. The tetradentate ligand involved contains a trimethylene bridge as does tsalpd.



(4)

The data for compound (4) when fitted to a simple Heisenberg model yielded similar parameters to those for [Fe(tsalpd)], *viz.* $g = 2.15$, $J = -26$ cm^{-1}, $N\alpha = 775 \times 10^{-6}$ c.g.s. units, although the fit was not as good as in the present case. The quadrupole splitting of (4), 3.45 mm s^{-1}, is very similar to that found for [Fe(tsalpd)]. In view of the similarity of the magnetic properties and Mössbauer parameters, it seems possible that [Fe(tsalpd)] may have a distorted trigonal bipyramidal dimeric structure of the same type as that shown by *X*-ray crystallography for compound (4). It can be concluded that the detailed co-ordination environment around Fe in [Fe(tsalen)] will be different to that in [Fe(tsalpd)] on the basis of the lower observed quadrupole splitting in [Fe(tsalen)] as well as the differences in magnetic properties between the two compounds. The more flexible tsalpd ligand presumably allows these structural differences to occur.

Magnetic and Mössbauer studies have been reported [4,5,22] for the salicylideneimine complex [Fe(salen)] and related species although no crystal structures have been described. The results have been interpreted in terms of high-spin $\mathrm{Fe^{II}}$ centres situated within a polymeric structure in which the iron atoms are probably six-co-ordinate. The spin state of [Fe(salen)] is therefore different to that of [Fe(tsalen)]. A recent variable-temperature susceptibility study of [Fe(salen)] has shown the presence of ferromagnetic coupling between iron(II) centres; [23] further details of this rather unexpected mode of coupling will be reported separately.

[Fe(mptsaln)$_2$].—This complex is a representative example of the bidentate complexes previously reported.[1] The magnetic moment of the *p*-methoxyphenyl derivative is typical of the values expected for high-spin $\mathrm{Fe^{II}}$ complexes. It remains constant at *ca.* 5.01 B.M. between 300 and 50 K and then decreases rapidly to 4.1 B.M. at 4.3 K (Figure 7). Such behaviour is that expected for an orbitally non-degenerate quintet state in which zero-field splitting is apparent at low temperatures. This kind of ground state could arise from either distorted tetrahedral or distorted octahedral ligand fields. While the former geometry might be expected from the stoicheiometry of the compound, the latter is supported by the Mössbauer spectral results which are more comparable with a pseudo-octahedral geometry, possibly arising through the association of molecules of the complex in the solid state. The quadrupole splitting parameter, ΔE, is 2.23 mm s^{-1}, similar to that observed for both [Fe(tsal)$_2$] and [Fe(tsalen)], neither of which would seem to possess tetrahedral geometry. There is no appreciable exchange coupling in [Fe(mptsaln)$_2$] since it would be evident in both the low temperature magnetic susceptibilities and in the 4.2 K applied-field Mössbauer spectrum. The latter, shown in Figure 8, confirms that the complex has a paramagnetic ground state with an effective magnetic field of 100 kOe at the Mössbauer nucleus. The lower-energy 'doublet' and higher-energy triplet in the applied-field spectrum of [Fe(mptsaln)$_2$] demonstrate that the principal component of the electric field gradient tensor, V_{zz}, is negative. It is possible, in principle, to deduce the nature of any distortions and bonding effects about the high-spin $\mathrm{Fe^{II}}$ ion from the sign of V_{zz}.[24] From a simple crystal

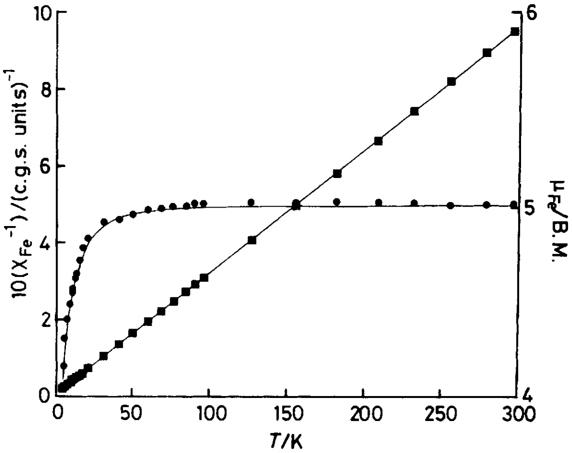


Figure 7. The magnetic behaviour of [Fe(mptsaln)$_2$]: (■) χ_{Fe}^{-1} experimental; (●) μ_{Fe} experimental; (——) calculated from equation (iv) with $g = 2.04$ and $D = -9.0$ cm^{-1}

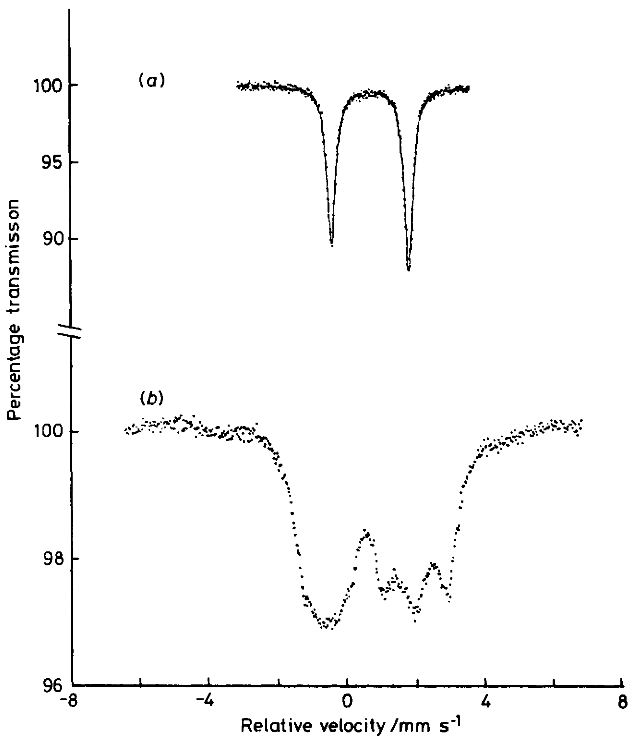


Figure 8. Zero-field (a) and applied field (b) Mössbauer spectra of [Fe(mptsaln)$_2$] at 4.2 K

field point of view the order of the one-electron d orbitals, assuming a tetragonally distorted octahedral geometry, is $d_{xz,yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$ with the sixth electron occupying one of lowest-bonding d_{xz} or d_{yz} orbitals. Such an order is compatible with a negative V_{zz} and with an orbital singlet ground state which is in agreement with the magnetic results (see below).

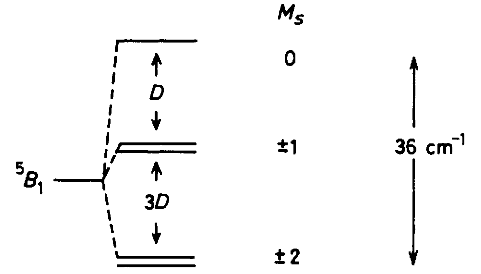
It is interesting to note that V_{zz} is positive in a number of other distorted five- or six-co-ordinate Fe^{II} sulphur-containing chelates.[11,20] Unfortunately, the sign of V_{zz} is not known for the bis(salicylideneimine) Fe^{II} analogue of the present compound which precludes any comparative correlations of Fe–ligand bonding effects.

The magnitude of the zero-field splitting of the ground state was obtained from analysis of the magnetic susceptibility data. Susceptibility values were calculated following computer diagonalization of the matrices obtained *via* the axial spin Hamiltonian in equation (iv). After allowing the size and sign

$$\mathcal{H} = D\,[S_z^2 - S(S+1)/3] + g\beta HS \qquad \text{(iv)}$$

of D to vary it was found that the best fit of the data was obtained for a negative value of D, with $g = 2.04 \pm 0.01$ and $D = -9.0 \pm 0.5$ cm^{-1}.

There was noticeably better agreement in the region 4.2 to 50 K when a negative D was employed, although single-crystal magnetic measurements would be required to confirm this sign and to estimate any rhombic ligand field components (which have been ignored). The calculated best fit is shown in Figure 7. A negative value of D means that the spin-orbit splitting of the ground $S = 2$ state is as shown below.



Zero-field splittings of this magnitude have been observed in various distorted high-spin Fe^{II} complexes, although D was deduced to be positive in most cases.[25,26]

Analogous bis-bidentate salicylideneimine chelates of Fe^{II} have been studied by means of susceptibility and Mössbauer measurements.[4,5,22] The compounds are high spin with temperature-independent μ_{Fe} values in the limited range 300—80 K and have Mössbauer parameters similar to those observed for the present bidentate complex. These Fe^{II} complexes were considered to be associated [4,22] in the solid state, having the Fe^{II} centres in distorted octahedral environments. The S_2N_2 bidentate compounds are, therefore, similar in their structural and electronic properties, which contrasts with the situation found in the tetradentate systems described above.

Acknowledgements

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