Iron Complexes of *N*-Substituted Thiosalicylideneimines. Part 3.[1] Structure, Magnetism, and Mössbauer Spectra of the Complex Chloro[*N,N'*-ethylenebis(thiosalicylideneiminato)]iron(III), an Intermediate-spin Complex which exists in three Crystalline Forms †

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Chloro[*N,N'*-ethylenebis(thiosalicylideneiminato)]iron(III), [Fe(tsalen)Cl], has been prepared by reaction of [Tl_2(tsalen)] with anhydrous $FeCl_3$. A crystal-structure determination has revealed the existence of three modifications of the complex. The α form predominates (96%) and contains equal numbers of weakly interacting Fe–S bridged dimer units (type 1 molecules) and monomers (type 2 molecules) with the Fe having a square-based pyramidal distribution of bonds. The β form consists of monomer species alone, while the γ form has weakly interacting dimer units. A variable-temperature magnetic study and Mössbauer spectral measurements on a bulk sample of the complex indicate that the Fe atoms have the intermediate $S = \frac{3}{2}$ spin state.

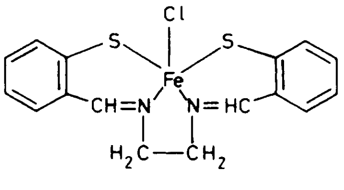
A variety of complexes of Fe^{II} and Fe^{III} with various *N*-substituted thiosalicylideneimines has been prepared [1,2] enabling comparisons to be made of various chemical and physical properties of these compounds with those of the analogous iron complexes of the oxygen-containing ligands, the salicylideneimines. The outstanding influence of sulphur is that it can modify the electronic configurations of the metal in most d^6 or d^5 iron compounds other than those containing bidentate ligands of this type.

This paper reports the synthesis of chloro[*N,N'*-ethylenebis(thiosalicylideneiminato)]iron(III), [Fe(tsalen)Cl] (1), by the reaction between [Tl_2(tsalen)] and $FeCl_3$, the determination of its molecular and crystal structure, and examination of its magnetic behaviour and Mössbauer spectrum. This enables a detailed comparison to be made with [Fe(salen)Cl], the oxygen analogue. The latter complex, first reported by Pfeiffer and Tsumaki [3] in 1933, has become a model for many of the recent studies on magnetic exchange phenomena in polynuclear, high-spin d^5 iron(III) systems [4] and hence a knowledge of the behaviour of the sulphur analogue is of considerable interest.

Experimental

Synthesis.—Thiosalicylaldehyde was prepared and purified as described,[2] with diethyl ether being used as eluant in the chromatographic purification stage.

(*Thiosalicylaldehydato*)*thallium*(I) [Tl(tsal)]. Thiosalicylaldehyde (1.12 g, 8.1 mmol) in ethanol (50 cm^3) was added to a warm solution of thallium(I) acetate (2.14 g, 8.1 mmol) in ethanol (50 cm^3). The mixture was stirred at room temperature for 30 min. The orange-red crystalline precipitate was filtered off, washed with ethanol, and dried *in vacuo* to yield the title complex (2.31 g, 83%), m.p. 152—153 °C (Found: C, 24.9; H, 1.75; S, 9.70. Calc. for C_7H_5OSTl: C, 24.6; H, 1.50; S, 9.40%). I.r. spectrum (Nujol, strong and medium bands only): 1 663m, 1 635s, 1 573m, 1 446m, 1 432m, 1 281m, 1 260m, 1 190m, 1 109m, 1 040m, 831m, 740s, and 710m cm^{-1}.



(1)

Mass spectrum: m/e = 342 (10) (M^+), 205 (30), 203 (13), 138 (74), 137 (100) ($tsal^+$), 109 (72), 104 (74), 77 (37), 65 (33), and 32 (33%).

[N,N'-*Ethylenebis*(*thiosalicylideneiminato*)*dithallium*(I), [Tl_2(tsalen)]. The complex [Tl(tsal)] (1 g, 2.9 mmol) was dissolved in boiling 2-methoxyethanol (100 cm^3) and the solution rapidly filtered. Ethylenediamine (0.09 g, 1.5 mmol) dissolved in 2-methoxyethanol (10 cm^3) was immediately added and the hot solution stirred rapidly until it had cooled to room temperature. The yellow microcrystalline solid which formed was filtered off, washed with ethanol, and dried *in vacuo* (yield 0.86 g, 83%) (Found: C, 27.4; H, 2.20; N, 3.80. Calc. for $C_{16}H_{14}N_2S_2Tl_2$: C, 27.2; H, 2.00; N, 3.95%). I.r. spectrum (Nujol): 1 635s, 1 579s, 1 425s, 1 364m, 1 278m, 1 123m, 1 112m, 1 057s, 1 031m, 753s, and 700m cm^{-1}. Mass spectrum: m/e = 298 (22), 205 (89), 203 (37), 136 (93), 135 (100), 109 (28), 104 (19), 77 (41), and 32 (74%); M^+ = (m/e 502) not detected.

Chloro[N,N'-*ethylenebis*(*thiosalicylideneiminato*)]*iron*(III), [Fe(tsalen)Cl]. The synthesis was carried out under a dry nitrogen atmosphere using degassed solvents. A mixture of anhydrous iron(III) chloride (54 mg, 0.33 mmol) and [Tl_2(tsalen)] (25 mg, 0.33 mmol) in dimethylformamide (20 cm^3) was stirred at 80—90 °C for 90 min and the solution filtered. The volume of solvent was reduced to *ca.* 10 cm^3 under vacuum, ethanol (40—50 cm^3) was added dropwise to the red-brown solution cooled in ice, and the resulting mixture allowed to stand for 24 h. The red-brown crystalline compound formed was filtered off, washed with ethanol, and dried *in vacuo* (yield 18 mg, 14%). Higher yields of the complex (up to 60%) could be obtained if diethyl ether was used instead of ethanol as precipitant but the crystallinity of the sample was greatly decreased (Found: C, 49.2; H, 3.90; Cl, 9.10; N, 7.10. Calc. for $C_{16}H_{14}ClFeN_2S_2$: C, 49.3; H, 3.6; Cl, 9.10; N, 7.20%).

The dimethylformamide used in the preparation was dried carefully before use by treatment with molecular sieves (BDH

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† *Supplementary data available* (No. SUP 56042, 6 pp.): thermal parameters of the α form, atomic co-ordinates, thermal parameters, and equations of mean planes for β and γ forms. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. units employed: B.M. ≈ 9.27 × 10^{-24} A m^2, Oe = 1 000/4π A m^{-1}, G = 10^{-4} T.

Table 1. Final atomic parameters for [Fe(tsalen)Cl] with their estimated standard deviations in parentheses

	α Form, type 1 molecules			α Form, type 2 molecules		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Fe	0.462 8(1)	0.341 8(3)	0.421 4(1)	0.085 5(2)	0.294 5(3)	0.553 8(2)
Cl	0.457 8(3)	0.159 1(6)	0.339 7(3)	0.149 8(3)	0.105 8(5)	0.516 8(3)
S(1)	0.577 6(3)	0.404 9(5)	0.433 7(3)	0.082 2(3)	0.419 7(6)	0.451 3(3)
S(2)	0.458 1(3)	0.512 1(5)	0.344 4(3)	0.167 8(3)	0.441 5(6)	0.591 4(3)
N(1)	0.467 5(9)	0.228 1(16)	0.512 3(9)	−0.015 7(8)	0.221 8(6)	0.533 1(9)
N(2)	0.354 1(9)	0.347 9(17)	0.443 7(17)	0.065 6(8)	0.234 4(16)	0.659 4(9)
C(1)	0.626 3(10)	0.304 5(18)	0.495 3(10)	0.0185 (11)	0.326 6(21)	0.387 6(11)
C(2)	0.702 9(10)	0.323 6(19)	0.497 2(10)	0.018 7(11)	0.415 8(22)	0.315 3(11)
C(3)	0.746 7(12)	0.250 9(20)	0.546 4(11)	−0.028 6(11)	0.377 8(20)	0.260 8(12)
C(4)	0.718 0(12)	0.160 4(23)	0.595 1(11)	−0.081 6(12)	0.277 7(23)	0.270 8(12)
C(5)	0.645 0(10)	0.139 9(19)	0.594 7(10)	−0.0851 (12)	0.224 3(23)	0.342 6(12)
C(6)	0.599 2(10)	0.211 7(19)	0.545 6(10)	−0.035 9(11)	0.267 3(20)	0.399 2(11)
C(7)	0.521 7(11)	0.181 6(24)	0.550 0(11)	−0.052 8(10)	0.208 1(19)	0.472 0(10)
C(8)	0.369 6(11)	0.530 8(20)	0.307 4(11)	0.187 2(10)	0.435 8(20)	0.690 1(10)
C(9)	0.363 4(12)	0.610 0(20)	0.242 8(11)	0.242 6(12)	0.522 0(22)	0.714 4(13)
C(10)	0.295 8(13)	0.638 8(24)	0.207 1(13)	0.258 1(12)	0.531 7(22)	0.789 0(13)
C(11)	0.235 5(14)	0.592 4(23)	0.241 8(13)	0.222 9(12)	0.450 5(21)	0.842 6(12)
C(12)	0.236 8(13)	0.515 0(22)	0.304 2(13)	0.169 0(11)	0.365 2(20)	0.816 5(11)
C(13)	0.306 8(11)	0.482 4(19)	0.339 7(10)	0.151 7(10)	0.353 6(20)	0.741 1(11)
C(14)	0.302 5(10)	0.402 9(18)	0.405 4(10)	0.093 5(10)	0.262 9(19)	0.723 7(11)
C(15)	0.341 7(12)	0.273 4(22)	0.514 0(12)	0.008 9(12)	0.126 0(22)	0.654 1(12)
C(16)	0.394 0(12)	0.171 3(24)	0.527 6(13)	−0.047 2(12)	0.172 9(23)	0.606 0(11)

grade 3A) and the dry ethanol or ether precipitants were also freshly distilled from appropriate agents immediately before use (Mg, EtOH; Na, diethyl ether).

Magnetic susceptibility data and Mössbauer spectra were recorded as previously described.[1] Detailed values of χ_{Fe} *vs.* T are available on request from the authors.

Structural Determinations.—Crystalline samples prepared as described above were found to contain three distinct crystalline forms.

Crystal data. $C_{16}H_{14}ClFeN_2S_2$, α form, $M = 389.7$, monoclinic, $a = 18.249(12)$, $b = 9.994(6)$, $c = 17.823(11)$ Å, $\beta = 91.04(8)°$, $U = 3\,250.0$ Å^3 (by least-squares refinement of diffractometer angles for 24 automatically centred reflections, $\lambda = 0.7107$ Å), space group $P2_1/n$ (alternative $P2_1/c$, no. 14), $D_m = 1.59(3)$, $Z = 8$, $D_c = 1.59$ g cm^{-3}, $F(000) = 1\,591.8$. Dark red tabular crystals, dimensions (distance to faces from centre) 0.05 (111,$\bar{1}\bar{1}\bar{1}$) × 0.05 (1$\bar{1}$1,$\bar{1}$1$\bar{1}$) × 0.038 (101,101) mm; μ(Mo-K_α) = 12.8 cm^{-1}.

β form, monoclinic, $a = 14.847(10)$, $b = 7.650(5)$, $c = 14.169(10)$ Å, $\beta = 96.17(9)°$, $U = 1\,600.0$ Å^3, space group $P2_1/n$, $D_m = 1.63(3)$, $Z = 4$, $D_c = 1.62$ g cm^{-3}, $F(000) = 795.9$. Dark red acicular crystals, dimensions (distances to faces from centre) 0.069 (010,0$\bar{1}$0) × 0.031 ($\bar{1}$01,10$\bar{1}$) × 0.019 (101,$\bar{1}$0$\bar{1}$) mm; μ(Mo-K_α) = 12.8 cm^{-1}.

γ form, orthorhombic, $a = 13.764(10)$, $b = 17.788(12)$, $c = 13.087(9)$ Å, $U = 3\,204.1$ Å^3, space group $Pbca$, $D_m = 1.61(3)$, $Z = 8$, $D_c = 1.62$ g cm^{-3} $F(000) = 1\,591.8$. Dark red plates, dimensions (distances to faces from centre) 0.006 (010,0$\bar{1}$0) × 0.044 (201,$\bar{2}$0$\bar{1}$) × 0.094 (212,$\bar{2}\bar{1}\bar{2}$) mm; μ(Mo-K_α) = 12.8 cm^{-1}.

Data collection and processing.[5] Data-collection parameters were common to all three sets of data except where specified: Philips PW1100 diffractometer, ω scan mode with ω scan width = 1.4 + 0.2 tan θ (α form) and 1.2 + 0.2 tan θ (β and γ forms), ω scan speed 0.03° s^{-1}, graphite-monochromated Mo-K_α radiation; reflections measured ($3 \leqslant \theta \leqslant 25°$), 5 706 (α form, $hk \pm l$), 2 806 (β form, $hk \pm l$), 2 812 (γ form, hkl), absorption correction [maximum, minimum transmission factors = 0.96, 0.88 (α form), 0.96, 0.92 (β form), 0.98, 0.93 (γ form)] giving 1 464, 736, and 367 with $I \geqslant 3\sigma(I)$ for the α, β, and γ forms respectively.

Structure analysis and refinement. Direct methods (Fe and Cl) for the α form and normal heavy-atom procedures for the β and γ forms. Full-matrix least-squares refinement, with Fe, Cl, and S anisotropic and hydrogens in calculated positions with one, overall, refined U[= 0.103 (α form), 0.069 (β form), and 0.093 Å^2 (γ form)]. Final R and R' [= $(\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] values were 0.071, 0.061; 0.061, 0.051; 0.067, 0.060 with $w = 1/\sigma^2(F)$ for the α, β, and γ forms respectively.

The major program used was that due to Sheldrick[6] on a DEC-VAX 11/780 computer. Scattering factor data were taken from ref. 7. Atomic parameters for all non-hydrogen atoms of the α form are given in Table 1, together with their estimated standard deviations.

Results

Synthesis.—Earlier attempts to synthesize [Fe(tsalen)Cl] by direct reaction of anhydrous $FeCl_3$ with a mixture of thiosalicylaldehyde and ethylenediamine in the presence of a Lewis base or *via* a (presumed) intermediate, $Fe(tsal)_2Cl$ with diamine, led to the formation of bis[*N*-(2-aminoethyl)-thiosalicylideneiminato]iron(III) chloride $[Fe(Haetsaln)_2]Cl$.[2]

A successful route to the desired complex has been devised which involves reaction of the thallium complex $[Tl_2(tsalen)]$ with anhydrous $FeCl_3$ in dry dimethylformamide. The thallium complex in turn can be readily prepared by the reaction of [Tl(tsal)] with ethylenediamine. Thallium complexes of salicylideneimines[8] have proved useful intermediates in the synthesis of a variety of complexes, particularly of the second and third transition series[9] and thiosalicylideneimine–thallium compounds are likely to be of similar use in view of the complications already observed in the direct synthesis of metal complexes from the free ligands.

The iron compound is poorly soluble in non-polar organic solvents such as benzene but is very soluble in donor solvents such as dimethylformamide and pyridine. It is quite sensitive to traces of water in solution and considerable care was

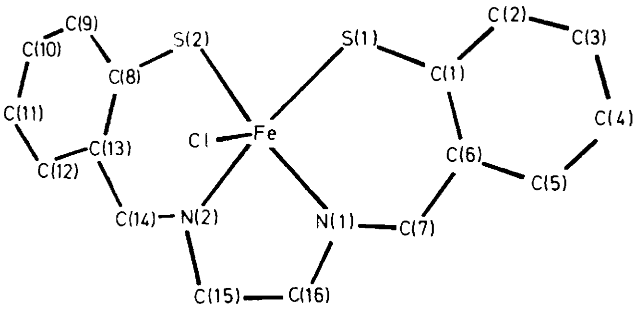

Figure 1. The numbering scheme for each of the [Fe(tsalen)Cl] molecules

Table 2. Equations of mean planes and deviations (Å) of individual atoms therefrom (in square brackets) for the α form. *X*, *Y*, *Z* are orthogonal co-ordinates related to the fractional co-ordinates *x*, *y*, *z* in the crystal system by the equation:

$$\begin{pmatrix} 18.2490 & 0.0000 & -0.3235 \\ 0.0000 & 9.9940 & 0.0000 \\ 0.0000 & 0.0000 & 17.8201 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \begin{matrix} = \\ = \\ = \end{matrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

(*a*) Type 1 molecules

Plane: S(1), S(2), N(1), N(2)

$0.0724X - 0.7232Y - 0.6868Z + 7.3999 = 0$

[S(1) −0.082(5), S(2) 0.080(5), N(1) 0.088(16), N(2) −0.087(16), Fe 0.374(3), Cl 2.690(6)]

(*b*) Type 2 molecules

Plane: S(1), S(2), N(1), N(2)

$-0.5896X - 0.7448Y - 0.3125Z + 4.8633 = 0$

[S(1) 0.024(6), S(2) −0.024(6), N(1) −0.027(16), N(2) 0.027(16), Fe 0.402(3), Cl 2.711(5)]

necessary to prevent decomposition when handling solutions which were required to be kept for periods of several hours.

Crystal and Molecular Structure.—The bulk sample of [Fe(tsalen)Cl] used for crystallographic analysis was found to contain three distinct crystalline forms termed hereafter the α, β, and γ forms. The α form represented the bulk of the sample, *ca*. 96%, while each of the other forms made up 2% of the sample. The numbering scheme for the atoms in each molecule of the complex is shown in Figure 1.

α *Form*. The α form was found to contain two independent molecules in the asymmetric unit which are termed 'type 1' and 'type 2' molecules. Both these molecules have an approximate square-pyramidal stereochemistry with the Fe atoms out of the mean planes through the donor N and S atoms by 0.374 Å in ' molecule 1 ' and 0.402 Å in ' molecule 2.' The deviations of the S and N atoms from the mean plane are quite small for both types of molecule but are larger for molecules of type 1 (Table 2). This may be contrasted with the structure of the monomeric form of [Fe(salen)Cl] [10] where the Fe atom was reported to be *ca*. 0.46 Å above the mean plane of the O_2N_2 group. The two thiosalicylideneimine chelate rings are virtually coplanar with the S_2N_2 plane for molecules of type 1. The ethylene bridge in this type is in the *gauche* position [Figure 2(*a*)] with a torsion angle of 45(2)° (Table 3).

Type 2 molecules, however, have a stepped configuration [Figure 3(*a*)] as found for many salicylideneimine complexes,[11,12] with the angles of the ligand planes to the S_2N_2 plane being small, 4.5 and 12.4°. The ethylene bridge in these molecules has a torsion angle of 52(2)° (Table 3). Intramolecular bond lengths for both molecules are similar to those found for other sulphur-containing Schiff-base iron complexes.[1,13,14]

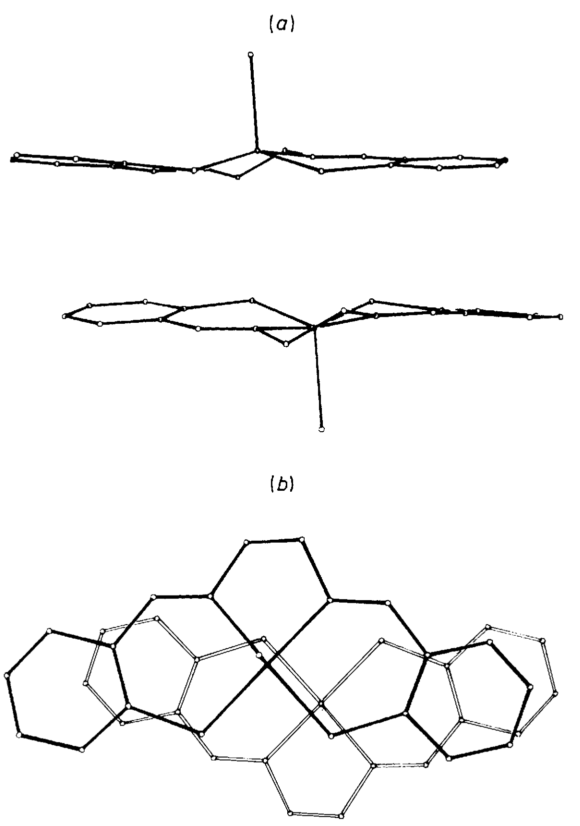

Figure 2. Pairs of type 1 molecules of the α form of [Fe(tsalen)Cl] viewed from the side (*a*) and top (*b*)

The type 1 molecules occur in the crystal in centrosymmetrically related pairs of molecules with intermolecular contacts of 3.700(6) Å between the Fe atom of the lower molecule in the pair and the S(1′) atom lying immediately above it in the second molecule [Figure 2(*b*)]. This contrasts with the complex [Co(tsalen)],[15] in which intermolecular Co–S distances of 2.445 Å indicate a considerable degree of bonding and justify the dimeric formulation [{Co(tsalen)}$_2$].

The distance observed between Fe and S in neighbouring molecules in the type 1 species, therefore, indicates weak interaction. The corresponding distance Fe–S(1′) between type 2 molecules is 4.186(6) Å and there is a considerable lateral shift between nearest-neighbour pairs of molecules [Figure 3(*b*)] so that any Fe–S′ interaction must be slight or negligible. Indeed, the shortest intermolecular contact between Fe and other atoms in neighbouring molecules of type 2 is between Fe and Cl(1′) at 4.06(2) Å.

The Fe–Fe′ distances between ' near ' neighbours are 4.423(6) Å in type 1 molecules and 5.483(6) Å in type 2.

The [{Fe(salen)Cl}$_2$] dimer species [16] has Fe–O(1′) contacts at 2.178(7) Å and represents a classical case of intermolecular bonding utilizing a donor atom O, primarily bound to one metal but still capable of bonding to a second. In these dimer units the Fe atoms are close to being octahedrally co-ordinated and are almost in the planes of the O_2N_2 donor groups. The binding between molecules in the dimeric form of [Fe(salen)Cl], however, is recognised as relatively weak and recrystallization of this form from nitromethane results in the ' monomer '

Table 3. Selected interatomic distances (Å), bond angles and torsion angles (°) in the three crystalline modifications of [Fe(tsalen)Cl]

(*a*) Interatomic distances

	α Form			
	type 1 molecule	type 2 molecule	β Form	γ Form
Fe–Cl	2.336(5)	2.323(6)	2.305(5)	2.295(11)
Fe–S(1)	2.196(6)	2.214(6)	2.204(5)	2.201(14)
Fe–S(2)	2.187(6)	2.197(6)	2.211(5)	2.216(13)
Fe–N(1)	1.98(2)	2.01(2)	2.01(1)	1.98(3)
Fe–N(2)	2.03(2)	2.02(2)	2.03(1)	1.95(4)
S(1)–C(1)	1.72(2)	1.71(2)	1.74(2)	1.77(4)
S(2)–C(8)	1.74(2)	1.79(2)	1.77(2)	1.76(4)
N(1)–C(7)	1.27(2)	1.28(2)	1.30(2)	1.30(4)
N(1)–C(6)	1.49(2)	1.51(2)	1.50(2)	1.50(4)
N(2)–C(14)	1.28(2)	1.28(2)	1.28(2)	1.33(5)
N(2)–C(15)	1.48(2)	1.50(2)	1.46(2)	1.47(4)
C(1)–C(2)	1.41(2)	1.39(2)	1.41(2)	1.38(4)
C(2)–C(3)	1.38(2)	1.34(2)	1.40(2)	1.42(5)
C(3)–C(4)	1.36(2)	1.41(2)	1.37(2)	1.35(5)
C(4)–C(5)	1.35(2)	1.39(2)	1.34(2)	1.32(5)
C(5)–C(6)	1.40(2)	1.41(2)	1.38(2)	1.41(5)
C(6)–C(1)	1.39(2)	1.39(2)	1.43(2)	1.43(4)
C(6)–C(7)	1.45(2)	1.46(2)	1.40(2)	1.39(5)
C(8)–C(9)	1.40(2)	1.39(3)	1.39(2)	1.50(4)
C(9)–C(10)	1.41(3)	1.36(2)	1.41(2)	1.38(5)
C(10)–C(11)	1.35(3)	1.42(3)	1.38(3)	1.32(5)
C(11)–C(12)	1.36(3)	1.38(2)	1.39(2)	1.45(5)
C(12)–C(13)	1.45(3)	1.38(2)	1.41(2)	1.42(5)
C(13)–C(8)	1.38(2)	1.39(2)	1.40(2)	1.39(4)
C(13)–C(14)	1.42(2)	1.43(2)	1.42(2)	1.46(4)
C(15)–C(16)	1.41(3)	1.40(3)	1.51(2)	1.29(5)
(*b*) Bond angles				
S(1)–Fe–S(2)	82.3(2)	83.2(2)	82.6(2)	82.0(5)
S(1)–Fe–N(1)	93.3(5)	92.4(5)	93.3(4)	92.8(10)
S(2)–Fe–N(2)	94.1(5)	92.7(5)	91.2(4)	93.9(10)
N(1)–Fe–N(2)	83.4(6)	83.3(6)	82.8(5)	83.0(13)
S(1)–Fe–Cl	108.2(2)	103.4(2)	107.8(2)	104.4(5)
S(2)–Fe–Cl	102.5(2)	106.5(2)	104.2(2)	106.9(5)
N(1)–Fe–Cl	93.6(5)	97.0(5)	97.6(3)	97.8(11)
N(2)–Fe–Cl	96.8(5)	97.1(5)	98.7(4)	95.0(10)
C(1)–S(1)–Fe	112.1(7)	111.6(7)	112.1(6)	113.7(14)
C(8)–S(2)–Fe	110.2(7)	113.6(7)	109.3(5)	109.6(13)
C(7)–N(1)–Fe	131.5(4)	131.6(13)	134.0(11)	129.5(27)
C(14)–N(2)–Fe	128.5(13)	134.1(14)	129.7(10)	134.3(26)
(*c*) Torsion angles for the group N(1), C(16), C(15), N(2). Sign is positive if, when viewed from C(16) to C(15), clockwise rotation of N(1) would superimpose it on N(2)				
	45(2)	52(2)	53(2)	18(7)

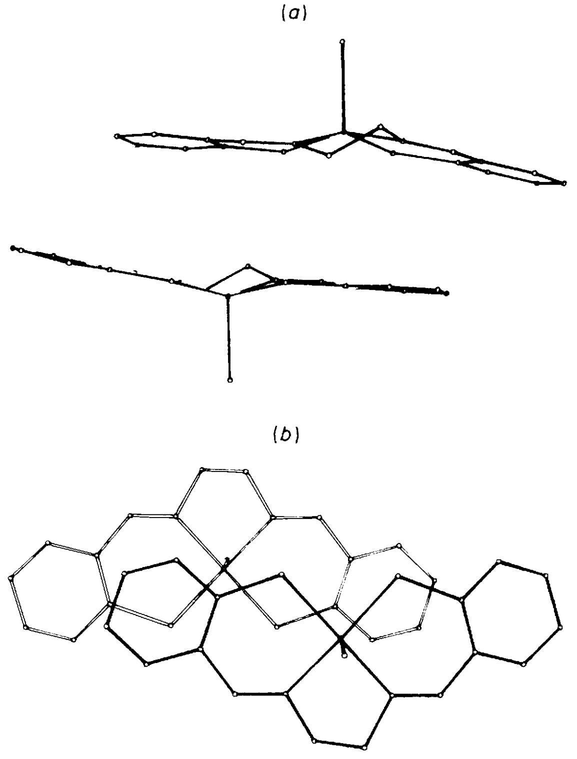

Figure 3. Pairs of type 2 molecules of the α form of [Fe(tsalen)Cl] viewed from the side (*a*) and top (*b*)

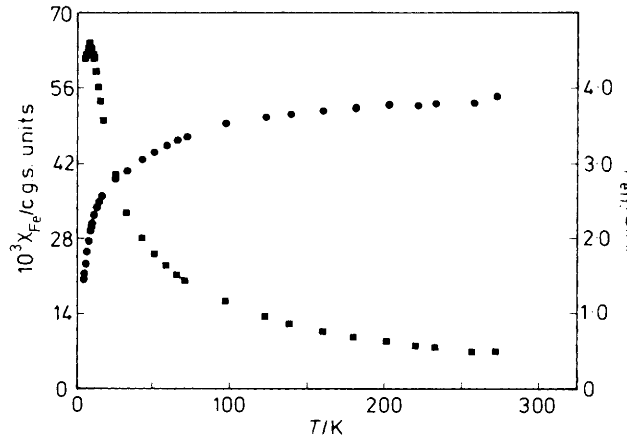

Figure 4. The magnetic behaviour of bulk [Fe(tsalen)Cl]: (■), χ_{Fe} experimental; (●), μ_{Fe} experimental

form of the compound with individual molecules of [Fe(salen)Cl] being separated by CH_3NO_2 molecules.[10] An interaction between pairs of molecules of type 1 of [Fe(tsalen)Cl] is clearly indicated by the intermolecular Fe–S(1′) distances but it must be very weak. The Fe atoms still lie above the S_2N_2 planes, away from the location of the weakly co-ordinating sulphurs.

A further point of difference between the molecular structures of [Fe(tsalen)Cl] and [Fe(salen)Cl] lies in the small amount of ' twist ' associated with the positions of the S_2N_2 atom group around the Fe compared to that shown by the O_2N_2 series. This twist has been ascribed [10] in part as being due to the strain involved in accommodating the short CH_2CH_2 chain and is accompanied by considerable twisting of the two salicylideneimine planes with respect to one another in the monomer. This distortion is partly offset in the dimer by adoption of a stepped configuration for the two chelate rings. Such twisting of the different parts of the chelate molecule is much less apparent in the tsalen compound possibly due to a combination of effects such as the larger size of S compared to O and the decrease in size of Fe^{III} having an $S = \frac{3}{2}$ configuration compared to $S = \frac{5}{2}$ for the [Fe(salen)Cl] compound.

β *and* γ *forms.* The compound [Fe(tsalen)Cl] was found to occur in two further modifications in the bulk sample examined, both in relatively small proportions. The five-co-ordinate square-pyramidal geometry is maintained for both forms of the complex with relatively minor variations determining their difference. Thus, the ligand chelate rings assume a ' stepped ' configuration in the β form with the angles of the ligand planes

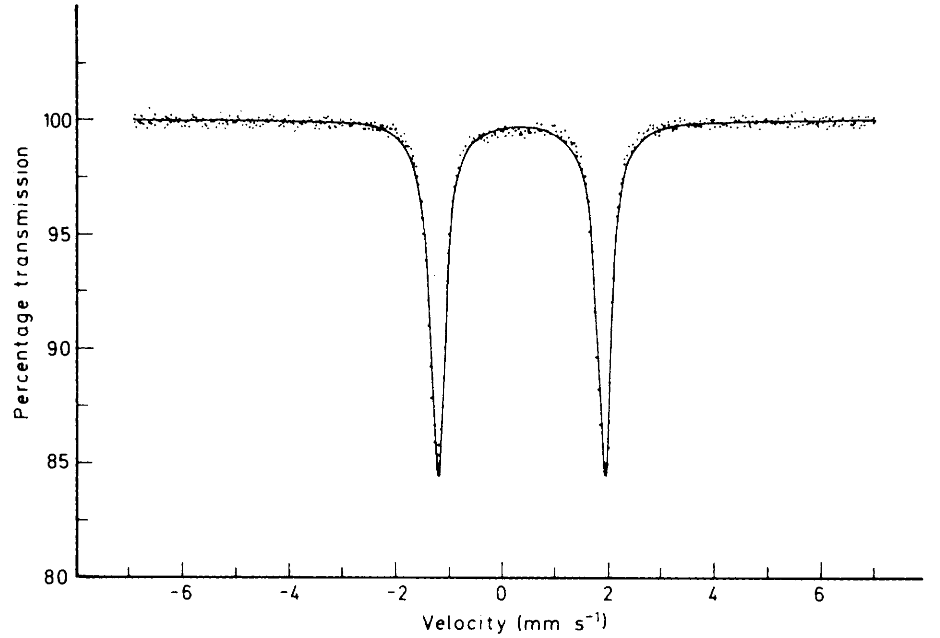

Figure 5. Zero-field Mössbauer spectrum of bulk [Fe(tsalen)Cl] at 4.2 K. The solid line is the fit assuming one doublet and using the parameters given in Table 4

to the S_2N_2 plane being 21.90 and 15.0° and a flat or planar arrangement in the γ form.

The Fe atoms in neighbouring pairs of molecules of the β form are packed ' base-to-base ' and lie above one another at a distance of 4.862(5) Å, too far apart to result in any interaction. The shortest intermolecular Fe–S(1′) interaction is at 4.806(5) Å, again too long for significant bonding to occur. The γ form, on the other hand, has a notably shorter Fe–S(2′) distance of 3.801(5) Å as its shortest intermolecular distance, followed by Fe–S(1′) at 4.780(14) Å with Fe–Fe contacts at 4.534(11) Å. The molecules of this form of the complex may be considered to couple, albeit weakly, through the Fe–S(2′) bridges, as in type 1 molecules of the α form.

Thus, overall, in the bulk sample examined, 50% of the Fe atoms will be interacting through the formation of weakly bound dimers and this will be reflected in the magnetic properties of the compound.

Magnetic Susceptibilities and Mössbauer Spectra.—Susceptibility measurements were made on two bulk samples, including the one used for the crystallographic determinations, and the results are similar except for a small movement in the position of the $\chi_{max.}$ at low temperature. For the sample used for the structural studies the μ_{Fe} value at 295 K is 3.90 B.M. which is in the usual range for $S = \frac{3}{2}$ systems. The moment remains almost constant down to 100 K then decreases (slowly, at first, then more rapidly), reaching 1.5 B.M. at 4.2 K (Figure 4). The susceptibility data similarly pass through a sharp maximum at 7 K. Above 7 K the susceptibilities follow Curie–Weiss behaviour with a θ value of *ca.* −26 K. Weak antiferromagnetic coupling is therefore occurring and zero-field splitting of the quartet ground state may also be contributing to the decrease in μ_{Fe} at low temperatures.

The Mössbauer spectrum of [Fe(tsalen)Cl] at 4.2 K is displayed in Figure 5 and shows one sharp symmetrical quadrupole doublet with isomer shift $\delta = 0.38$ mm s^{-1} and quadrupole splitting $\Delta E = 3.13$ mm s^{-1}. These parameters are symptomatic of a single $S = \frac{3}{2}$ Fe site being present at 4.2 K and suggest that if the β and γ iron sites are electronically different to the α sites they are not present in large enough concentrations to be observed by the Mössbauer effect. The magnitudes of δ and Δ*E* for the present compound are similar to those reported [17–21] for other intermediate-spin iron(III) complexes (Table 4).

Table 4. Mössbauer parameters of some five-co-ordinate iron(III) complexes

Complex [a]	$\frac{T}{K}$	$\frac{\delta^{b}}{\text{mm s}^{-1}}$	$\frac{\Delta E}{\text{mm s}^{-1}}$	Spin state	Ref.
[Fe(tsalen)Cl]	4.2	0.38	3.13	$\frac{3}{2}$	This work
[Fe(salen)Cl]	4.2	0.44	1.34	$\frac{5}{2}$	17
[{Fe(tsalen)}$_2$O]·py	4.2	0.43	1.10	$\frac{1}{2}$	14
[Fe(S_2CNEt_2)Cl]	77	0.49	2.70	$\frac{3}{2}$	18
[Fe(pc)Cl]	4.2	0.28	2.94	$\frac{3}{2}$ [c]	19
[Fe(tpp)]ClO_4	4.2	0.38	3.50	$\frac{3}{2}$ [c]	20
[FeL(SPh)]	77	0.13	2.55	$\frac{3}{2}$	21

[a] py = Pyridine, pc = phthalocyaninate(2−), tpp = 5,10,15,20-tetraphenylporphyrinate(2−), and L = the dianion of a 15-membered macrocycle, $C_{23}H_{24}N_4^{2-}$. [b] Relative to metallic iron. [c] Admixed with $S = \frac{5}{2}$ state.

In an applied magnetic field of 25 kOe at 4.2 K the quadrupole doublet of [Fe(tsalen)Cl] shows only a small effective hyperfine field (Figure 6) quite unlike the large hyperfine splitting observed, for instance, for various monomeric $S = \frac{3}{2}$ iron(III) dithiocarbamate paramagnets.[18] This is because of the weak antiferromagnetic ordering below 7 K giving rise to population of a spin-zero ground state in a related manner to that which occurs in the binuclear (high-spin) analogue, [{Fe(salen)Cl}$_2$].[22]

We have tried a number of approaches to fit the χ_{Fe} *vs.* *T* data shown in Figure 4 quantitatively including simple Heisenberg Hamiltonians of type $-2JS_1 \cdot S_2$, appropriate to either an $S = \frac{3}{2}$ dimer or $S = \frac{3}{2}$ linear chain with and without inclusion of a zero-field parameter *D* for the iron(III) ion. None of the approaches reproduced the data with the desired accuracy.

In the light of the crystal-structure determination showing

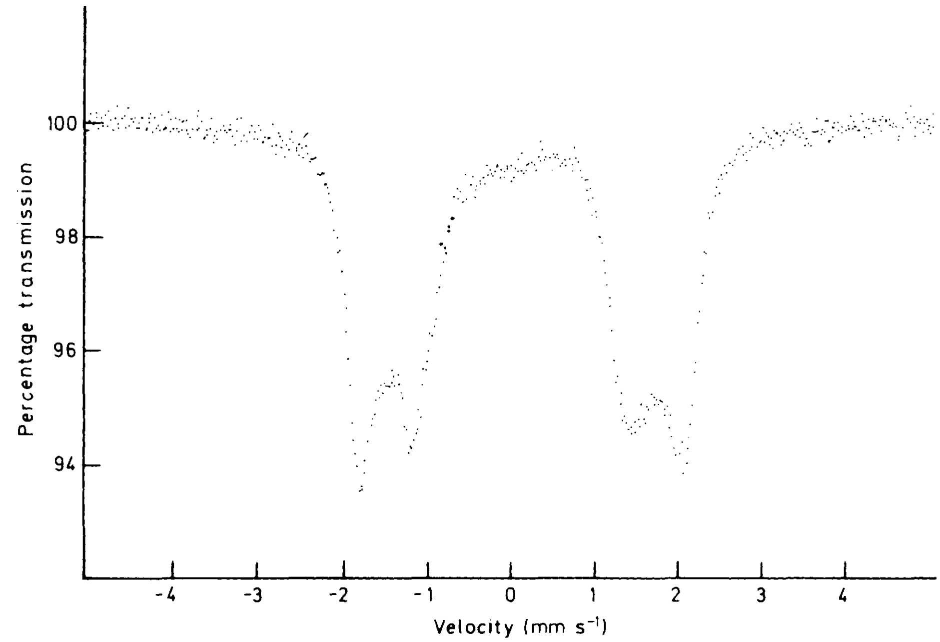

Figure 6. 25-kG Applied-field Mössbauer spectrum of bulk [Fe(tsalen)Cl] at 4.2 K

Table 5. Comparison of bulk magnetic properties of [Fe(tsalen)Cl] and [Fe(salen)Cl]

Property	[Fe(tsalen)Cl]	[{Fe(salen)Cl}$_2$] (Refs. 4, 17, 22)	[Fe(salen)Cl]* (Refs. 10, 17, 24)
μ_{Fe} (295 K)/B.M.	3.90	5.36	5.9
Spin state on Fe	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$
Magnetic coupling	Very weak Antiferromagnetic (α form)	Weak Antiferromagnetic	Nil
Coupling constant, J/cm^{-1}	$\frac{3}{2}$–$\frac{3}{2}$ *ca.* −2	$\frac{5}{2}$–$\frac{5}{2}$ −7.5	0
Isomer shift, δ/mm s^{-1}	0.38	0.27	0.44
Quadrupole splitting at 4.2 K, ΔE/mm s^{-1}	3.13	1.38	1.34

* Nitromethane solvate.

that the bulk of the sample was in the α form, a further model was examined assuming a 50% mixture of monomer and $S = \frac{3}{2}$ dimer but this was inadequate. The data curve in the 50—150 K region proved the most intractable in all models tried. The best fit to date would suggest that two magnetically distinct moieties are contributing to the overall susceptibility, one with very weak antiferromagnetic exchange, the other with a significantly stronger coupling.

Despite the failure to obtain an exact fit of the data, the results clearly show that [Fe(tsalen)Cl] is an $S = \frac{3}{2}$ system and displays very weak exchange coupling. Magnetic and Mössbauer properties are compared in Table 5 with those of the binuclear and mononuclear forms of the salicylideneimine analogue, [Fe(salen)Cl]. In contrast to the present complex, the binuclear form [{Fe(salen)Cl}$_2$] obtained from acetone solutions appears to crystallize in a single phase and its bulk magnetic properties can be fitted exactly to a simple $S = \frac{5}{2}$ dimer model.[4] The superexchange pathway in this molecule occurs *via* the intermolecular Fe–O(phenoxide)–Fe bridging moieties. A variety of behaviour including both antiferromagnetic and weak exchange coupling has been observed, however, in the various solvent-rich phases used to isolate the mononuclear form of [Fe(salen)Cl]. Such species could well contain multiple phases of monomer and dimer molecules. The Mössbauer parameters of a large number of polycrystalline [Fe(salen)Cl] preparations are generally similar and indicative of $S = \frac{5}{2}$ Fe^{III}, with very little noticeable effect on the crystal-field environment of the Fe atom being caused by dimerization.[17,23,24] For the present compound, however, there is a marked increase in the size of the quadrupole splitting compared to that of the salen complex.

Discussion

It is apparent that there is need to exercise caution in relating spectroscopic and magnetic measurements on polycrystalline samples to the structures of individually chosen crystals. In the present study, while recognizing that the α form represents virtually the bulk of the sample, albeit with two structurally distinct molecules, a complete understanding of the electronic structure of the system would require magnetic and Mössbauer measurements on the minor β and γ forms. Unfortunately, we have not been able to prepare or separate sufficient of these to carry out such measurements. Despite this, the results show that [Fe(tsalen)Cl] is another example of the growing list of intermediate-spin iron(III) complexes, most of which have related five-co-ordinate geometries and possess donor sets such as {S$_4$Cl},[18] {N$_4$Cl},[19] {N$_4$S},[21] and {N$_4$O}[20] (*cf.* the present {S$_2$N$_2$Cl}).

The iron–ligand bond lengths in Schiff-base complexes provide a guide to spin state in a similar way to that deduced for iron(III) porphyrins.[25] Thus, Fe–S distances in [Fe(tsalen)Cl] and in [Fe(Haetsaln)$_2$]Cl[13] are identical (2.21 Å), even though the spin states are $\frac{3}{2}$ and $\frac{1}{2}$ respectively. This is because the $d_{x^2-y^2}$ orbital is unoccupied in both cases. The Fe–N distances are likewise similar but shorter than those found in the $S = \frac{5}{2}$ molecule [Fe(salen)Cl] in which the $d_{x^2-y^2}$ orbital is occupied.[7,12] The Fe–Cl distance in [Fe(tsalen)Cl] is slightly longer than that in [Fe(salen)Cl], a phenomenon also noted in intermediate- and high-spin iron(III) porphyrins.[25] The out-of-plane displacements of the Fe atoms in each compound are similar.

The occurrence of weak exchange coupling in the present system is a feature common to high- and intermediate-spin five-co-ordinate iron(III) chelates containing a variety of donor groups and in which exchange pathways are not always clearly defined. Iron–sulphur bridges presumably provide the pathways in the present compound. The intermolecular Fe–S bridging distances in type 1 molecules of form α are considerably longer than the Co–S distance in the well defined dimer [{Co(tsalen)}$_2$][15] and the corresponding Fe–O distance in [{Fe(salen)Cl}$_2$].[16] There is no obvious reason why this should be so apart from the displacement of the Fe atom out of the S$_2$N$_2$ plane towards the chlorine atom and away from the neighbouring Fe(S$_2$N$_2$) moiety. Thiolate groups are known to be capable of using differently orientated orbitals in bridging metal ions compared to analogous oxo-groups,[26] but this was not the case in the [{Co(salen)}$_2$] and [{Co(tsalen)}$_2$] analogues which adopt very similar phenoxide and thiophenoxide bridging geometries.[15]

The change in spin state from high to intermediate in going from [Fe(salen)Cl] to [Fe(tsalen)Cl] is fundamentally related to the change in donor atoms from O to S, which in turn gives rise to an interdependence of equatorial and axial ligand-field effects. The antiferromagnetic coupling observed in [Fe(tsalen)Cl] is weaker than that in [{Fe(salen)Cl}$_2$], even allowing for spin-state differences. This is because of the much longer intermolecular bridging distances found in form α (type 1) and form γ of [Fe(tsalen)Cl].

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