Iron Complexes of *N*-Substituted Thiosalicylideneimines. Part 1. Synthesis and Reactions with Oxygen and Carbon Monoxide †

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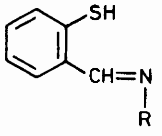
Iron(II) complexes with *N*-substituted bidentate and tetradentate thiosalicylideneimines can be prepared by the reaction of bis(thiosalicylaldehydato)iron(II) with appropriate primary amines. The bidentate compounds show $S = 2$ spin states while a number of the tetradentate compounds have the unusual $S = 1$ state. The tetradentate complexes react with CO to form monocarbonyl complexes and with O_2 to form Fe^{III} μ-oxo-bridged derivatives. Some evidence is presented to support the preliminary formation at low temperatures of a dinuclear iron(III) peroxo-species as the precursor of the μ-oxo-compounds. Several spin-paired Fe^{III} compounds containing SN_2-bonded tridentate ligands are also reported.

Only a small number of Fe^{II} complexes have been characterized involving chelate ligands containing both sulphur and nitrogen donors. These include the Fe^{II} complexes of 2-aminobenzenethiol,[1] several *NN'*-dimethyl-*NN'*-bis(2-mercaptoethyl)alkylenediamines,[2,3] and cysteine.[4] An Fe^{II} complex derived from *NN'*-ethylenebis(thioacetylacetonimine) has been reported [5] but a full characterisation of the complex has not been given subsequently.

As part of a study of the metal complexes of thiosalicylideneimines a series of Fe complexes has been prepared involving bidentate, tridentate, and tetradentate ligand types. Their syntheses, magnetic and Mössbauer spectral properties, together with some reactions towards oxygen and carbon monoxide are reported in this paper. The ligands are the sulphur-containing analogues of the well known salicylideneimines and studies of these compounds provide an excellent means of comparing directly the influence on co-ordination of the substitution of sulphur for oxygen, all other components of the ligand remaining the same.

A preliminary account [6] of some of the properties of the ethylene-bridged Fe^{II} tetradentate complex and the structure of a tridentate Fe^{III} complex [7] have been reported.

The thiosalicylideneimine ligands investigated in the present work can be divided into three groups (1)—(3) as shown. Various other systems of nomenclature and abbreviations have been used previously [6-10] for these compounds.



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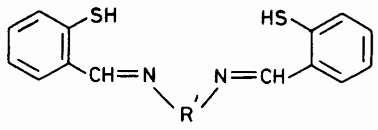

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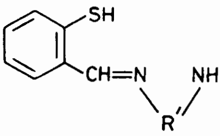

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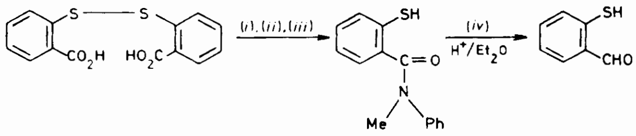
Structure	Name (abbreviation)
(1); R = Ph	*N*-phenylthiosalicylideneimine (H-Phtsaln)
(1); R = *p*-MeC_6H_4	*N*-*p*-tolylthiosalicylideneimine (Httsaln)
(1); R = *p*-$MeOC_6H_4$	*N*-(*p*-methoxyphenyl)thiosalicylideneimine (Hmptsaln)
(1); R = Bu^t	*N*-t-butylthiosalicylideneimine (H-Bu^ttsaln)
(1); R = H	thiosalicylideneimine (Htsaln)
(2); R′ = CH_2CH_2	*NN'*-ethylenebis(thiosalicylideneimine) (H_2tsalen)
(2); R′ = CH_2CHMe	*NN'*-propane-1,2-diylbis(thiosalicylideneimine) (H_2tsalpn)
(2); R′ = $CH_2CH_2CH_2$	*NN'*-propane-1,3-diylbis(thiosalicylideneimine) (H_2tsalpd)
(2); R′ = *o*-C_6H_4	*NN'*-*o*-phenylenebis(thiosalicylideneimine) (H_2tsalphen)
(3); R′ = CH_2CH_2	*N*-(2-aminoethyl)thiosalicylideneimine (H_2aetsaln)
(3); R′ = $CH_2CH_2CH_2$	*N*-(3-aminopropyl)thiosalicylideneimine (H_2aptsaln)
(3); R′ = $CHMeCH_2$	*N*-(2-amino-1-methylethyl)thiosalicylideneimine (H_2ametsaln)

Results and Discussion

Synthesis of Thiosalicylaldehyde.—Some difficulties have been experienced with the two procedures previously reported for the synthesis of the parent compound, thiosalicylaldehyde.

That due to Leaver *et al.*[11] requires the reduction of an anilide derived from 2,2′-dithiodibenzoic acid to give thiosalicylaldehyde (Scheme 1). It suffers from the disadvantage that the final reduction step is critically dependent on the nature and amount of reducing agent. The overall yield of aldehyde is much reduced by the accompanying formation of the related alcohol even when $NaAlH_2(OCH_2CH_2OCH_3)_2$ is used instead of $LiAlH_4$.[8]



Scheme 1. (*i*) $SOCl_2$; (*ii*) NHMePh; (*iii*) $NaBH_4$; (*iv*) $LiAlH_4$ or $NaAlH_2(OCH_2CH_2OMe)_2$

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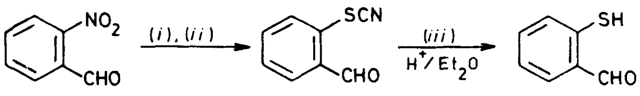
† *Non-S.I. units employed*: B.M. = 9.27×10^{-24} A m^2; atm = 101 325 Pa; G = 10^{-4} T; eV ≈ 1.60×10^{-19} J.

The method due to Friedländer and Lenk [12] involves reaction of sodium sulphide nonahydrate with 2-thiocyanatobenzaldehyde to give thiosalicylaldehyde (Scheme 2). In the



Scheme 2. (*i*) Reduction to amine by $FeSO_4/NH_4OH$; (*ii*) diazotisation and reaction with CuSCN/KSCN; (*iii*) $Na_2S{\cdot}9H_2O$

present work the yield of thiosalicylaldehyde was found to vary (0—30%) depending on the source and age of the samples of sodium sulphide used. It has subsequently been established that hydroxide ions are capable of cleaving the thiocyanate group to yield the desired thiosalicylaldehyde. Therefore the variation in yield due to different samples of sodium sulphide is related only to the amount of OH^- in the sample.

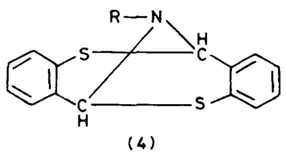
Some 2,2′-dithiodibenzaldehyde has also been isolated in reactions involving hydroxyl cleavage. This is in accord with the formation of disulphides by the reaction of organic thiocyanates with alkali, equations (1) and (2). Such reactions however have generally required elevated temperatures for their initiation in the examples hitherto known.[13]

$$RSCN + OH^- \longrightarrow RS^- + HOCN \qquad (1)$$

$$H_2O + HOCN + 2\,RS^- \longrightarrow R{-}S{-}S{-}R + NH_3 + CO_2 \qquad (2)$$

The overall yield of thiosalicylaldehyde has been found to reach 70% by this alkaline cleavage route which has thus become the preferred method of synthesis in this study.

Synthesis of Bi- and Tetra-dentate Complexes.—Condensation reactions involving thiosalicylaldehyde and primary amines and leading to the formation of the dithiocins (4) have been shown to compete with the formation of metal complexes from the Schiff base forms of thiosalicylideneimines.[8,14]



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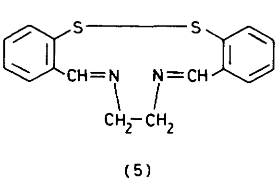

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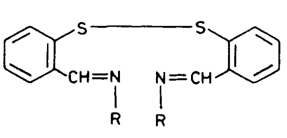


(6) (R = p-$MeOC_6H_4$)

Consequently, the Fe^{II} compounds have been prepared by isolation of the iron(II)–thiosalicylaldehydato-complex followed by reaction with the appropriate amine. This method was applied by Hoyer and Lorentz [15] in the first preparation of nickel thiosalicylideneimines and subsequently used by Corrigan and West [8] to isolate Co^{II} derivatives of such ligands. The complex $[Fe(tsal)_2]$ (Htsal = thiosalicylaldehyde) was obtained as a black microcrystalline solid by reaction of iron(II) acetate with the free aldehyde in dimethylformamide with careful exclusion of air.

The metal–imine derivatives (Table 1) were subsequently prepared by stirring a suspension of $[Fe(tsal)_2]$ with an equivalent amount of amine in either methanol or 2-methoxyethanol, followed by a short period under reflux. Prolonged heating under reflux conditions was found to lead to impure products. The bidentate complexes are freely soluble in solvents such as chloroform, benzene, and tetrahydrofuran (thf) whereas the tetradentate complexes are generally insoluble, or at best sparingly soluble, in common non-polar solvents. They have limited solubilities in donor solvents such as pyridine or 1-methylimidazole. The related tetradentate Co^{II} derivatives [8] also show this limited solubility and this suggests that the Fe^{II} complexes may have similar dimeric structures to their Co^{II} counterparts [16] in the solid state, or may be associated in other ways. Solutions of the Fe^{II} complexes are not stable in air whereas the dry, solid complexes do not appear to react, at least for several days. It was essential that all spectral or other measurements carried out on the compounds used freshly prepared samples or samples that had been stored under nitrogen.

An alternative synthesis was devised which involved reaction of $[Fe(CO)_5]$ with the di-imine disulphide derivatives (5) or (6), prepared by oxidising thiosalicylaldehyde to 2,2′-dithiodibenzaldehyde and reacting this with amines or diamines.

Table 1. Analytical and magnetic moment data obtained for thiosalicylideneimine complexes

Complex [a]	Analysis (%) [b] C	H	N	μ_{Fe}/B.M.[c]
$[Fe(tsal)_2]$ [d]	50.7	3.35	—	5.01
	(50.9)	(3.05)	—	
$[Fe(Bu^ttsaln)_2]$	59.5	6.6	6.15	5.18
	(60.0)	(6.4)	(6.35)	
$[Fe(ttsaln)_2]$	66.3	4.8	5.6	5.05
	(66.1)	(4.75)	(5.5)	
$[Fe(mptsaln)_2]$	62.3	4.6	5.35	5.16
	61.9 [e]	4.7 [e]	5.15 [e]	
	(62.2)	(4.5)	(5.2)	
$[Fe(Phtsaln)_2]$	64.5	4.4	5.65	5.10
	(65.0)	(4.2)	(5.85)	
[Fe(tsalen)]	54.2	4.1	7.8	1.90
	54.1 [e]	4.2 [e]	7.6 [e]	
	(54.2)	(4.0)	(7.9)	
[Fe(tsalpn)]	55.6	4.45	7.4	1.81
	(55.4)	(4.4)	(7.6)	
[Fe(tsalpd)]	55.0	4.55	7.45	4.16
	(55.4)	(4.4)	(7.6)	
[Fe(tsalphen)]	59.5	3.85	6.9	1.91
	(59.7)	(3.5)	(6.95)	
$[\{Fe(tsalen)\}_2O]{\cdot}py$	55.5	4.45	8.7	1.89
	(55.3)	(4.15)	(8.7)	
$[\{Fe(tsalen)\}_2O]{\cdot}\gamma$-pic	55.5	4.35	8.7	2.00
	(55.8)	(4.3)	(8.55)	
$[\{Fe(tsalpd)\}_2O]$	53.8	4.9	7.2	2.88
	(54.3)	(4.3)	(7.45)	
$[\{Fe(tsalphen)\}_2O]{\cdot}py$	60.4	3.95	7.9	2.06
	(60.1)	(3.7)	(7.8)	
[Fe(tsalen)(CO)(py)]	56.9	4.25	9.2	0.5
	(57.2)	(4.15)	(9.1)	
[Fe(tsalphen)(CO)(py)]	61.2	3.85	8.25	0.7
	(61.3)	(3.75)	(8.25)	
$[Fe(Haetsaln)_2]Cl$	48.2	5.2	12.4	2.00
	(48.1)	(4.9)	(12.4)	
$[Fe(Haptsaln)_2]Cl{\cdot}MeOH$	49.7	5.6	11.1	1.97
	(49.7)	(5.9)	(11.0)	
$[Fe(Hametsaln)_2]Cl{\cdot}MeOH$	49.5	5.9	10.6	1.95
	(49.7)	(5.9)	(11.0)	

[a] py = Pyridine, γ-pic = γ-picoline. [b] Calculated values in parentheses. [c] At 295 K. [d] Found: S, 19.2. Requires: S, 19.4%. [e] Prepared by reaction of $[Fe(CO)_5]$ with di-imine disulphides.

Table 2. I.r. spectra of iron(II) complexes of *N*-substituted thiosalicylideneimines

Compound	ν(C=N)/cm^{-1}	ν(C=C)/cm^{-1}
[Fe(Bu^{t}tsaln)$_2$]	1 581	1 529
[Fe(ttsaln)$_2$]	1 603, 1 568	1 521
[Fe(mptsaln)$_2$]	1 602, 1 571	1 529
[Fe(Phtsaln)$_2$]	1 585, 1 560	1 530
[Fe(tsalen)]	1 620, 1 583	1 529
[Fe(tsalpn)]	1 619, 1 583	1 529
[Fe(tsalpd)]	1 618, 1 609, 1 583	1 546, 1 535
[Fe(tsalphen)]	1 588, 1 566	1 520

The appropriate Fe^{II} complexes could be readily prepared by this route but it did not have any marked advantage over that using [Fe(tsal)$_2$] as the starting material.

Spectral Data.—The i.r. spectrum of [Fe(tsal)$_2$] showed four strong peaks in the region 1 500—1 650 cm^{-1}, similar to that of the corresponding Co^{II} compound.[8] The spectra of the thiosalicylideneiminato-complexes showed the absorption bands typical of Schiff base complexes. There were generally three major peaks in the region 1 500—1 650 cm^{-1} which could be assigned to C=N and C=C stretching frequencies (Table 2) with shoulders observed on these peaks in a number of cases. The complexes having aryl groups attached to N showed a further peak at approximately 1 500 cm^{-1}. In contrast to the other complexes, [Fe(tsalpd)] displayed five peaks in the region 1 500—1 650 cm^{-1} which may be related to a distortion of the ligand from a planar disposition about the Fe atom.

The mass spectrum of [Fe(tsal)$_2$] showed a molecular ion for the parent compound although the most intense peak in the spectrum corresponded to the appearance of the free ligand, *i.e.* the co-ordinated group with an added proton.

The bidentate thiosalicylideneimine complexes showed mass spectra with the same general features already described for Co^{II} derivatives,[8] *i.e.* molecular ion peaks (generally the most intense); metal-containing fragments resulting from (*a*) the loss of a substituent R from one or both of the nitrogen atoms in the molecule, (*b*) the complete loss of one ligand grouping (O-SC$_6$H$_4$CHNR) to leave [Fe(*o*-SC$_6$H$_4$CHNR)]$^+$, (*c*) the loss of one or both –CH=N–R– groupings. The complete ligands *o*-HSC$_6$H$_4$CHNR and their various decomposition products have also been detected in the mass spectra of the bidentate-ligand complexes.

The tetradentate complexes gave the molecular ions as the only metal-containing fragments to be observed.

The visible spectra of all the Fe^{II} complexes showed broad bands with maxima in the region of 470 nm with molar absorption coefficients of the order of 10^4 dm^3 mol^{-1} cm^{-1}. Due to the similarities between the peak positions for both bidentate and tetradentate complexes with different stereochemistries, the bands have been assigned to iron–ligand charge-transfer bands. The spectrum of [Fe(tsalen)] in pyridine at room temperature is virtually the same as that in methylene dichloride which indicates only weak interaction with pyridine. However, when a pyridine solution of this complex was cooled to -23 °C a dramatic colour change from blue-black to red occurred and the absorption peak maximum shifted to 508 nm which is consistent with pyridine co-ordination. The analogous Co^{II} complex [Co(tsalen)] has also been observed to co-ordinate pyridine at low temperatures, but not at room temperature.[17]

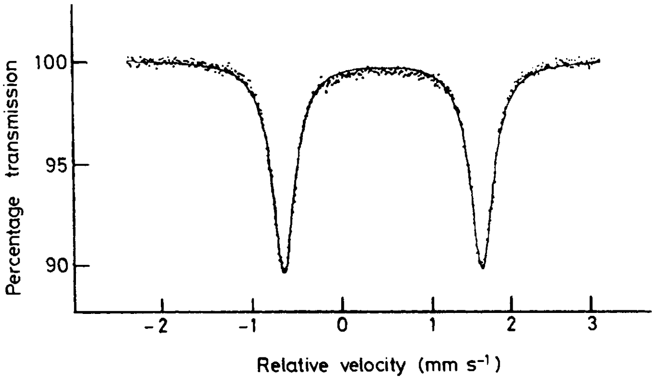


Figure 1. Mössbauer spectrum of [Fe(tsalen)] at 4.2 K

Table 3. Mössbauer parameters for iron(II) and iron(III) complexes of thiosalicylaldehyde and *N*-substituted thiosalicylideneimines [a]

Compound	δ [b]/mm s^{-1}	ΔE/mm s^{-1}	*S*
[Fe(tsal)$_2$]	1.08	2.49	2
[Fe(mptsaln)$_2$]	0.70	2.23	2
[Fe(tsalen)]	0.44	2.20	1
[Fe(tsalpd)]	0.87	3.32	2
[Fe(tsalen)(CO)(py)]	0.18	0.56	0
[{Fe(tsalen)}$_2$O]·py	0.43	1.10	½

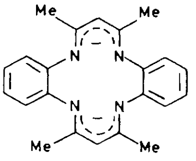
[a] Recorded at 4.2 K. [b] Relative to Fe metal.

Spin States of Iron(II) *Complexes*.—The magnetic moments at 22 °C of the Fe^{II} complexes of thiosalicylaldehyde and *N*-substituted thiosalicylideneimines are shown in Table 1. The [Fe(*o*-SC$_6$H$_4$CHNR)$_2$] and [Fe(tsal)$_2$] complexes have moments of the order of 5.1 B.M., which are similar to those observed for the analogous salicylaldehyde [18] and salicylideneimine [19] complexes, and fall in the range expected for high-spin d^6 systems (5.0—5.5 B.M.). By contrast, the tetradentate thiosalicylideneiminato-complexes have unusual magnetic moments which do not correspond to either low-spin or high-spin d^6 systems. Three complexes, [Fe(tsalen)], [Fe(tsalpn)], and [Fe(tsalphen)], have moments in the range 1.81—1.91 B.M., while the other complex, [Fe(tsalpd)], has a moment of 4.16 B.M. The analogous tetradentate salicylideneiminatoiron(II) derivatives are high-spin compounds [19,20] with moments in the range 4.8—5.3 B.M.

Mössbauer spectral measurements have been carried out on a member of each group of complexes at 4.2 K and the results are summarized in Table 3. The spectra consist of a single, quadrupole-split doublet in all cases. A typical spectrum of [Fe(tsalen)] is shown in Figure 1. The observed isomer shift (δ) and quadrupole splitting (ΔE) parameters for [Fe(tsal)$_2$] and [Fe(mptsaln)$_2$] are consistent with the presence of high-spin Fe^{II}.

Similar values have been found for Fe^{II} salicylideneimines which contain the related ON-donor ligands.[21] The high-spin tetradentate, trigonal-bipyramidal complexes studied by Karlin and Lippard,[2] which contain saturated S$_2$N$_2$ ligands within a sulphur-bridged dinuclear structure, display similar δ values but much larger ΔE values (3.4—3.6 mm s^{-1}). These higher quadrupole splittings reflect in part the different geometry displayed by the trigonal-bipyramidal molecules compared to the probable tetragonal geometries of [Fe(tsal)$_2$] and [Fe(*o*-SC$_6$H$_4$CHNR)$_2$] .The higher ΔE value observed for the other high-spin complex, [Fe(tsalpd)], strongly suggests distortions away from the geometries of the bidentate complexes towards that observed by Karlin and Lippard. This seems reasonable in view of the longer diamine chain in

Table 4. Bond distances (Å) and angles (°) in iron–carbonyl compounds



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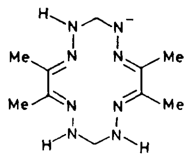

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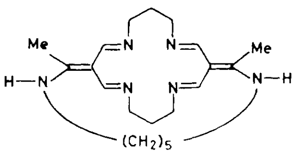


L^3

		Distances (Å)		Angle (°)	
Compound	Fe–CO	Fe–N(pyridine)	Fe–N(ligand)	Fe–C–O	Ref.
[Fe(tsalen)(CO)(py)]	1.74(3)	2.10(2)	1.97(2)	174(2)	30
[Fe(tpp)(CO)(py)] [a]	1.77(2)	2.10(2)	2.02(1)	179(2)	[b]
[Fe(L^1)(CO)]	1.694(4)	—	1.927(4)	177.2(3)	28
[Fe(L^1)(CO)(py)]	1.730(3)	2.088(3)	1.941(4)	178.2(3)	28
[Fe(L^1)(CO)(NH_2NH_2)]	1.751(6)	2.122(5)	1.944(4)	177.6(5)	28
[Fe(L^2)(CO)(CH_3)]	1.772(5)	—	1.900(2)	180.0(0)	27
[Fe(L^3)(CO)(py)][PF_6]$_2$	1.792(4)	2.052(3)	1.992(5)	170.6(5)	31

[a] tpp = 5,10,15,20-Tetraphenylporphyrinate(2−). [b] J. A. Ibers and S.-M. Peng, *J. Am. Chem. Soc.*, 1976, **98**, 8032.

tsalpd. In contrast, though, the ΔE value for [Fe(tsalen)] is similar to those for [Fe(tsal)$_2$] and [Fe(mptsaln)$_2$], the isomer shift is much smaller and corresponds to neither high-spin nor low-spin Fe^{II}. It is closer to the values observed for Fe^{II} compounds with phthalocyanin [22] ($\delta_{4.2\text{ K}} = 0.48$ mm s^{-1}) and tetraphenylporphyrin [23] ($\delta_{4.2\text{ K}} = 0.52$ mm s^{-1}) which could implicate the unusual intermediate $S = 1$ spin state.

A more detailed account of the variable-temperature susceptibility and Mössbauer studies of these complexes will be reported separately.

Reaction with Carbon Monoxide.—Iron(II) complexes of tetradentate *N*-substituted salicylideneimines do not readily co-ordinate with CO.[20,24] However, the thio-analogues of these complexes do react. Thus, when CO is passed into a pyridine solution of a tetradentate thiosalicylideneiminatorion(II) complex the blue-black solution rapidly changes to deep red. Monocarbonyl complexes of empirical formulae [Fe(tsalen)(CO)(py)] and [Fe(tsalphen)(CO)(py)] have been isolated from solutions. [Fe(tsalpd)] also reacts but only a red oil has been obtained from solution which has not been brought to crystallization. The solution reactions appear to be irreversible at room temperature. [Fe(tsalen)(CO)(py)] does not decompose *in vacuo* below 90 °C but loses both pyridine and CO between 90 and 120 °C.

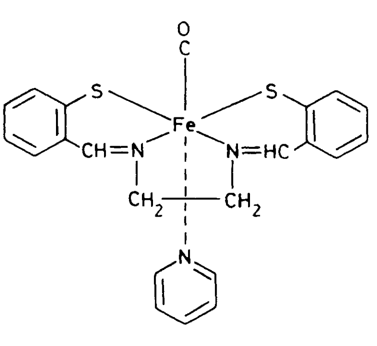
The complexes showed strong i.r. absorptions due to CO at 1 940 cm^{-1} (Nujol) and 1 969 cm^{-1} (pyridine solution) for [Fe(tsalen)(CO)(py)] and 1 938 cm^{-1} (Nujol) and 1 948 cm^{-1} (pyridine) for [Fe(tsalphen)(CO)(py)]. A wide range of ν(CO) values has been reported for other Fe^{II} monocarbonyl complexes with a variety of tetradentate ligands in the range 1 925—2 040 cm^{-1} and including ' synthetic ' and natural porphyrins, including haemoproteins [25] and macrocyclic annulene type ligands.[26,27] The influence of a sixth ligand in modifying the value of ν(CO) and presumably the strength of binding of CO has been shown [28] by the low value of 1 921 cm^{-1} observed for the five-co-ordinate macrocyclic complex [Fe($C_{22}H_{22}N_4$)(CO)] compared to 1 935 cm^{-1} for the pyridine derivatives [Fe($C_{22}H_{22}N_4$)(CO)(py)].

A small number of other Fe^{II} complexes containing sulphur-bonded ligands have also been observed to react with CO. Dicarbonyl derivatives have been observed to form in each case with *NN'*-dimethyl-*NN'*-bis(2-mercaptoethyl)alkylenediamines,[2] cysteine,[4] and dialkyldithiocarbamates.[29] These species each display two ν(CO) values, in the regions 2 010—2 030 cm^{-1} and 1 940—1 970 cm^{-1}, indicating *cis* co-ordination.

There has been no evidence obtained in the present work for the co-ordination of a second molecule of CO to [Fe(tsalen)] or [Fe(tsalphen)] at atmospheric pressure in pyridine. Experiments in other solvents are severely limited by the low solubility of the complexes in other media, however.

The two complexes obtained are essentially diamagnetic at room temperature but both show small temperature-independent paramagnetic moments {[Fe(tsalen)(CO)(py)] 0.5 B.M., [Fe(tsalphen)(CO)(py)] 0.7 B.M.} of the same order as is generally found for low-spin Fe^{II} d^6 compounds. The Mössbauer spectrum of [Fe(tsalen)(CO)(py)] at 4.2 K is also consistent with the presence of low-spin Fe^{II}.

The structure of [Fe(tsalen)(CO)(py)] (7) has been determined by single crystal *X*-ray analysis [30] and shows a *trans* relationship for CO and pyridine. The average Fe–S and Fe–N(plane) distances are 2.27(1) and 1.97(2) Å respectively. The Fe–N(plane), Fe–N(pyridine), and Fe–C(carbonyl) distances are comparable with those of other structurally characterised low-spin iron(II)–carbonyl compounds containing tetradentate ligands (Table 4). The Fe atom is essentially coplanar with the S- and N-donor atoms of the ligand.



(7)

The Fe–C–O angle shows only slight deviation from linearity as has been found for other Fe(CO) compounds with various macrocyclic ligands. However, Busch *et al.*[31] have

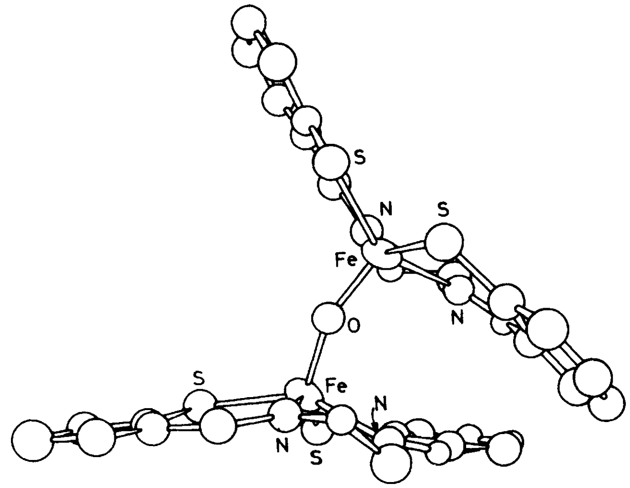


Figure 2. Molecular structure of $[\{\mathrm{Fe(tsalen)}\}_2\mathrm{O}]$ (hydrogen atoms are not shown)

observed a considerable distortion of the order of 10° from linearity in an Fe(CO) complex containing a ligand which produces considerable steric restrictions on the free space available for co-ordination by a CO molecule. Such steric influences are believed to cause much greater distortions from linearity for the Fe–C–O bonds in carbonyl haemoprotein and myoglobin compounds [32] leading to Fe–C–O angles in the range 135—145°.

Reaction with Oxygen.—The passage of oxygen through the blue-black solutions of the $\mathrm{Fe^{II}}$ tetradentate complexes in dry pyridine causes a rapid colour change to brown. In the case of [Fe(tsalen)] and [Fe(tsalphen)], black crystals of the μ-oxo-complexes $[\{\mathrm{Fe(tsalen)}\}_2\mathrm{O}]\cdot\mathrm{py}$ and $[\{\mathrm{Fe(tsalphen)}\}_2\mathrm{O}]\cdot\mathrm{py}$ appear within a few minutes.

The μ-oxo-compound $[\{\mathrm{Fe(tsalpd)}\}_2\mathrm{O}]$ is precipitated from pyridine upon addition of n-heptane. It did not contain any associated pyridine. [Fe(tsalen)] also reacts with oxygen in other donor solvents such as γ-picoline and 1-methylimidazole; however, a μ-oxo-complex has only been isolated from γ-picoline. The complexes obtained are listed in Table 1. These are the first reported μ-oxo-iron(III) complexes containing *S*-donors as ligands. The compounds are stable in the solid state or solution in the presence of dry oxygen. However, if suspensions or solutions of these compounds are allowed to stand in moist air decomposition occurs at different rates depending on the complex. Thus $[\{\mathrm{Fe(tsalpd)}\}_2\mathrm{O}]$ decomposes within an hour of exposure while the other compounds are stable for several hours. The products are red-brown solids of unknown composition showing i.r. spectral evidence for the presence of OH groups or H_2O. The disulphide of the ligand [*e.g.* (5)] was also detected amongst the products. The sensitivity of the oxo-compounds to moisture requires that they be prepared using carefully dried solvents.

Table 5. E.s.r. spectral data for the μ-oxo-compounds

Compound	*g* Values at 77 K	
	Solid	Pyridine glass
$[\{\mathrm{Fe(tsalen)}\}_2\mathrm{O}]\cdot\mathrm{py}$	2.159, 2.105, 2.005	2.61, 2.098, 1.999
$[\{\mathrm{Fe(tsalphen)}\}_2\mathrm{O}]\cdot\mathrm{py}$	2.107, 2.028 [a]	*b*
$[\{\mathrm{Fe(tsalpd)}\}_2\mathrm{O}]$	2.041 [c]	2.028 [c]

[a] Line also at $g = 4.28$ of similar width to g 2.107 line; g 2.028 line much narrower. [b] The complex was insufficiently soluble in pyridine to yield a spectrum. [c] Broad line.

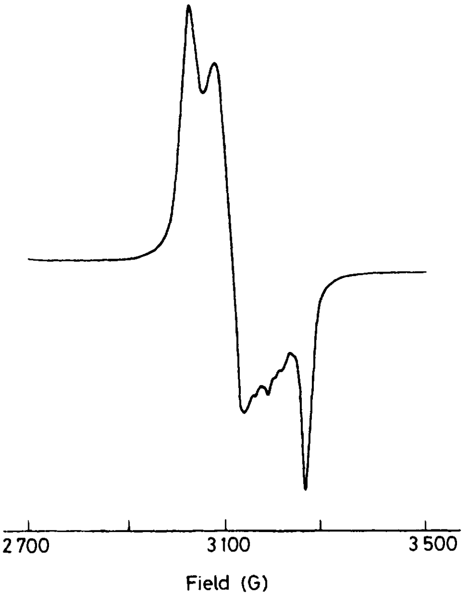


Figure 3. E.s.r. spectrum (9 148 MHz) of a pyridine solution of $[\{\mathrm{Fe(tsalen)}\}_2\mathrm{O}]\cdot\mathrm{py}$ at 77 K

The passage of oxygen through solutions of bidentate complexes did not yield isolable μ-oxo-complexes. A series of rapid colour changes was observed and the disulphide of the ligand was obtained.

A partial crystal structure determination [33] has been carried out on the complex $[\{\mathrm{Fe(tsalen)}\}_2\mathrm{O}]\cdot\mathrm{py}$ * which has confirmed the μ-oxo-linkage and established a distorted square-pyramidal arrangement for each Fe(tsalen) unit (Figure 2). The pyridine molecule exists solely as a lattice molecule and is not co-ordinated to either Fe atom. The Fe–O–Fe angle of 159 (3)° lies between those found for various $[\{\mathrm{Fe(salicylideneiminate)}\}_2\mathrm{O}]$ species [34] (139—144°) and the bidentate complexes μ-oxo-bis[(*N*-isopropylsalicylideneiminato)iron(III)] [35a] (164°) and μ-oxo-bis{[*N*-(*p*-chlorophenyl)salicylideneiminato]iron(III)} [35b] (175°). The Fe–(μ-O) [1.78 (1) Å] and Fe–Fe [3.50 (1) Å] distances are similar to those in $[\{\mathrm{Fe(salicylideneiminate)}\}_2\mathrm{O}]$ derivatives. The average Fe-S and Fe-N(ligand) distances, 2.32(2) and 2.06 (4) Å respectively, are both comparable to those found for [Fe(tsalen)(CO)(py)].

Magnetic Moments of μ-Oxo Complexes.—The room temperature magnetic moments of the μ-oxo-complexes are given in Table 1. The tsalen and tsalphen compounds have magnetic moments per Fe in the range 1.89—2.06 B.M. which are similar to those found for the analogous μ-oxo-salicylideneiminate complexes [36] and other μ-oxo-compounds.[37] The complex $[\{\mathrm{Fe(tsalpd)}\}_2\mathrm{O}]$ has a notably larger moment of 2.88 B.M., although it was difficult to obtain reproducible magnetic moments for this rather unstable derivative.

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* It was reported previously [6] that considerable difficulty has been experienced in obtaining crystals of $[\{\mathrm{Fe(tsalen)}\}_2\mathrm{O}]\cdot\mathrm{py}$ entirely suitable for *X*-ray diffraction studies. The disorder of the unco-ordinated pyridine molecules has complicated the task of locating these atoms and in the best determination made the refinement of the structure converged at *R* 0.11. However, the essential features of the structure, namely the Fe–O–Fe angle, the square-pyramidal array about each Fe, and the average Fe–S and Fe–N distances have been determined with sufficient accuracy to enable adequate comparisons to be made with other Schiff base Fe–O–Fe derivatives.

A variable-temperature magnetic susceptibility measurement on [{Fe(tsalen)}$_2$O]·py shows quite different behaviour to that observed for [{Fe(salen)}$_2$O] (salen = salicylideneiminate) and the results can be fitted to a weakly coupled Fe^{III}($S = \frac{1}{2}$)-Fe^{III} ($S = \frac{1}{2}$) model.[6] The occurrence of low-spin Fe^{III} centres contrasts with the well authenticated high-spin centres in the salen compound.[37] While the Mössbauer isomer shift value, $\delta = 0.43$ mm s^{-1}, does not unequivocally lend support to this spin assignment, e.s.r. spectral measurements on a neat powder or pyridine-glass sample show three g values in the $g \sim 2$ region (Table 5) which are characteristic of rhombically distorted Fe^{III} ($S = \frac{1}{2}$). The e.s.r. spectrum of [{Fe(tsalen)}$_2$O] in frozen pyridine (Figure 3) displays unusual structure on the middle line which, at first sight appears due to N(pyridine) hyperfine coupling, but may be due to superposition of lines from species with slightly differing g values. This structure is not evident in the powder spectrum although the middle line is broader than the other two.

The e.s.r. spectra of the tsalpd and tsalphen μ-oxo-compounds show differences in detail to that of [{Fe(tsalen)}$_2$O], the tsalpd complex giving a very broad $g \sim 2$ line in the powder spectrum, which is perhaps due to lack of solvated pyridine capable of acting as diamagnetic diluent. A full description of the magnetic and spectroscopic properties of these and the Fe^{II} compounds will be reported separately.

*Evidence for Peroxo-*Fe^{III} *Complexes.*—If oxygen is bubbled through a pyridine solution of [Fe(tsalen)] (*ca.* 1.5 mmol) at room temperature for several minutes the initial blue-black solution changes to a distinct dark brown and crystals of the μ-oxo-compound are observed to form. Replacing the oxygen stream with nitrogen does not cause any change in the colour of the solution indicating that the compound in solution does not readily dissociate again to [Fe(tsalen)] and oxygen. However, if the solution is heated to 40—50 °C with nitrogen continually passing through it the colour does return to that of the initial [Fe(tsalen)] although the precipitated crystals of the μ-oxo-compound are unaffected. Cooling to room temperature and again passing through oxygen causes a return to the dark brown solution and more crystals of the μ-oxo-complex separate. Once more, heating to 40—50 °C and purging with nitrogen reverses the colour of the solution. This cycle can be repeated several times before all the [Fe(tsalen)] has finally been converted to [{Fe(tsalen)}$_2$O].

At low temperatures the rate of conversion to μ-oxo-complex can be slowed considerably. Thus at 250 K oxygen reacts with [Fe(tsalen)] in pyridine causing a change in colour of the solution to brown but crystals of the μ-oxo-complex do not separate. The colour change cannot be reversed by passing in nitrogen at 250 K but if such a solution is rapidly heated to 40—50 °C in a nitrogen stream then the colour reversal does occur. Under these conditions some crystals of the μ-oxo-complex also make their appearance as the temperature rises.

Measurements of the volume of oxygen absorbed by a pyridine–[Fe(tsalen)] solution at 250 K indicate a ratio of Fe : O$_2$ close to 2 : 1, suggesting the formation of a peroxo-type dinuclear species [{Fe(tsalen)}$_2$O$_2$] as the product predominating at low temperatures and hence the likely precursor of [{Fe(tsalen)}$_2$O]. It is probable that pyridine is also co-ordinated to [Fe(tsalen)] at low temperatures in the light of the observed colour change in pyridine solutions when the temperature is lowered and this may aid co-ordination of oxygen as is known for reactions involving Co^{II} complexes. Low temperatures also facilitate pyridine co-ordination to [Co^{II}(tsalen)] and subsequent attachment of oxygen.

The e.s.r. spectra at 77 K of pyridine solutions of [Fe(tsalen)], [Fe(tsalpd)], and [Fe(tsalphen)] which had been equilibrated with oxygen at 250 K showed distinctly different features from those of the μ-oxo-complexes containing the three ligands. Three g values could be derived for each ' oxygenated ' system: [Fe(tsalen)]/O$_2$, g = 2.156, 2.109, 2.004; [Fe(tsalpd)]/O$_2$, g = 2.234, 2.127, 1.976; [Fe(tsalphen)]/O$_2$, g = 2.222, 2.132, 1.979. The general form of the spectra agrees with the Fe species having weakly coupled $S = \frac{1}{2}$ spin states as previously suggested for the μ-oxo-complexes.

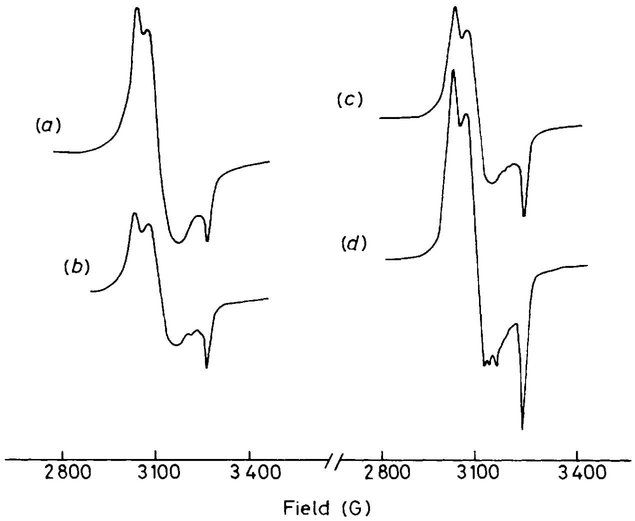

Figure 4. E.s.r. spectra (9 148 MHz) at 77 K: (*a*) pyridine solution of [Fe(tsalen)] cooled to 250 K and then treated with oxygen; (*b*) solution (*a*) warmed to room temperature for 15 min and then remeasured; (*c*) cooled solution (*b*) warmed to room temperature for an additional 15 min and then remeasured; (*d*) solution (*c*) warmed to room temperature for an additional 30 min and then remeasured

It is therefore suggested that the evidence supports the existence of peroxo-species such as [(tsalen)Fe–O–O–Fe(tsalen)] being formed initially. The need to go to higher temperatures in order to reverse the formation of such compounds is similar to the situation observed with the well known μ-peroxo-species formed by Co; *e.g.* [{Co(salen)(py)}$_2$O$_2$] is formed at room temperature but requires notably higher temperatures, in pyridine, to cause dissociation. It was possible to monitor the conversion of the first formed complex (the suggested peroxo-compound) to the final μ-oxo-species by following the change in the e.s.r. spectrum. A pyridine solution of [Fe(tsalen)] was equilibrated at 250 K with oxygen then warmed to room temperature, left for 15 min, then cooled to 77 K for e.s.r. spectral measurement. The solution under oxygen was then warmed again to room temperature and kept for a further 15 min, and again cooled to 77 K and remeasured. Eventually, the solution showed only the e.s.r. spectrum of the μ-oxo-complex (Figure 4).

The analogous O$_2$N$_2$ complex [Fe(salen)] was also allowed to react with oxygen in pyridine at 250 K but the solution showed only the g = 4.28 spectrum at 77 K of the known μ-oxo-compound [{Fe(salen)}$_2$O] with no evidence for another species. If similar mechanisms are involved in those reactions involving the different donor ligands S and O then the peroxo-[Fe(salen)] intermediate must break down to give a μ-oxo-complex more rapidly than the S$_2$N$_2$ systems. Evidence has previously been presented for the formation of similar peroxo-species in the reaction of oxygen with Fe^{II} porphyrins [38] at low temperatures.

Other Fe^{III} *Complexes.*—Attempts have been made to synthesise Fe^{III} derivatives such as [Fe(tsalen)Cl] for comparison with the well known salicylideneiminate complexes such as [Fe(salen)Cl]. However, whether by reaction of anhydrous $FeCl_3$ with a mixture of thiosalicylaldehyde and a diamine in the presence of NEt_3, or by an initial reaction of $FeCl_3$ with thiosalicylaldehyde followed by addition of the appropriate diamine, the only products isolated have been bis(tridentate iminate)iron(III) chloride derivatives, *e.g.* $[Fe(Haetsaln)_2]Cl$.

The three complexes prepared (Table 1) are dark brown in colour and are sparingly soluble in common polar solvents. In the presence of moist air the complexes decompose in solution giving precipitates having i.r. spectra similar to hydrated Fe_2O_3.

The complexes are each low spin, in contrast to the analogous salicylideneiminate complexes $[Fe(o\text{-}OC_6H_4CHNCH_2CH_2NH_2)_2]X$ (X = Cl or I) which are high spin.[39] The crystal structure [7] of the complex has revealed a significant shortening of the Fe–S distances compared to the sum of the covalent radii together with shorter Fe–N(imino) distances than occur in high-spin salicylideneiminate–Fe^{III} complexes. These observations are in line with the low-spin nature of the complex. The S-donor groups clearly influence the spin state in these thiosalicylideneiminate compounds. However it has recently been shown that subtle effects can lead to low-spin or spin-equilibrium behaviour in the related salicylideneiminate derivatives. These effects include hydrogen bonding of H_2O to the donor nitrogen atoms in low-spin $[Fe(o\text{-}OC_6H_4CHNCH_2CH_2NH_2)]Cl{\cdot}H_2O$,[40] variation in the non-co-ordinated anion, and variation in substituents on the $-NH_2$ fragment.[41]

The e.s.r. spectrum of $[Fe(Haetsaln)_2]Cl$ at 77 K further confirms the $S = \frac{1}{2}$ ground state as evidenced by lines at g = 2.166, 2.115, and 2.008. These nearly-axial g values arise through a splitting of the t_{2g} orbital levels brought about by the distorted six-co-ordinate ligand field.[42] The anisotropy in g is much smaller than that generally observed in low-spin Fe^{III} porphyrins [43] but is similar to that displayed, for example, by a six-co-ordinate salicylideneiminate complex,[44] $[Fe(salen)(CN)_2]^-$, and a β-dithioketonate, $[Fe(dtacac)_3]$ (dtacac = dithioacetylacetonate).[45] The odd electron most likely occupies the d_{xy} orbital in these non-porphyrin species. The spectral lineshape and g values of the present tridentate complexes are similar to those of $[\{Fe(tsalen)\}_2O]{\cdot}py$ described above.

Experimental

Materials and Methods.—2-Aminobenzaldehyde was prepared by reduction of 2-nitrobenzaldehyde (EGA Chemie) with iron(II) sulphate as described by Smith and Opie.[46] 2-Methoxyethanol and dimethylformamide (dmf) were analytical reagents and were used without further purification; ethanol and methanol were dried by standard methods. Pyridine and n-heptane were dried by refluxing over barium oxide and sodium metal–benzophenone ketyl, respectively. Iron(II) acetate was prepared by the method of Calderazzo *et al.*[20] All amines were distilled prior to use.

The synthesis and manipulations of the iron(II) complexes were carried out under a dry nitrogen atmosphere using degassed solvents. For analytical purposes, the iron(II) complexes were sealed in glass ampoules under nitrogen and opened just before the analysis was carried out. Nitrogen was purified by passage through BASF catalyst R3-11 and molecular sieves.

Solution electronic spectra were recorded under nitrogen with a Varian Superscan spectrophotometer using 1-cm matched Pyrex cells. I.r. spectra were recorded as Nujol mulls between sodium chloride plates on a Perkin-Elmer 180 spectrometer. Mass spectra were recorded with a V.G. Micromass 7070F, using an electron energy of 70 eV and an ion chamber temperature of 200 °C.

Room temperature magnetic susceptibilities were measured by the Faraday method over three field strengths, $Hg[Co(NCS)_4]$ and $[Ni(en)_3][S_2O_3]$ being used to calibrate the balance. The diamagnetic corrections for ligands were calculated using Pascal's constants. Mössbauer spectra were recorded on an instrument which has previously been described.[47] E.s.r. spectra were recorded on a Varian E-12 spectrometer using quartz sample tubes.

Synthesis of Thiosalicylaldehyde.—(*a*) *2-Thiocyanatobenzaldehyde.* A cold solution (0 °C) of sulphuric acid (13.5 cm^3 in 200 cm^3 water) was added dropwise to a vigorously stirred suspension of 2-aminobenzaldehyde (10 g, 0.08 mol) in cold sodium nitrite solution (6 g in 500 cm^3 water). The diazonium salt was filtered off and then added dropwise to a cold, stirred solution of copper(I) thiocyanate (10 g, 0.08 mol) and potassium thiocyanate (100 g) in water (60 cm^3). The resulting black-green mixture was stirred at room temperature for 1 h and then at 60 °C for 30 min. The mixture was cooled and the yellow-brown solid was collected by filtration. The solid was extracted three times with boiling light petroleum (200 cm^3, b.p. 40—60 °C) to obtain creamy white needles (4.5 g, 33%), m.p. 73 °C (lit.,[12] 76 °C).

(*b*) *2-Thiosalicylaldehyde.* A freshly prepared solution of sodium hydroxide (5 g in 40 cm^3 water) was added, with vigorous stirring, to 2-thiocyanatobenzaldehyde (1 g, 6 mmol). After 5 min the mixture was filtered to remove a yellow solid (0.12 g) and the filtrate was cooled by addition of ice. This solution was acidified with concentrated sulphuric acid (15 cm^3) and extracted with peroxide-free diethyl ether. The extract was dried over sodium sulphate. The yield of 2-thiosalicylaldehyde was determined by precipitation of the red-orange 2,4-dinitrophenylhydrazone derivative from an aliquot of the ether solution, m.p. 269—270 °C (lit.,[11] 270 °C). Yields of thiosalicylaldehyde were of the order of 60—70% (0.56 g). The compound was not recovered from ether solution but used immediately after purification.

(*c*) *Purification of thiosalicylaldehyde.* Thiosalicylaldehyde was purified by column chromatography prior to reaction with iron(II) acetate. The ether solution was reduced to 2—3 cm^3 by rotary evaporation and then chromatographed on Florisil (100–200 mesh) using benzene as eluant. Dimethylformamide (12 cm^3) was then added to the benzene solution and the benzene removed by rotary evaporation.

Synthesis of 2,2′-Dithiodibenzaldehyde and Related Benzylideneimines.—An ethereal solution of thiosalicylaldehyde (1.12 g, 8.1 mmol) was added to an excess of dimethyl sulphoxide (10 cm^3). The ether was removed by rotary evaporation and the solution warmed at 60 °C for 8 h. After cooling, ice–water (100 cm^3) and sodium chloride (3 g) were added and the mixture was stirred for 15 min. The precipitate was collected, dried, and recrystallized from 95% ethanol to give the white-yellow crystalline disulphide (1.08 g, 98%), m.p. 144 °C (lit.,[12] 145 °C) (Found: C, 61.1; H, 3.75; S, 23.1. Calc. for $C_{14}H_{10}O_2S_2$: C, 61.3; H, 3.65; S, 23.35%). ^1H N.m.r. spectrum: $\delta(CDCl_3)$ 10.22 (s, 2 H, CHO), 7.23—7.93 p.p.m. (m, 8 H, aromatic); $\delta(CD_3SOCD_3)$ 10.19 (S, 2 H, CHO). 7.17—8.14 p.p.m. (m, 8 H, aromatic).

(*a*) *7,8-Dihydrodibenzo*[c,k][1,2,6,9]*dithiadiazacyclododecin* (5). Ethylenediamine (65 mg, 1.08 mmol) dissolved in methanol (5 cm^3) was added to a suspension of 2,2′-dithiodibenzaldehyde (274 mg, 1 mmol) in methanol (20 cm^3). The mixture was stirred at room temperature for 15 min and then refluxed for 60 min. After cooling, the solid was collected and recrystallized from dmf to give white crystals (170 mg, 57%), m.p. 181—182 °C (Found: C, 64.1; H, 5.1; N, 9.6. $C_{16}H_{14}N_2S_2$ requires C, 64.4; H, 4.75; N, 9.4%). The compound was insufficiently soluble in solvents to allow measurement of its ^{1}H n.m.r. spectrum.

(*b*) The use of *p*-methoxyaniline allowed the preparation of the bis-*p*-methoxyphenylimine derivative as pale orange crystals, recrystallized from ethanol (73% yield), m.p. 131—132 °C (Found: C, 69.3; H, 4.95; N, 5.65. $C_{28}H_{24}N_2S_2O_2$ requires C, 69.4; H, 5.0; N, 5.8%). ^{1}H n.m.r. spectrum: δ($CDCl_3$) 8.85 (s, 2 H, CH=N), 6.80—7.97 (m, 16 H, aromatic), 3.83 p.p.m. (s, 6 H, CH_3); δ (CD_3SOCD_3) 8.93 (s, 2 H, CH=N), 6.94—7.97 (m, 16 H, aromatic), 3.79 p.p.m. (s, 6 H, CH_3).

Iron(II) *Complexes.—Bis(thiosalicylaldehydato)iron*(II), [Fe(tsal)$_2$]. A dmf solution of thiosalicylaldehyde (0.56 g, 4.3 mmol) was added to iron(II) acetate (0.35 g, 2.1 mmol). The mixture was stirred at 80 °C for 30 min and then filtered. Ethanol (40—50 cm^3) was added dropwise to the cooled black-green solution and the mixture was allowed to stand for at least 3 h. The black microcrystalline precipitate was filtered off, washed with ethanol, and dried *in vacuo* to give [Fe(tsal)$_2$] (0.33 g, 50%). I.r. spectrum (Nujol, strong and medium bands only): 1 628s, 1 614s, 1 584s, 1 537s, 1 409m, 1 309m, 1 194m, 1 162m, 1 122m, 1 072m, 854m, 754m, 739s, 675m, and 649m cm^{-1}. Mass spectrum: *m*/*e* = 330(60%) (M^+), 302 (5), 193 (15), 165 (15), 138 (100) (ligand), 137 (32), 56 (12), 32 (79).

[NN′-*Ethylenebis(thiosalicylideneiminato)*]*iron*(II), [Fe(tsalen)]. (*a*) Ethylenediamine (65 mg, 1.08 mmol) dissolved in 2-methoxyethanol was added to [Fe(tsal)$_2$] (330 mg, 1 mmol). The mixture was stirred at room temperature for 75 min and then refluxed for 5 min. After cooling, the solid was filtered off. washed with ethanol, and dried *in vacuo* to yield the title compound as a black powder (234 mg, 84%). Essentially the same procedure was used to prepare [Fe(tsalpn)] (yield 65%, black crystals), [Fe(tsalpd)] (yield 77%, purple-black crystals), and [Fe(tsalphen)] (yield 66%, black powder).

(*b*) Iron pentacarbonyl (392 mg, 2 mmol) dissolved in toluene (40 cm^3) was added to a suspension of compound (5) (596 mg, 2 mmol) in toluene (10 cm^3) and the resulting mixture refluxed until the evolution of carbon monoxide had ceased (*ca.* 3 h). The black microcrystalline precipitate was filtered off, washed with ethanol, and dried under vacuum to yield [Fe(tsalen)] (495 mg, 70%).

Bis[N-(p-*methoxyphenyl)thiosalicylideneiminato*]*iron*(II), [Fe(mptsaln)$_2$]. (*a*) *p*-Methoxyaniline (270 mg, 2.05 mmol) dissolved in methanol (40 cm^3) was added to [Fe(tsal)$_2$] (330 mg, 1 mmol). The mixture was stirred at room temperature for 60 min and then refluxed for 2 min. After cooling the solid was filtered off, dried, and recrystallized from ethanol to give maroon crystals (380 mg, 70%).

The remaining bidentate complexes [Fe(*o*-$SC_6H_4CHNR)_2$] were prepared by using the appropriate amines: R = *p*-MeC_6H_4 (maroon crystals, 65%), Ph(maroon crystals, 60%), Bu^t (red crystals, 65%, recrystallized from $CHCl_3$–n-hexane).

(*b*) Iron pentacarbonyl (392 mg, 2 mmol) dissolved in toluene (40 cm^3) was added to a solution of (6; R = *p*-$MeOC_6H_4$) (972 mg, 2 mmol) in toluene (10 cm^3) and the mixture refluxed until CO evolution had ceased. The complex was precipitated by addition of n-hexane (40 cm^3) and the crude product recrystallized from ethanol (45%).

Carbonyl[NN′-*ethylenebis(thiosalicylideneiminato)*](*pyridine*)*iron*(II), [Fe(tsalen)(CO)(py)]. [Fe(tsalen)] (300 mg, 0.85 mmol) was dissolved in pyridine (20 cm^3) and carbon monoxide bubbled through the solution for 1 h. The resulting deep red solution was filtered and n-heptane added dropwise to the solution. The precipitate was filtered off, washed with n-heptane, and dried under vacuum to yield burgundy-red crystals of the complex (272 mg, 72%).

The complex [Fe(tsalphen)(CO)(py)] was isolated as purple-red crystals (90% yield) by slow diffusion of n-heptane into a pyridine solution.

Iron(III) *Complexes.—Bis*[N-(2-*aminoethyl)thiosalicylideneiminato*]*iron*(III) *chloride*, [Fe(Haetsaln)$_2$]Cl. Ethylenediamine (60 mg, 1.0 mmol) in cold methanol (10 cm^3) was added to a cold solution of Htsal (276 mg, 2.0 mmol) in methanol (50 cm^3). After stirring this solution for 5 min, $FeCl_3$ (163 mg, 1.0 mmol) in benzene or dry diethyl ether (50 cm^3) and triethylamine (202 mg, 2 mmol) in methanol (10 cm^3) were added to the solution. After stirring for 15 min the solution volume was reduced and the tridentate complex precipitated as brown needles (43% yield). I.r. spectrum: 1 615, 1 540 [ν(C=N)]; 3 200, 3 090 cm^{-1} [ν(N–H)].

Bis[*N*-(3-aminopropyl)thiosalicylideneiminato]iron(III) chloride and [Fe(Hametsaln)$_2$]Cl (both 30% yield) were similarly prepared. Both these complexes precipitated as monomethanol solvates. The MeOH molecules were removed by heating *in vacuo* at temperatures above 100 °C. They each show a broad band in the i.r. centred at 3 400 cm^{-1} due to the presence of MeOH, together with the bands ν(C=N) 1 616, 1 541 [$(CH_2)_3NH_2$]; 1 616, 1 540 ($CHMeCH_2NH_2$); ν(NH) 3 200, 3 090 cm^{-1}.

μ-*Oxo-bis*{[NN′-*ethylenebis(thiosalicylideneiminato)*]*iron*(III)}, [{Fe(tsalen)}$_2$O]. [Fe(tsalen)] (300 mg, 0.85 mmol) was dissolved in pyridine (20 cm^3) under a nitrogen atmosphere and the solution filtered. Oxygen was bubbled through the solution. Black crystals began to separate after several minutes. The stream of oxygen was continued for 1 h, after which the solution was filtered, the crystalline product (255 mg, 75%) washed with ethanol and dried under vacuum. The compound separated containing one mole of pyridine.

The use of γ-picoline as solvent resulted in the formation of the picoline solvate. Reaction also occurred in 1-methylimidazole but a crystalline product could not be isolated.

Similar procedures were followed to isolate the tsalphen and tsalpd derivatives, also as black crystals. The phenylene complex separated readily as a mono-pyridine solvate, [{Fe(tsalphen)}$_2$O], whereas the propane-1,3-diyl derivative required precipitation by the addition of n-heptane. It did not contain any additional solvent molecules.

Experiments on Oxygen Reactivity with Iron(III) *Complexes.*—(*a*) *E.s.r. measurements.* A solution of the iron complex (*ca.* 1.5 mmol) in pyridine was prepared under nitrogen and the solution cooled to 250 K. The solution was kept at this temperature for at least 30 min, then oxygen was bubbled through the solution for a further 5 min. An aliquot of this solution was transferred under oxygen to a pre-cooled e.s.r. tube and held in a 195 K cold-bath until placed in the e.s.r. spectrometer cavity cooled to 77 K.

(*b*) *Oxygen absorption.* Oxygen uptake was determined using a modified version of an apparatus previously described.[48] The Fe^{II} complex was added to a small bucket which was placed in a modified Schlenk solids container, fitted to a flask containing pyridine which could be agitated by a magnetic stirrer. The flask was then attached to the gas burette apparatus, cooled to 250 K, and the solution allowed to equilibrate with oxygen at 1 atm. The Schlenk container was rotated to place the bucket in the pyridine, and the change in volume measured.

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