Iron Complexes of *N*-Substituted Thiosalicylideneimines. Part 4.[1] Preparation, Structure,† and Reactivity of Pentadentate [*N*,*N*′-4-Azaheptane-1,7-diylbis-(thiosalicylideneiminato)]iron(II) Derivatives

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The complex [*N*,*N*′-4-azaheptane-1,7-diylbis(thiosalicylideneiminato)]iron(II), [Fe(tsalah)], and the 4-methyl-4-azaheptane derivative, [Fe(tsalmah)], have been prepared by reaction of the parent thiosalicylaldehyde (Htsal) complex, [Fe(tsal)$_2$], with the appropriate amine. The molecular structure of [Fe(tsalmah)] has been determined. The compound crystallizes from dimethylformamide–ethanol in space group $P2_1/n$ with unit-cell dimensions a = 21.018(9), b = 13.015(7), c = 15.476(8) Å, β = 91.98(9)°, and Z = 8. The structure has been refined to R = 0.071 and R' = 0.061 on the basis of 1 576 independent reflections. The molecule has a distorted trigonal-bipyramidal structure with the two S atoms and the aza N atom in the trigonal plane. The complexes are high spin and react with CO. Molecular oxygen causes rapid decomposition with the formation of the disulphides of the ligands.

Iron(III) derivatives of tetradentate thiosalicylideneimines differ from their high-spin oxygen-donor salicylideneimine counterparts in that they show intermediate spin properties[2] and react with CO to form diamagnetic species such as [Fe(py)(tsalen)(CO)] (py = pyridine).[3] Both classes of complexes react with oxygen, however, to yield μ-oxo homobinuclear species such as [{Fe(salen)}$_2$O] and [{Fe(tsalen)}$_2$O][3] although the spin states of the Fe^{III} ions in each complex are different.[2,4]

The Fe^{II} complexes of the oxygen-donor pentadentate salicylideneimines H$_2$salah and H$_2$salmah show similar high-spin magnetic properties to those of the related tetradentate complexes, *e.g.* [Fe(salen)], and also react with oxygen to form μ-oxo complexes.[5]

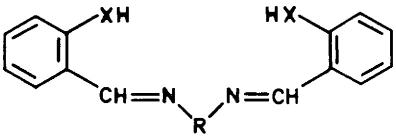
The analogous Fe^{II} compounds with the pentadentate thiosalicylideneimine ligands H$_2$tsalah and H$_2$tsalmah have now been prepared in order to compare the influence of substituting S for O in such molecules.

Results and Discussion

Synthesis, Spectral and Magnetic Data.—The procedure previously used for the successful synthesis of Ni^{II},[6] Co^{II},[7] and Fe^{II} [3] thiosalicylideneimines was employed. The thiosalicylaldehyde (Htsal) complex [Fe(tsal)$_2$] was refluxed with the appropriate di(3-aminopropyl)amine in 2-methoxyethanol with careful exclusion of air and the products obtained as deep red crystalline products on reduction of volume of solvent. Both complexes are readily soluble in polar solvents such as pyridine, 2-methoxyethanol, dichloromethane, and dimethylformamide, poorly soluble in ethanol and insoluble in toluene, hexane, and diethyl ether. The tetradentate derivatives were found to be only sparingly soluble in pyridine and other donor solvents.

The i.r. spectra of the molecules show the general features of salicylideneimine complexes, notably the three major peaks in the 1 500—1 650 cm^{-1} region assignable to combination of C=N and C=C stretching frequencies. The 4-azaheptane derivative also displays a sharp band at 3 280 cm^{-1} arising from the N–H bond vibration.

Both complexes display broad absorption bands in their visible spectra in CH$_2$Cl$_2$ with maxima at 556 and 375 nm for each. There is virtually no change in the positions of the absorption maxima in pyridine indicating only weak interaction between Fe and that Lewis base.



Ligand names and abbreviations

X = O, R = CH$_2$CH$_2$: *N*,*N*′-ethane-1,2-diylbis(salicylideneimine) (H$_2$salen)
X = O, R = (CH$_2$)$_3$NH(CH$_2$)$_3$: *N*,*N*′-4-azaheptane-1,7-diylbis(salicylideneimine) (H$_2$salah)
X = O, R = (CH$_2$)$_3$NCH$_3$(CH$_2$)$_3$: *N*,*N*′-4-methyl-4-azaheptane-1,7-diylbis(salicylideneimine) (H$_2$salmah)
X = S, R = CH$_2$CH$_2$: *N*,*N*′-ethane-1,2-diylbis(thiosalicylideneimine) (H$_2$tsalen)
X = S, R = CH$_2$CH$_2$CH$_2$: *N*,*N*′-propane-1,3-diylbis(thiosalicylideneimine) (H$_2$tsalpd)
X = S, R = (CH$_2$)$_3$NH(CH$_2$)$_3$: *N*,*N*′-4-azaheptane-1,7-diylbis(thiosalicylideneimine) (H$_2$tsalah)
X = S, R = (CH$_2$)$_3$NCH$_3$(CH$_2$)$_3$: *N*,*N*′-4-methyl-4-azaheptane-1,7-diylbis(thiosalicylideneimine) (H$_2$tsalmah)

The deep red colour of the five-co-ordinate compounds in solution corresponding to the absorption at 556 nm recalls the observation[3] that blue-black solutions of [Fe(tsalen)], although showing little spectral evidence for co-ordination of pyridine at room temperature, change colour to red on cooling with an accompanying shift in absorption peak from 470 to 508 nm. The change was ascribed to pyridine co-ordination and is thus in line with the spectral behaviour of the pentadentate chelate complexes being discussed.

The complexes each show molecular ions in their mass spectra as the most intense (100%) peaks. Fragmentation of the complex and the thiosalicylideneiminate ligand is evident but a peak corresponding to the metal-free (disulphide) ligand was not observed.

The room-temperature magnetic moments indicate that each complex contains high-spin Fe^{II} {$\mu_{eff.}$ = 5.06 for [Fe(tsalah)],

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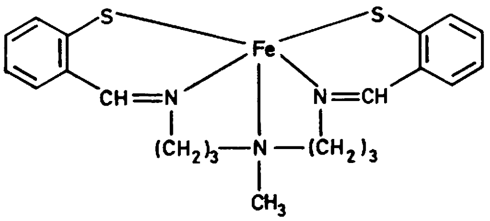
† *Supplementary data available* (No. SUP 56600, 6 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Selected interatomic distances (Å) and bond angles (°) for molecules 1 and 2 of [Fe(tsalmah)] *

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
Fe(1)–S(11)	2.325(6)	Fe(2)–S(21)	2.355(6)	N(13)–C(114)	1.30(2)	N(23)–C(214)	1.30(3)
Fe(1)–S(12)	2.351(6)	Fe(2)–S(22)	2.340(6)	N(13)–C(121)	1.49(2)	N(23)–C(221)	1.51(3)
Fe(1)–N(11)	2.11(2)	Fe(2)–N(21)	2.12(2)	C(11)–C(16)	1.42(3)	C(21)–C(26)	1.43(3)
Fe(1)–N(12)	2.20(1)	Fe(2)–N(22)	2.23(2)	C(16)–C(17)	1.46(3)	C(26)–C(27)	1.45(3)
Fe(1)–N(13)	2.14(2)	Fe(2)–N(23)	2.15(2)	C(116)–C(117)	1.50(3)	C(216)–C(217)	1.54(3)
S(11)–C(11)	1.73(2)	S(21)–C(21)	1.74(2)	C(117)–C(118)	1.54(3)	C(217)–C(218)	1.54(3)
S(12)–C(18)	1.76(2)	S(22)–C(28)	1.75(2)	C(119)–C(120)	1.55(3)	C(219)–C(220)	1.57(4)
N(11)–C(17)	1.29(2)	N(21)–C(27)	1.28(2)	C(120)–C(121)	1.52(3)	C(220)–C(221)	1.47(3)
N(11)–C(116)	1.49(2)	N(21)–C(216)	1.46(2)	C(18)–C(113)	1.40(3)	C(28)–C(213)	1.39(3)
N(12)–C(115)	1.45(3)	N(22)–C(215)	1.45(3)	C(113)–C(114)	1.43(3)	C(213)–C(214)	1.43(3)
N(12)–C(118)	1.48(3)	N(22)–C(218)	1.47(3)	S(11)–S(12)	4.23(1)	S(21)–S(22)	4.18(1)
N(12)–C(119)	1.49(3)	N(22)–C(219)	1.43(3)				

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
S(11)–Fe(1)–S(12)	129.4(2)	S(21)–Fe(2)–S(22)	125.7(2)	Fe(1)–N(12)–C(119)	111.8(12)	Fe(2)–N(22)–C(219)	112.9(16)
S(11)–Fe(1)–N(11)	91.0(4)	S(21)–Fe(2)–N(21)	90.9(5)	Fe(1)–N(13)–C(114)	130.6(12)	Fe(2)–N(23)–C(214)	130.4(14)
S(11)–Fe(1)–N(12)	117.2(4)	S(21)–Fe(2)–N(22)	120.3(5)	Fe(1)–N(13)–C(121)	112.1(11)	Fe(2)–N(23)–C(221)	110.3(12)
S(11)–Fe(1)–N(13)	88.3(4)	S(21)–Fe(2)–N(23)	90.0(4)	S(11)–C(11)–C(16)	126.2(14)	S(21)–C(21)–C(26)	126.1(14)
S(12)–Fe(1)–N(11)	93.9(4)	S(22)–Fe(2)–N(21)	94.9(4)	C(11)–C(16)–C(17)	127.2(17)	C(21)–C(26)–C(27)	126.8(17)
S(12)–Fe(1)–N(12)	113.3(4)	S(22)–Fe(2)–N(22)	113.9(5)	C(16)–C(17)–N(11)	128.2(17)	C(26)–C(27)–N(21)	130.0(17)
S(12)–Fe(1)–N(13)	89.6(4)	S(22)–Fe(2)–N(23)	90.8(5)	N(11)–C(116)–C(117)	111.4(15)	N(21)–C(216)–C(217)	108.0(16)
N(11)–Fe(1)–N(12)	88.1(6)	N(21)–Fe(2)–N(22)	86.5(6)	C(116)–C(117)–C(118)	114.8(16)	C(216)–C(217)–C(218)	115.0(18)
N(11)–Fe(1)–N(13)	176.1(6)	N(21)–Fe(2)–N(23)	172.4(6)	C(117)–C(118)–N(12)	114.8(18)	C(217)–C(218)–N(22)	117.1(18)
N(12)–Fe(1)–N(13)	88.8(6)	N(22)–Fe(2)–N(23)	86.5(6)	N(12)–C(119)–C(120)	113.7(17)	N(22)–C(219)–C(220)	109.6(21)
Fe(1)–S(11)–C(11)	111.5(7)	Fe(2)–S(21)–C(21)	113.6(7)	C(119)–C(120)–C(121)	119.7(17)	C(219)–C(220)–C(221)	120.8(20)
Fe(1)–S(12)–C(18)	110.5(7)	Fe(2)–S(22)–C(211)	115.7(3)	C(120)–C(121)–N(13)	109.7(14)	C(220)–C(221)–N(23)	109.7(17)
Fe(1)–N(11)–C(17)	130.7(12)	Fe(2)–N(21)–C(27)	132.5(13)	N(13)–C(114)–C(113)	127.0(17)	N(23)–C(214)–C(213)	128.5(19)
Fe(1)–N(11)–C(116)	112.7(11)	Fe(2)–N(21)–C(216)	113.1(12)	C(114)–C(113)–C(18)	129.1(17)	C(214)–C(213)–C(28)	128.3(19)
Fe(1)–N(12)–C(115)	115.3(12)	Fe(2)–N(22)–C(215)	111.2(14)	C(113)–C(18)–S(12)	124.9(14)	C(213)–C(28)–S(22)	126.9(16)
Fe(1)–N(12)–C(118)	111.8(12)	Fe(2)–N(22)–C(218)	108.4(13)				

* The labelling scheme is such that the first figure after the atomic symbol designates the molecule (1 or 2) to which the atom belongs.



[Fe(tsalmah)]

5.15 for [Fe(tsalmah)]} as do the analogous oxygen-donor complexes.[5] Bis-bidentate thiosalicylideneiminate Fe^{II} complexes are also high-spin molecules[2] while those tetradentate ligands, *e.g.* tsalen, best able to provide a square-planar field about Fe^{II}, produce spin pairing and give rise to molecules of intermediate low-spin characteristics.[2] The tetradentate ligand having a propane-1,3-diyl linkage (tsalpd) which would allow the ligand to adopt a non-planar configuration about a metal, shows a notably higher magnetic moment than other tetradentate complexes.[2]

Since oxygen-donor tetradentate salicylideneiminate Fe^{II} complexes have been found to be high spin, it seems clear that a combination of S-donor and four-co-ordinate square-planar field is necessary to bring about spin pairing in the Fe^{II} thiosalicylideneiminate complexes in the absence of contributions by other ligands. It should be noted that low-spin complexes are formed by Fe^{III} in the five-co-ordinate, [Fe(tsalen)Cl],[1] and six-co-ordinate bis-tridentate thiosalicylideneiminate Fe^{III}[3,8] complexes, illustrating the important role of the charge on the metal ion in determining the spin state of an Fe complex even when S-donor sites are involved.

Structure of [Fe(tsalmah)].—The structure of [Fe(tsalmah)] has been determined. The Fe atom is at the centre of a distorted trigonal-bipyramidal array of two S and three N atoms. The asymmetric unit of the complex contains two molecules, 1 and 2, differing only slightly in molecular parameters. A molecular drawing of molecule 1 is shown in the Figure. The equatorial plane is defined by the donor atoms S(11), S(12), and N(12) with the azomethine nitrogen atoms N(11) and N(13) occupying the axial positions. This type of trigonal-prismatic structure has also been observed for the analogous O_2N_3-donor complex [Fe^{II}(salmah)][9] as well as for [Ni(salah)],[10] [Ni(salmah)],[11] and [Co(salmah)].[12] Representative bond distances and angles in molecules 1 and 2 of [Fe(tsalmah)] are listed in Table 1. The two axial and the equatorial Fe–N distances for each type of molecule are slightly longer than the corresponding distances in [Fe(salmah)][9] while the S–Fe–S angles are smaller than the O–Fe–O angle (136.9°).

The S–S distances are larger than twice the van der Waals radius for S and therefore no S–S bonding contribution can be contemplated in the complex. The formation of the disulphide of the ligand when oxygen reacts with the complex as described later must therefore be accompanied by a major reorganization of the ligand structure during or after the oxidation step producing the disulphide.

The remaining S–Fe–N angles in the trigonal plane are larger than the corresponding O–Fe–N angles (111.3 and 111.8°). The axial N–Fe–N angles are slightly less than 180° as is also found for the N–Fe–N angle in [Fe(salmah)]. The Fe–S distances are greater than those found in the spin-paired complexes [Fe(py)(tsalen)(CO)][3] (av. 2.27 Å) and [Fe^{III}(tsalen)Cl] (av. 2.20 Å).[1] The strain inherent in the molecular configuration adopted by the ligand is shown in the bond angles of the C

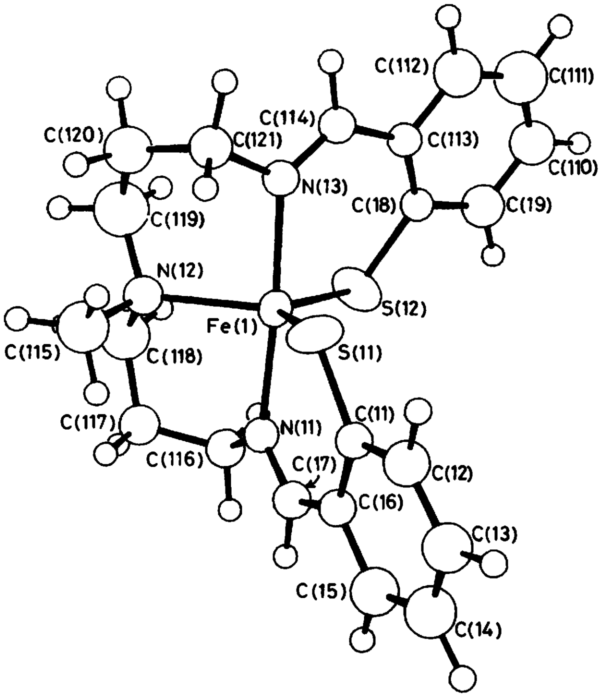


Figure. Molecular structure of [Fe(tsalmah)] (molecule 1). Thermal ellipsoids are drawn at the 50% probability level, except hydrogens which are drawn as spheres of arbitrary radius for clarity

atoms in the trimethylene chains which exceed the tetrahedral angle by up to 10° in several instances [*e.g.* C(119)–C(120)–C(121), 119.7°].

The Fe atoms lie somewhat out of the mean free planes defined by the sulphur atoms and N(12) or N(22) in molecules 1 or 2. The displacement is towards N(11) and N(21) respectively (Table 2). By contrast, the Fe^{II} ion in [Fe(salmah)] lies essentially within the corresponding O_2N plane of that compound.

Reactions with Carbon Monoxide.—The pentadentate thiosalicylideneiminate Fe^{II} complexes dissolved in pyridine or dichloromethane react readily with carbon monoxide to yield dark red complexes which can be precipitated from solution by addition of hexane. The solid products show strong i.r. spectral bands at 1 922 cm^{-1}, [Fe(tsalah)(CO)], and 1 942 cm^{-1}, [Fe(tsalmah)(CO)], indicating the presence of co-ordinated CO. The band due to the N–H bond has shifted to 3 160 cm^{-1} in the tsalah complex. The co-ordination of CO is not reversed in CH_2Cl_2 solution by passing nitrogen through the solution for some time but CO can be displaced by this technique in pyridine solution. Solutions of the CO complexes in each solvent have been found to decompose readily on exposure to the atmosphere just as do solutions of the parent Fe^{II} compounds.[3] The complexes isolated from solution are found to occlude solvent molecules and have not been obtained analytically pure. The magnetic moments of the isolated solid products are higher ($\mu_{eff.} > 1$) than would be expected for such d^6 Fe^{II} compounds when temperature-independent paramagnetism is expected to be the only source of paramagnetism.[3] Incorporation of small amounts of unreacted high-spin Fe^{II} complexes in the products could be the major cause of the paramagnetism.

Reaction with Oxygen.—The tetradentate thiosalicylideneiminate Fe^{II} complexes react with oxygen in pyridine solution to form μ-oxo-bridged complexes. Indeed, [{Fe(tsalen)}$_2$O] crystallizes from solution as reaction proceeds, whereas [{Fe(tsalpd)}$_2$O] remains in solution.[3] Both these oxo complexes decompose further in solution on exposure to air, [{Fe(tsalpd)}$_2$O] more readily than [{Fe(tsalen)}$_2$O], yielding the disulphides derived from the ligands together with hydrated iron oxides.

The pentadentate thiosalicylideneiminate Fe^{II} compounds also react readily with oxygen in pyridine solution but μ-oxo compounds have not been isolated in a pure state. Extensive decomposition of the complexes occurs in the presence of oxygen as evidenced by the rapid disappearance of the absorption band at 546 nm shown by each complex. The addition of hexane to such an 'oxidised' solution of [Fe(tsalah)] gave a hygroscopic precipitate having a high Fe and low S content which was found to be heterogeneous by electron microprobe examination. Infrared spectral examination did not disclose any substantial organic component in the product although its mass spectrum showed a peak corresponding to the $[Fe(tsalah)]^+$ molecular ion as well as some peaks of higher *m/e* values. The authentic μ-oxo derivatives [{Fe(tsalpd)}$_2$O] and [{Fe(tsalphen)}$_2$O][tsalphen = *N,N'-o*-phenylenebis(thiosalicylideneiminate)] fail to give molecular ions but do show ions corresponding to the monomer units, $[Fe(tsalpd)]^+$ *etc.*, as their most intensive peaks together with some peaks of higher *m/e* values, presumably resulting from the breakdown of the parent oxo complexes. Very weak peaks due to the disulphides of the ligands (L) can be observed (< 2% of $[FeL]^+$ intensities) in each case. The product from the reaction of [Fe(tsalah)] with oxygen does however show a significant peak corresponding to the *m/e* value for the disulphide {120% of the $[Fe(tsalah)]^+$ peak height}. The filtrate from this precipitation process contains a material showing an intense mass spectral peak corresponding to the presence of the disulphide. This fraction of the reaction product, however, also displays a much weaker peak corresponding to the $[Fe(tsalah)]^+$ ion.

These results indicate a rapid decomposition of the Fe^{II} complex [Fe(tsalah)] by oxygen to give the disulphide of the ligand as a major product together presumably with a hygroscopic iron oxide by-product. However, the observation of mass spectral peaks due to the $[Fe(tsalah)]^+$ ion together with a number of higher *m/e* values in the isolated products is consistent with the separation of some μ-oxo complex which had not completely decomposed at the time of separation of the products.

A possible sequence for the reaction is shown below, assuming the formation of μ-oxo complexes follows the route *via* peroxo Fe^{III} and Fe^{IV} formation found for the oxidation of Fe^{II} porphyrins.[13]

$$2[Fe^{II}L] + O_2 \rightleftharpoons [LFe^{III}\text{–}O_2\text{–}Fe^{III}L] \rightleftharpoons 2[LFe^{IV}O]$$

$$[LFe^{IV}O] + [Fe^{II}L] \rightleftharpoons [LFe^{III}\text{–}O\text{–}Fe^{III}L]$$

$$[LFe^{IV}O] \longrightarrow Fe^{II}O + L \text{ as disulphide}$$

Experimental

The synthesis of thiosalicylaldehyde and the chemical and instrumental techniques used in studying thiosalicylideneiminate Fe^{II} complexes have previously been described.[3] Electron microprobe analyses were made with a Cambridge S410 scanning electron microscope linked to a Packard Multi Channel Analyzer. Mass spectra were recorded with a V.G. Micromass 7070F instrument.

Bis(thiosalicylaldehydato)iron(II), [Fe(tsal)$_2$].—The reported synthesis of this complex[3] used anhydrous iron(II) acetate reacting with thiosalicylaldehyde. In view of the air-reactivity of Fe^{II} acetate an alternative synthesis was devised using the less air-sensitive $[Fe(py)_4(SCN)_2]$[14] as the Fe^{II} reagent.

Table 2. Least-squares planes (X, Y, Z in Å) in [Fe(tsalmah)] and distances (Å) of Fe(1) and Fe(2) from their respective planes*

Plane 1 $0.0822X + 0.7506Y - 0.6557Z - 3.4633 = 0$
Plane 2 $-0.1628X - 0.7719Y - 0.6146Z + 4.8261 = 0$

Plane 1		Plane 2	
S(11)	0.000(6)	S(21)	0.000(6)
S(12)	0.000(6)	S(22)	0.000(6)
N(12)	0.000(16)	N(22)	0.000(18)
Fe(1)	−0.045(3)	Fe(2)	0.034(3)

* The iron is displaced towards N(11) or N(21) respectively.

Dry, deoxygenated ethanol (50 cm^3) was added to [Fe(py)$_4$(NCS)$_2$] (2.06 g, 4 mmol) followed by a solution of triethylamine (1.10 g, 10 mmol) and thiosalicylaldehyde (1.22 g, 8.8 mmol) in further ethanol (50 cm^3). The mixture was refluxed under nitrogen for 30 min and then cooled to 0 °C. After standing for 1 h at this temperature the precipitated solid was filtered off and the product washed with ethanol and dried at 10^{-3} Torr (*ca.* 0.13 Pa). Yield: 1.2 g (92%).

[N,N′-4-*Azaheptane*-1,7-*diylbis*(*thiosalicylideneiminato*)]-*iron*(II), [Fe(tsalah)].—[Fe(tsal)$_2$] (0.66 g, 2 mmol) was suspended in dry, deoxygenated 2-methoxyethanol (30 cm^3), di(3-aminopropyl)amine (0.284 g, 2.2 mmol) was added with further solvent (50 cm^3) and the mixture refluxed for 45 min. After cooling the solution was filtered and the volume reduced until crystallization began. The mixture was then cooled in ice. The red-black product was filtered under nitrogen, washed with dry, deoxygenated ethanol and dried *in vacuo*. Yield: 0.42 g (50%) (Found: C, 56.6; H, 5.23; N, 10.1. Calc. for $C_{20}H_{23}FeN_3S_2$: C, 56.5; H, 5.55; N, 9.90%). I.r. (Nujol) [very strong (vs), strong (s), medium (m) peaks only]: 3 280m, 1 627vs, 1 595vs, 1 547s, 1 414s, 1 314m, 1 257s, 1 206m, 1 159m, 1 127m, 1 104m, 1 086s, 1 072m, 1 036s, 1 000m, 972s, 932m, 896m, 880m, 869m, 826m, 768vs, 754vs, and 692s cm^{-1}. Mass spectrum: m/e = 425 (100%, M^+), 392 (22), 322 (48), 294 (14), 287 (29), 274 (29), 261 (38), 248 (15), 220 (10), 207 (15), 192 (20), 177 (10), 164 (12), 149 (10), 135 (36), 121 (17), 105 (15), 91 (32), 77 (15), 69 (28), and 56 (15). No peak at m/e = 369 (ligand disulphide) detected.

[N,N′-4-*Methyl*-4-*azaheptane*-1,7-*diylbis*(*thiosalicylideneiminato*)]*iron*(II), [Fe(tsalmah)].—This was prepared by essentially the same procedure except that dimethylformamide was used as the solvent and di(3-aminopropyl)methylamine as the amine. The product was quite soluble in the solvent used and dry hexane was finally added to precipitate the product as red-black crystals. Yield: 0.35 g (40%) (Found: C, 57.0; H, 5.65; N, 9.35. Calc. for $C_{21}H_{25}FeN_3S_2$: C, 57.4; H, 5.75; N, 9.55%). I.r. (Nujol): 1 612vs, 1 583vs, 1 532s, 1 413s, 1 323m, 1 278m, 1 266m, 1 199m, 1 166m, 1 133s, 1 076s, 1 056m, 1 036m, 1 010m, 969m, 871m, 840m, 759vs, and 691s cm^{-1}. Mass spectrum: m/e = 439 (100%, M^+), 289 (11), 276 (14), 263 (26), 220 (12), 192 (10), 178 (10), and 135 (15). A peak at m/e = 383 (ligand disulphide) was <0.2% of the M^+ peak.

Reaction with Oxygen.—Dry oxygen was passed into a solution of [Fe(tsalah)] (0.15 g) in pyridine (10 cm^3). The dark red solution initially became darker but within 1 min the colour had changed to light brown and eventually after bubbling oxygen for 30 min the solution had become a clear yellow-brown. No obvious solid precipitate had formed at this stage. Hexane (20 cm^3) was added to the solution and a dark brown powder was deposited. The solid was collected under dry oxygen and then dried *in vacuo*. The final product (A) was hygroscopic and its i.r. spectrum, obtained as a Nujol mull, showed pronounced OH bands in the 3 440 cm^{-1} region but only slight indications of bands around 1 600 cm^{-1} due to organic moieties. Electron microprobe examination of (A) indicated that it was a heterogeneous mixture with varying Fe:S ratios, the maximum being 1:0.6. The mass spectrum of (A) contained peaks common to the starting material [Fe(tsalah)] although the molecular ion peak at 425 was no longer the dominant feature. An additional peak corresponding to the disulphide of the ligand (m/e = 369) was also present (samples collected after reaction at −77 °C appeared to contain more of this material). Low-intensity peaks (10% of peak at 425) were also found in the region m/e = 430—580.

The filtrate from the above reaction was evaporated to dryness leaving a light yellow solid (B). I.r. (Nujol): 3 060w, 1 640vs, 1 595vs, 1 583m, 1 300w, 1 270m, 1 220m, 1 162s, 1 138m, 1 086s, 1 040s, 1 000m, 976w, 950w, 911w, 892m, 878m, 869m, 761vs, and 685m cm^{-1}.

The most intense peak in the mass spectrum of (B), m/e = 135, corresponds to SC_6H_4CHN. Peaks with higher m/e values occur with decreasing intensity with the peak corresponding to the disulphide molecular ion (m/e = 369) being only a few percent of the intensity of the peak at 135. Peaks at m/e = 149, 163, 177, 192, 206, 220, 234, 248, 261, and 337 correspond to the fragmentation of the disulphide. Peaks of lower intensity than that at 369 occur at higher m/e values with a peak at m/e = 425 indicating the presence of some iron complex.

In a similar experiment at −77 °C in CH_2Cl_2 the [Fe(tsalah)] solution rapidly darkened on entry of oxygen and this colouration remained for a considerable period without lightening. Deoxygenating the solvent by bubbling through N_2 for some time (30 min) did not reverse the colouration and if the dark solutions (under O_2 or N_2) were allowed to warm the solutions lightened as described above.

Addition of hexane to the dark solutions obtained at low temperature produced a somewhat darker brown solid precipitate than that recovered from the room-temperature experiments. The material was again inhomogeneous and had similar spectral properties to those already discussed. The filtrate yielded a similar yellow product on evaporation.

Comparable behaviour was observed when 2-methoxyethanol was used as solvent.

Mass Spectra of [{Fe(tsalpd)}$_2$O] *and* [{Fe(tsalphen)}$_2$O].—Samples of oxo complexes were prepared as previously described.[3] [{Fe(tsalpd)}$_2$O]: m/e = 368 [100%, Fe(tsalpd)], 233 (13), 192 (20), 190 (22), 178 (23), 164 (10), 159 (10), 150 (12), 135 (16), 121 (15), 91 (10), and 56 (20). The peak corresponding to the disulphide (m/e = 312) was *ca.* 1% of that of Fe(tsalpd). Peaks above m/e = 368 were <1% (378 and 474). [{Fe(tsalphen)}$_2$O]: m/e = 402 [100%, Fe(tsalphen)], 376 (10), 338 (15), 314 (12), 237 (18), 224 (60), 201 (14), 190 (14), 184 (16), 135 (13), 121 (10), 108 (10), 77 (14), 69 (36), 64 (18), and 56 (20). The peak corresponding to the disulphide (m/e = 346) was *ca.* 1% of that of Fe(tsalphen). Peaks above m/e = 402 were < 1% (416, 431, 449, 475, 508, and 541).

Reaction with Carbon Monoxide.—The complexes [Fe(tsalah)] or [Fe(tsalmah)] were dissolved in pyridine or dichloromethane and CO passed through the solutions for 1 h. Dry hexane (40 cm^3) was then added to precipitate red-brown solid products. The solids were filtered off and pumped dry at 10^{-3} Torr for 10 min. I.r. (Nujol): [Fe(tsalah)(CO)], 3 160m, 1 922vs, 1 606vs, 1 581vs, 1 542m, 1 306m, 1 252s, 1 212s, 1 150m, 1 098m, 1 082m, 1 068m, 1 058m, 1 028vs, 965m, 947s, 908m, 897m, 878m, and 761vs cm^{-1}; [Fe(tsalmah)(CO)], 1 942vs, 1 612vs, 1 590vs, 1 542s, 1 408m, 1 307m, 1 260s, 1 238s,

Table 3. Atomic parameters for [Fe(tsalmah)] with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	0.147 3(1)	0.521 0(2)	0.189 0(2)	C(21)	0.790 9(9)	−0.002 8(15)	0.060 0(12)
Fe(2)	0.660 6(1)	0.125 9(2)	0.134 5(2)	C(22)	0.856 8(9)	−0.024 5(16)	0.052 5(13)
S(11)	0.080 7(3)	0.434 5(5)	0.090 4(4)	C(23)	0.877 3(11)	−0.100 6(18)	0.000 2(14)
S(12)	0.121 5(3)	0.641 2(5)	0.295 6(3)	C(24)	0.836 1(11)	−0.164 5(18)	−0.042 7(24)
S(21)	0.771 0(3)	0.102 8(4)	0.122 6(4)	C(25)	0.772 4(10)	−0.152 3(15)	−0.031 7(12)
S(22)	0.596 1(3)	0.233 0(5)	0.047 3(4)	C(26)	0.747 2(9)	−0.073 5(14)	0.019 4(12)
C(11)	0.038 3(8)	0.338 5(14)	0.140 1(12)	C(27)	0.678 4(9)	−0.070 0(15)	0.021 1(11)
C(12)	−0.015 1(9)	0.299 1(15)	0.095 2(13)	C(28)	0.607 5(9)	0.363 1(16)	0.073 3(13)
C(13)	−0.054 7(10)	0.226 3(16)	0.127 7(13)	C(29)	0.579 2(9)	0.433 7(16)	0.012 2(13)
C(14)	−0.040 6(10)	0.185 0(16)	0.207 5(14)	C(210)	0.587 6(9)	0.536 7(18)	0.022 9(14)
C(15)	0.014 1(9)	0.216 2(16)	0.255 6(14)	C(211)	0.622 2(10)	0.576 9(17)	0.091 5(14)
C(16)	0.053 8(9)	0.292 7(14)	0.221 1(12)	C(212)	0.647 1(9)	0.510 1(15)	0.155 4(13)
C(17)	0.105 6(9)	0.321 0(15)	0.281 3(12)	C(213)	0.641 3(9)	0.402 5(15)	0.144 5(13)
C(18)	0.085 3(8)	0.750 5(14)	0.247 9(12)	C(214)	0.670 6(9)	0.347 5(16)	0.215 7(13)
C(19)	0.047 3(9)	0.808 2(16)	0.304 7(14)	C(215)	0.643 2(12)	−0.042 2(21)	0.270 9(16)
C(110)	0.018 3(10)	0.897 5(17)	0.275 2(15)	C(216)	0.574 1(9)	−0.028 5(17)	0.046 0(13)
C(111)	0.025 3(11)	0.928 4(19)	0.191 7(16)	C(217)	0.547 9(10)	−0.067 3(16)	0.131 4(14)
C(112)	0.060 4(10)	0.871 7(18)	0.133 8(14)	C(218)	0.547 1(10)	0.012 7(19)	0.204 3(15)
C(113)	0.089 6(8)	0.778 8(15)	0.160 7(12)	C(219)	0.590 2(13)	0.117 6(24)	0.306 2(19)
C(114)	0.126 0(8)	0.732 7(14)	0.094 7(12)	C(220)	0.651 0(11)	0.159 4(20)	0.356 5(15)
C(115)	0.268 2(10)	0.406 7(16)	0.131 1(14)	C(221)	0.703 1(10)	0.206 9(18)	0.310 1(14)
C(116)	0.192 7(8)	0.406 4(15)	0.349 1(12)	N(11)	0.146 1(7)	0.395 1(12)	0.274 7(9)
C(117)	0.259 9(8)	0.397 8(15)	0.320 5(12)	N(12)	0.250 2(7)	0.496 9(12)	0.179 0(10)
C(118)	0.282 5(10)	0.488 3(17)	0.264 8(13)	N(13)	0.153 3(6)	0.642 9(12)	0.097 2(9)
C(119)	0.281 7(11)	0.586 2(18)	0.138 1(15)	N(21)	0.642 0(7)	−0.008 0(12)	0.060 1(10)
C(120)	0.259 3(9)	0.605 0(17)	0.042 8(13)	N(22)	0.609 0(8)	0.048 1(14)	0.239 8(11)
C(121)	0.188 7(8)	0.611 7(15)	0.019 6(12)	N(23)	0.678 0(7)	0.248 9(13)	0.224 8(10)

1 210m, 1 161m, 1 136s, 1 082s, 1 058m, 1 038m, 1 011m, 983s, 937m, 890m, 877m, 843m, 823m, 758vs, and 750m cm^{-1}.

When nitrogen was passed through a solution of the product [Fe(tsalah)(CO)] in CH_2Cl_2 for 30 min and the solvent evaporated, the product recovered still showed a strong CO band at 1 922 cm^{-1}. A similar experiment in pyridine, however, gave a final solid product which no longer showed a band at 1 922 cm^{-1} but had the general i.r. features of [Fe(tsalah)].

The compounds were found to decompose rapidly in solution when exposed to air and were obtained from solution with solvent occlusions. Analytical data were generally poor {particularly for [Fe(tsalmah)] products} and somewhat irreproducible. Several of the better analyses are presented for comparison. [Fe(tsalah)CO)] from pyridine (Found: C, 57.1; H, 4.85; N, 10.1. Calc. for $C_{21}H_{23}FeN_3OS_2$·0.5 C_5H_5N: C, 57.1; H, 5.20; N, 9.90%). [Fe(tsalah)(CO)] from CH_2Cl_2 (Found: C, 48.7; H, 5.05; Cl, 11.0; N, 8.25; S, 12.7. Calc. for $C_{21}H_{23}FeN_3OS_2$·CH_2Cl_2: C, 49.1; H, 4,70; Cl, 13.2; N, 7.80; S, 11.9%). Magnetic moments were somewhat variable from sample to sample in line with the impure nature of the products but were generally found to be in the range $\mu_{eff.}$ = 1—3: *e.g.* [Fe(tsalmah)(CO)] from CH_2Cl_2, $\mu_{eff.}$ = 1.14; [Fe(tsalmah)-(CO)] from pyridine, $\mu_{eff.}$ = 2.78.

Structural Determination of [Fe(tsalmah)].—*Crystal data.* $C_{21}H_{25}FeN_3S_2$, M = 439.5, monoclinic, a = 21.018(9), b = 13.015(7), c = 15.476(8) Å, β = 91.98(9)°, U = 4 230.9 Å^3 (by least-squares refinement of diffractometer angles for 24 accurately centred reflections, λ = 0.7107 Å), space group $P2_1/n$, D_m = 1.38(2), Z = 8, D_c = 1.38 g cm^{-3}, $F(000)$ = 1 839.8. A representative dark red prismatic crystal was obtained from dimethylformanide–ethanol having dimensions (distance to faces from centre) 0.063 mm($111, 1\bar{1}\bar{1}, 1\bar{1}1, 110, \bar{1}10, \bar{1}\bar{1}0$, and $0\bar{1}0$); μ(Mo-K_α) = 8.8 cm^{-1}.

Data collection and processing. Intensity measurements were made on a Philips PW1100 diffractometer with graphite-monochromated Mo-K_α radiation with $6 < 2\theta \leqslant 60°$ operating in an ω-scan mode with a symmetric scan range of ± (1.30 + 0.2 tan θ)° in 2θ from the calculated Bragg scattering angle at scan rate of 0.07° s^{-1}. A total of 10 189 unique data were collected, 1 576 of which were considered to be observed [$I \geqslant 3\sigma(I)$]. The standard reflections monitored every 6 h showed no significant variation in intensity over the data collection period.

Intensity data were processed as described previously.[15] A numerical absorption correction was applied, the maximum and minimum transmission factors being 0.938 and 0.865 respectively. The atomic scattering factors for neutral atoms were corrected for anomalous dispersion using values from ref. 16. All calculations were performed on a DEC/VAX 11/780 computer. The SHELX 76 program[17] was used for least-squares refinement.

Structure analysis and refinement. The structure was solved by direct methods, the positions for two unique Fe and four S atoms being found in the first E-map. Subsequent difference-Fourier synthesis revealed the rest of the two molecules in the asymmetric unit. Full-matrix least-squares refinement employing anisotropic thermal parameters for Fe and S and isotropic thermal parameters for all other atoms, with hydrogen in geometrically idealized positions (C–H, 1.08 Å) and a common thermal parameter, reduced R to 0.071 and R' to 0.061 at convergence $\{R' = \Sigma w^{\frac{1}{2}}(||F_o| - |F_c||)/\Sigma w^{\frac{1}{2}}|F_o|$, with $w = [\sigma^2(F)]^{-1}\}$. Atomic parameters for all non-hydrogen atoms are given in Table 3, together with their estimated standard deviations.

Acknowledgements

This work was supported by a grant (to B. O. W.) from the Australian Research Grants Committee.

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Received 20th December 1985; *Paper* 5/2241