A Comparative Synthetic and Structural Study of μ-Oxo and μ-Sulphido Derivatives of *N,N'*-Ethylenebis(acetylacetoneiminato)iron(III), including the Synthesis and Structural Characterization† of the Parent Compound

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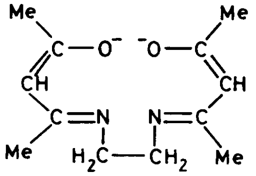
The synthesis of [{Fe(acen)}$_2$] (**1**) [acen = *N,N'*-ethylenebis(acetylacetoneiminate) dianion, $\mu_{eff.}$ = 4.84] was performed by treating anhydrous $FeCl_2$•1.5thf with H_2acen in the presence of Na(OMe). Complex (**1**) has a monomeric structure in solution (*M* = 288 in C_6H_6) but is dimeric in the solid state as shown by an *X*-ray analysis. It has good solubility in organic solvents. Iron(II) achieves five-co-ordination either through dimerization or by binding of a molecule of solvent, *e.g.* pyridine, to form [Fe(acen)(py)] (**2**). Complex (**1**) undergoes one-electron oxidation by molecular oxygen and elemental sulphur to form the corresponding iron(III) derivatives [{Fe(acen)}$_2$(μ-O)] (**3**) and [{Fe(acen)}$_2$(μ-S)] (**4**) respectively. In complexes (**3**) and (**4**) the two d^5 high-spin configurations are strongly antiferromagnetic [$\mu_{eff.}$ = 1.80 at 290 K for (**3**) and 2.16 at 293 K for (**4**)]. *X*-Ray analysis of (**3**) and (**4**) has allowed a comparison of the most significant parameters associated with the Fe–X–Fe backbone [Fe–O 1.775(13), Fe–S 2.210(3) and 2.204(2) Å; Fe–O–Fe 150.7(13), Fe–S–Fe 120.8(1)°].

Iron(II) Schiff-base complexes have long been one of the most investigated classes of organometallic compounds. Interest has centered mostly on the magnetic and spectroscopic properties of the metal as a function of the ligand and co-ordination number of the metal.[1] The reactivity of the metal site in terms of redox reactions[2] and organometallic derivatives[2a] has been relatively little explored, in spite of the fact that the ability of polydentate Schiff bases to provide a rather rich chemistry in these areas is well known.[3] A major difficulty encountered with some of the Fe(salen)-type complexes [salen = *N,N'*-ethylenebis(salicylideneiminate) dianion] is their low solubility in most organic solvents.

The purpose of this work was to find an iron(II)–quadridentate Schiff-base complex for use as a model compound for reactivity study. This first paper will deal with the synthesis of *N,N'*-ethylenebis(acetylacetoneiminato)iron(II), [Fe(acen)], which is an iron(II) chelate fairly soluble in organic solvents. Its oxidation to the corresponding iron(III) derivative was carried out using molecular oxygen and elemental sulphur. The resulting dinuclear compounds have dimeric structures with μ-oxo and μ-sulphido ligands, respectively, for which a comparative study was carried out. The Fe–O–Fe bridge is a constituent of synthetic iron complexes;[4–14] and is also of biological significance.[15] In contrast, the single bridge Fe–S–Fe has been structurally authenticated only recently[16] in [{Fe(salen)}$_2$(μ-S)] which was synthesized some years ago.[17,18]



acen

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Anhydrous $FeCl_2$•1.5thf (thf = tetrahydrofuran) was prepared from $FeCl_2$•$4H_2O$ by dehydration and recrystallization from thf. Its structure was recently published.[19] The ligand H_2acen was prepared as reported.[20] Infrared spectra were recorded with a Perkin-Elmer 983 spectrophotometer. Magnetic susceptibility was measured using a Faraday balance.

Synthesis of [Fe(acen)] (**1**).—A thf suspension (400 cm^3) of anhydrous $FeCl_2$•1.5 thf (70.4 g, 299.8 mmol) was treated with H_2acen (67.5 g, 300.9 mmol). The suspension was stirred for 2 h until a yellow solid formed. The addition of Na(OMe) (580.0 mmol) caused the solubilization of all solid except NaCl; the red solution was refluxed for 2 h. Sodium chloride was filtered off and the solution evaporated to dryness. The residue was dissolved in hot toluene (400 cm^3). The toluene solution, after standing at room temperature for 12 h, gave a crystalline red-green solid, [Fe(acen)] (**1**) (58.0 g, 72%) (Found: C, 51.95; H, 6.55; N, 9.95. Calc. for $C_{12}H_{18}FeN_2O_2$: C, 51.8; H, 6.50; N, 10.05%). The C=N stretching vibration (Nujol) is at 1 520 cm^{-1}; $\mu_{eff.}$ = 4.84 at 294 K. The complex is very sensitive to oxidation in solution, only slightly sensitive in the solid state. The molecular weight determined by cryoscopy in benzene was 288 (calc. 278).

Synthesis of [Fe(acen)(py)] (**2**).—Pyridine (1.5 cm^3) was added to a toluene solution (70 cm^3) of [Fe(acen)] (2.50 g, 9.0 mmol). The solution changed from green-red to deep red; after standing for 12 h at −35 °C it gave a black crystalline solid (2.0 g, 62%) of [Fe(acen)(py)] (Found: C, 57.9; H, 6.50; N, 11.8. Calc. for $C_{17}H_{23}FeN_3O_2$: C, 57.15; H, 6.50; N, 11.75%); ν(C=N) (Nujol) 1 500 cm^{-1}; $\mu_{eff.}$ = 4.95 at 295 K.

Reaction of [Fe(acen)] *with* O_2; *Synthesis of* [{Fe(acen)}$_2$(μ-O)] (**3**).—A thf solution (50 cm^3) of [Fe(acen)] (1.00 g, 3.59 mmol) was treated with dry O_2 in an apparatus which allowed the oxygen to diffuse very slowly into the thf solution. The solution changed from red-brown to red-orange

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

and gave on standing (12 h) a red crystalline solid (0.90 g, 43%) (Found: C, 50.05; H, 6.75; N, 9.60%. Calc. for $C_{24}H_{36}Fe_2N_4O_5$: C, 50.35; H, 6.35; N, 9.80%); ν(C=N) (Nujol) 1 515 cm^{-1}, ν(Fe–O–Fe) 840 cm^{-1}; $\mu_{eff.}$ = 1.80 at 290 K.

Reaction of [Fe(acen)] *with Elemental Sulphur.*—A toluene solution (70 cm^3) of crystalline sulphur (0.13 g, 4.06 mmol) was treated with [Fe(acen)] (1.12 g, 4.06 mmol). The red solution obtained gave on standing at room temperature a deep red crystalline solid (0.9 g, 37%) of [{Fe(acen)}$_2$(μ-S)] (**4**) (Found: C, 48.7; H, 6.05; N, 9.40; S, 5.30%. Calc. for $C_{24}H_{36}Fe_2N_4O_4S$: C, 49.0; H, 6.15; N, 9.50; S, 5.45%); ν(C=N) (Nujol) 1 507 cm^{-1}; $\mu_{eff.}$ = 2.16 per iron atom at 293 K.

Determination of the Structures.—*Crystal data.* Compoun (**1**) $(C_{12}H_{18}FeN_2O_2)_2$, M = 556.27, monoclinic, a = 11.687(4 b = 10.241(4), c = 12.237(6) Å, α = 118.07(5)°, U = 1 292. $Å^3$ (by least-squares refinement of diffractometer angles for 2 automatically centered reflections, λ = 0.710 69 Å), spac group $P2_1/n$ (no. 14), $Z = 2$, D_c = 1.429 g cm^{-3}, $F(000)$ = 58 Red-green crystals mounted in a 0.3-mm Lindemann capillar tube under nitrogen, μ(Mo-K_α) = 11.567 cm^{-1}.

Intensity data were collected on a CAD4 diffractomete θ—2θ scan, graphite-monochromated Mo-K_α radiation; 2 26 independent reflections measured [($\pm h$, $+k$, l); $2 < \theta < 24°$ 1 641 with $F > 2\sigma(F)$. No correction for absorbance wa applied. The structure was solved by direct method

Table 1. Final fractional co-ordinates for non-hydrogen atoms with estimated standard deviations in parentheses

Compound (**1**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Fe	−0.021 7(1)	0.156 2(1)	0.000 4(1)	C(5)	0.040 0(4)	0.251 4(4)	−0.325 0(4)
O(1)	0.120 7(2)	0.027 1(2)	0.017 4(2)	C(6)	−0.154 6(4)	0.277 9(3)	−0.242 6(3)
O(2)	0.009 1(2)	0.170 7(2)	0.173 2(2)	C(7)	−0.162 1(4)	0.386 7(3)	−0.160 8(4)
N(1)	−0.034 6(3)	0.204 3(3)	−0.170 6(3)	C(8)	−0.155 1(3)	0.398 0(3)	0.038 3(4)
N(2)	−0.127 5(3)	0.331 6(2)	−0.037 4(3)	C(9)	−0.223 3(4)	0.529 0(3)	0.001 5(5)
C(1)	0.195 5(3)	0.038 1(3)	−0.035 7(3)	C(10)	−0.123 0(4)	0.351 1(3)	0.159 3(3)
C(2)	0.311 7(3)	−0.048 8(3)	0.016 5(4)	C(11)	−0.049 8(3)	0.244 5(3)	0.216 9(3)
C(3)	0.168 3(3)	0.116 6(3)	−0.135 1(3)	C(12)	−0.030 9(4)	0.200 3(4)	0.342 6(4)
C(4)	0.055 1(4)	0.190 3(3)	−0.205 6(3)				

Compound (**3**)

Fe(1)	0.245 6(3)	0.499 0(3)	0.153 2(3)	C(8)	0.089 4(28)	0.658 1(30)	0.144 5(25)
Fe(2)	0.500 6(3)	0.753 8(3)	0.346 6(3)	C(9)	0.049 8(34)	0.765 9(36)	0.097 5(31)
O(1)	0.395 8(15)	0.603 0(15)	0.250 3(11)	C(10)	0.024 6(23)	0.594 2(25)	0.223 7(20)
O(2)	0.227 3(21)	0.319 5(16)	0.123 5(16)	C(11)	0.032 3(30)	0.498 4(34)	0.256 5(27)
O(3)	0.101 0(20)	0.433 9(22)	0.228 3(17)	C(12)	−0.052 9(34)	0.428 6(36)	0.339 2(29)
O(4)	0.680 7(16)	0.779 3(21)	0.378 0(13)	C(13)	0.741 8(24)	0.752 7(26)	0.450 6(20)
O(5)	0.571 1(20)	0.904 0(21)	0.274 0(15)	C(14)	0.883 9(38)	0.788 9(40)	0.437 4(32)
N(1)	0.307 0(19)	0.518 1(19)	0.012 7(12)	C(15)	0.686 6(35)	0.698 9(39)	0.535 4(30)
N(2)	0.170 2(17)	0.620 0(19)	0.105 1(14)	C(16)	0.562 4(28)	0.674 0(30)	0.551 6(23)
N(3)	0.476 2(20)	0.689 1(22)	0.493 0(19)	C(17)	0.526 6(33)	0.626 5(36)	0.655 4(29)
N(4)	0.379 0(19)	0.828 3(20)	0.399 6(14)	C(18)	0.340 8(32)	0.656 0(35)	0.501 7(30)
C(1)	0.256 1(32)	0.270 4(37)	0.030 7(29)	C(19)	0.316 6(25)	0.772 7(27)	0.480 6(23)
C(2)	0.210 3(41)	0.112 1(42)	0.042 8(36)	C(20)	0.347 7(23)	0.917 5(25)	0.352 1(20)
C(3)	0.304 2(24)	0.310 0(27)	−0.031 9(21)	C(21)	0.247 5(30)	0.959 5(31)	0.384 6(26)
C(4)	0.327 0(25)	0.447 5(26)	−0.062 2(22)	C(22)	0.414 0(34)	0.978 5(38)	0.281 0(31)
C(5)	0.372 2(26)	0.467 9(28)	−0.152 4(22)	C(23)	0.510 8(33)	0.975 7(34)	0.244 6(28)
C(6)	0.337 9(31)	0.658 0(32)	−0.003 7(26)	C(24)	0.585 3(45)	1.047 3(48)	0.179 7(39)
C(7)	0.222 5(30)	0.685 6(32)	0.016 1(26)				

Compound (**4**)

Fe(1)	0.330 8(1)	0.065 2(1)	0.252 1(1)	C(8)	0.036 9(13)	−0.149 6(11)	0.082 4(7)
Fe(2)	0.513 6(1)	0.434 8(1)	0.248 0(1)	C(9)	−0.041 0(16)	−0.220 6(15)	−0.018 1(9)
S(1)	0.301 0(3)	0.250 5(2)	0.250 4(2)	C(10)	−0.063 2(11)	−0.201 8(9)	0.136 4(8)
O(1)	0.491 5(7)	0.091 9(6)	0.373 8(4)	C(11)	−0.011 2(11)	−0.154 9(8)	0.229 4(7)
O(2)	0.141 0(7)	−0.054 7(6)	0.281 9(4)	C(12)	−0.130 7(14)	−0.218 0(12)	0.275 6(9)
N(1)	0.528 5(8)	0.067 9(6)	0.207 1(5)	C(13)	0.415 0(12)	0.653 9(9)	0.270 5(7)
N(2)	0.189 2(9)	−0.046 8(7)	0.117 7(5)	C(14)	0.314 1(19)	0.719 8(12)	0.223 1(9)
O(3)	0.413 6(8)	0.555 2(6)	0.217 8(4)	C(15)	0.502 8(14)	0.701 8(10)	0.362 3(8)
O(4)	0.524 9(7)	0.407 4(6)	0.126 3(4)	C(16)	0.605 3(11)	0.651 6(9)	0.416 7(6)
N(3)	0.618 2(9)	0.547 3(7)	0.382 0(5)	C(17)	0.697 9(17)	0.725 7(15)	0.516 2(9)
N(4)	0.754 0(8)	0.432 0(6)	0.294 6(5)	C(18)	0.720 2(16)	0.490 1(16)	0.435 5(7)
C(1)	0.647 1(11)	0.107 5(8)	0.403 1(6)	C(19)	0.829 2(14)	0.466 1(11)	0.393 2(7)
C(2)	0.729 4(13)	0.131 7(12)	0.503 1(7)	C(20)	0.846 6(10)	0.419 4(8)	0.246 0(7)
C(3)	0.742 6(11)	0.104 9(9)	0.348 5(7)	C(21)	1.026 2(13)	0.430 6(11)	0.293 2(8)
C(4)	0.680 7(11)	0.081 5(8)	0.252 5(6)	C(22)	0.791 9(12)	0.397 6(10)	0.153 2(7)
C(5)	0.802 3(13)	0.069 5(11)	0.206 6(8)	C(23)	0.636 7(11)	0.391 7(9)	0.096 6(6)
C(6)	0.470 7(13)	0.031 8(11)	0.107 2(7)	C(24)	0.595 6(15)	0.369 4(12)	−0.003 3(7)
C(7)	0.296 5(15)	0.013 1(15)	0.065 2(7)				

Table 2. Selected interatomic distances (Å) and angles (°)

Complex (**1**)							
Fe–O(1)	2.058(2)	O(1)–C(1)	1.318(6)	N(2)–C(7)	1.479(5)	O(1)–Fe–O(1′)	79.7(1)
Fe–O(2)	1.976(3)	O(2)–C(11)	1.295(5)	N(2)–C(8)	1.307(6)	O(1)–Fe–O(2)	102.0(1)
Fe–N(1)	2.084(4)	N(1)–C(4)	1.314(7)	Fe–Fe′	3.240(2)	O(1)–Fe–N(1)	85.8(1)
Fe–N(2)	2.105(3)	N(1)–C(6)	1.466(4)			O(2)–Fe–N(2)	87.9(1)
						N(1)–Fe–N(2)	79.6(1)
Complex (**3**)							
Fe(1)–O(1)	1.775(13)	Fe(2)–O(1)	1.775(13)	O(2)–C(1)	1.407(46)	O(4)–C(13)	1.253(37)
Fe(1)–O(2)	1.943(21)	Fe(2)–O(4)	1.916(20)	O(3)–C(11)	1.348(52)	O(5)–C(23)	1.345(53)
Fe(1)–O(3)	1.924(23)	Fe(2)–O(5)	1.957(22)	N(1)–C(4)	1.295(37)	N(3)–C(16)	1.256(44)
Fe(1)–N(1)	2.044(18)	Fe(2)–N(3)	2.138(26)	N(1)–C(6)	1.520(43)	N(3)–C(18)	1.434(45)
Fe(1)–N(2)	2.050(25)	Fe(2)–N(4)	2.069(26)	N(2)–C(7)	1.500(40)	N(4)–C(19)	1.404(36)
Fe(1)–Fe(2)	3.433(3)			N(2)–C(8)	1.314(45)	N(4)–C(20)	1.408(40)
O(1)–Fe(1)–O(2)	107.9(9)	O(1)–Fe(2)–O(4)	110.1(9)	O(2)–Fe(1)–O(3)	89.3(10)	O(4)–Fe(2)–O(5)	86.9(9)
O(1)–Fe(1)–O(3)	89.3(10)	O(1)–Fe(2)–O(5)	108.6(7)	O(2)–Fe(1)–N(1)	85.6(9)	O(4)–Fe(2)–N(3)	87.1(9)
O(1)–Fe(1)–N(1)	104.0(7)	O(1)–Fe(2)–N(3)	103.2(7)	O(3)–Fe(1)–N(2)	86.2(10)	O(5)–Fe(2)–N(4)	87.5(10)
O(1)–Fe(1)–N(2)	107.4(8)	O(1)–Fe(2)–N(4)	107.8(8)	N(1)–Fe(1)–N(2)	80.5(9)	N(3)–Fe(2)–N(4)	77.8(10)
				Fe(1)–O(1)–Fe(2)	150.7(13)		
Complex (**4**)							
Fe(1)–S	2.210(3)	Fe(2)–S	2.204(2)	O(1)–C(1)	1.269(12)	O(3)–C(13)	1.300(13)
Fe(1)–O(1)	1.966(6)	Fe(2)–O(3)	1.941(8)	O(2)–C(11)	1.314(8)	O(4)–C(23)	1.284(14)
Fe(1)–O(2)	1.932(6)	Fe(2)–O(4)	1.965(6)	N(1)–C(14)	1.287(12)	N(3)–C(16)	1.298(15)
Fe(1)–N(1)	2.084(9)	Fe(2)–N(3)	2.073(7)	N(1)–C(6)	1.475(12)	N(3)–C(18)	1.465(19)
Fe(1)–N(2)	2.076(6)	Fe(2)–N(4)	2.087(8)	N(2)–C(7)	1.472(16)	N(4)–C(19)	1.456(12)
Fe(1)–Fe(2)	3.838(2)			N(2)–C(8)	1.291(10)	N(4)–C(20)	1.318(14)
S–Fe(1)–O(1)	107.8(2)	S–Fe(2)–O(3)	106.6(2)	O(1)–Fe(1)–O(2)	88.6(2)	O(3)–Fe(2)–O(4)	88.5(3)
S–Fe(1)–O(2)	106.6(2)	S–Fe(2)–O(4)	107.9(2)	O(1)–Fe(1)–N(1)	86.1(3)	O(3)–Fe(1)–N(3)	87.6(3)
S–Fe(1)–N(1)	118.8(2)	S–Fe(2)–N(3)	101.5(2)	O(2)–Fe(1)–N(2)	87.7(3)	O(4)–Fe(2)–N(4)	86.6(3)
S–Fe(1)–N(2)	101.6(3)	S–Fe(2)–N(4)	111.5(2)	N(1)–Fe(1)–N(2)	78.4(3)	N(3)–Fe(2)–Ne(4)	78.1(3)
				Fe(1)–S–Fe(2)	120.8(1)		

Anisotropic blocked-matrix least-squares refinement. Final *R* and *R′* [$w = \sigma^2(2F_o) + g(F_o)^2]^{-1}$ = 0.038 and 0.033.

Compound (**3**), $C_{24}H_{36}Fe_2N_4O_5$, *M* = 572.27, triclinic, *a* = 11.389(5), *b* = 11.406(5), *c* = 13.030(6) Å, α = 97.37(4), β = 97.30(5), γ = 117.11(4)°, *U* = 1 460.90 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, λ = 0.710 69 Å), space group $P\bar{1}$ (no. 2), *Z* = 2, D_c = 1.301 g cm^{-3}, *F*(000) = 600. Red crystals (0.26 × 0.22 × 0.46 mm) mounted in a 0.3-mm Lindemann capillary tube under nitrogen, μ(Mo-K_α) = 10.274 cm^{-1}.

Data were collected using the same scan mode as above; 5 500 reflections measured [(±*h*, ±*k*, *l*); 2 < θ < 24°], 2 900 with *F* > 2σ(*F*). Crystals suffered an intensity loss of *ca.* 5% h^{-1}. Three different crystals were used for data collection. Intensity data were corrected for anisotropic decay with time and for absorbance using the program ABSCOR.[21] The structure was solved by Patterson techniques. Refinement by blocked-matrix least squares using unit weights, Fe, O, and N anisotropic, C atoms isotropic. Final *R* = 0.10; the high value is a consequence of the crystal quality.

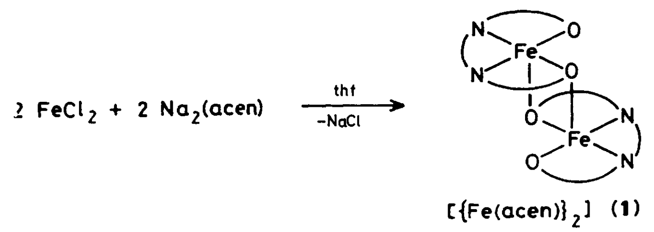
Compound (**4**), $C_{24}H_{36}Fe_2N_4O_4S$, *M* = 588.34, triclinic, *a* = 8.964(2), *b* = 11.268(2), *c* = 15.959(6) Å, α = 97.27(2), β = 106.38(3), γ = 113.44(2)°, *U* = 1 365.7 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, λ = 0.710 69 Å), space group $P\bar{1}$ (no. 2), *Z* = 2, D_c = 1.431 g cm^{-3}, *F*(000) = 616. Deep red crystals mounted in a 0.3-mm Lindemann capillary tube under nitrogen, μ(Mo-K_α) = 11.695 cm^{-1}.

Data were collected using the same scan mode as above; 4 291 reflections measured [(±*h*, ±*k*, *l*); 2 < θ < 24°], 3 038 with *F* > 4σ(*F*). No correction for absorbance was applied. The structure was solved by direct methods. Anisotropic blocked-matrix least-squares refinement. Final *R* and *R′* [$w = \sigma^2(2F_o) + g(F_o)^2]^{-1}$ = 0.0865 and 0.09.

Programs used (Sperry-Univac 1161, University of Basle) and sources of scattering factors were as reported in refs. 22 and 23. Fractional atomic co-ordinates for complexes (**1**), (**3**), and (**4**) are listed in Table 1.

Results and Discussion

The synthesis of the parent compound [Fe(acen)] was performed by treating anhydrous iron chloride[19] with the ligand H_2acen in the presence of Na(OMe) [equation (1)].



[{Fe(acen)}$_2$] (**1**)

Other synthetic methods led to adducts between the Schiff base and the iron salts, rather than to the iron complex.[24]

Complex (**1**), unlike many other iron(II)–Schiff-base complexes, is soluble in aromatic hydrocarbons. This allows study of its reactivity in different homogeneous systems. It is monomeric in solution, according to molecular weight determination by cryoscopy in benzene, dimeric in the solid state as shown by

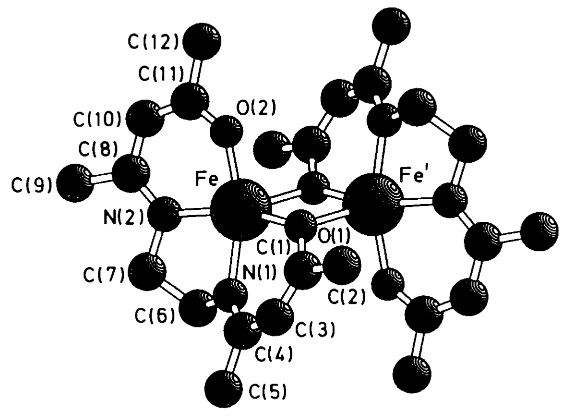
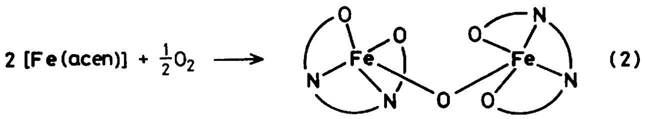


Figure 1. A view of complex (1) with the corresponding numbering scheme

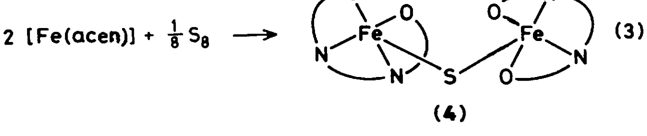
single-crystal *X*-ray analysis. Co-ordinating solvents like pyridine bind to iron, forming a five-co-ordinated iron(II) complex, [Fe(acen)(py)] (2).[25] The molecular structure of complex (1) is shown in Figure 1, while the most relevant bond distances and angles related to the co-ordination sphere of the metal are listed in Table 2. Each iron atom is in a nearly square-pyramidal geometry, with N_2O_2 donor atoms from acen defining the equatorial plane, while the axial position is filled by the oxygen of an adjacent unit. The iron atom is out of the mean plane through the N_2O_2 by 0.029 Å toward the apical oxygen, which is bonded at significantly longer distances [Fe(1)–O(1) 2.058(2) Å] than the other two oxygens [Fe–O(2) 1.976(3) Å]. The ligand acen shows an asymmetric 'umbrella' conformation in (1),[26] bond distances and angles within the ligand being in the usual ranges.[26] Complex (1), while only slightly sensitive to oxygen in the solid state, is very sensitive to various oxidizing agents in solution.

The reaction with oxygen leading to a μ-oxo dimeric compound, in this case (3) [equation (2)], is a common feature of



(1) (3)

high-spin iron(II)–Schiff-base derivatives.[2,5–14] Complex (3) crystallizes as a red solid from a thf solution of (1) after reaction with dry oxygen. A strong Fe–O–Fe band at 840 cm^{-1} in the i.r. spectrum is associated with a significant M–O multiple-bond character.[5–14] As in [{Fe(salen)}$_2$(μ-O)],[4–10] the bridging oxygen promotes a strong antiferromagnetic induction of the spin-only value expected for the d^5 high-spin configuration.[4,27–29] Similar properties are found for the μ-sulphido derivative (4), obtained by treating a thf solution of (1) with elemental sulphur[17] [equation (3)]. Reaction (3) is rather fast



(4)

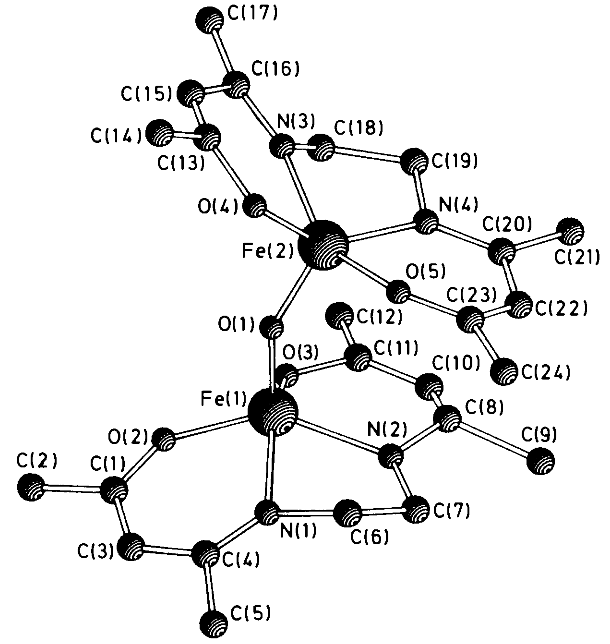


Figure 2. A view of complex (3) with the corresponding numbering scheme

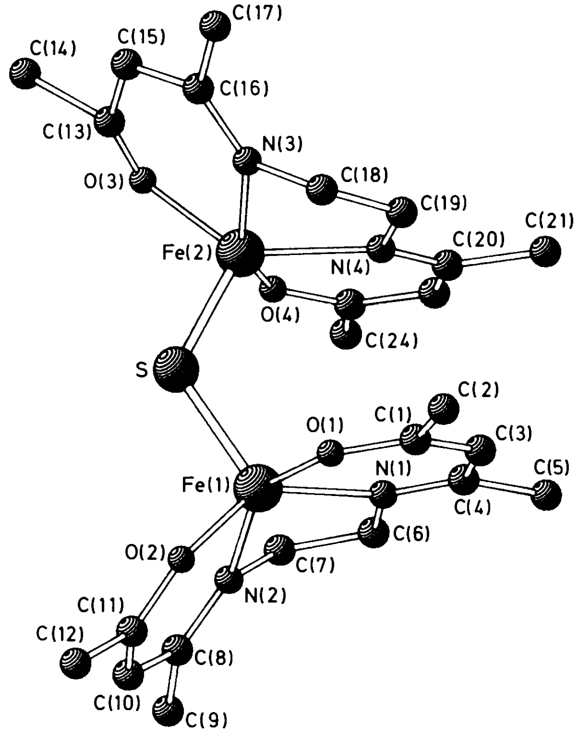
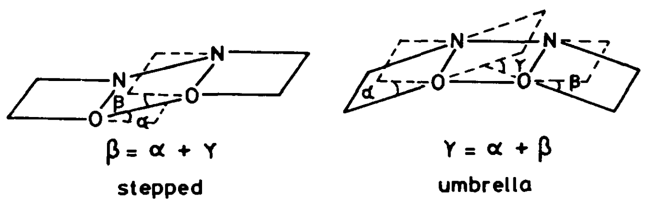


Figure 3. A view of complex (4) with the corresponding numbering scheme

and produces a crystalline material. The bridging sulphido ligand enables magnetic exchange, reducing the magnetic moment to 2.16 at 293 K. The strong Fe–O band at 840 cm^{-1} is absent from the i.r. spectrum of the sulphido complex. Because of the strong ligand bands in the far-i.r. spectra of the complexes, it was not possible to assign iron–sulphur vibrations, though a strong band appears at 405 cm^{-1}, which is absent for (1) and (3).

An interesting structural comparison can be made for complexes (3) and (4), the structures of which are shown in Figures 2 and 3 respectively. The most significant bond distances and angles related to the iron(III) co-ordination

Table 3. Comparison of some conformational data for acen and related salen complexes



Compound	Max. deviation from N_2O_2 plane/Å	Torsion angle NOON/°	d^a/Å		Angle/°			Ref.
					α^b	β^b	γ^c	
[{Fe(acen)}$_2$]	0.014	1.0	0.29	Umbrella	32.4	4.2	35.5	This work
[{Fe(acen)}$_2$O]	0.048	3.9	0.584	Umbrella	19.9	6.9	26.5	This work
[{Fe(acen)}$_2$S]	0.080	6.4	0.584	Umbrella	22.3	22.7	45.0	This work
[{Co(salen)}$_2$]	0.042	1.7	0.132	Stepped	2.4	26.1	23.6	24
[{Fe(salen)}$_2$O]	0.400	15.7	0.570	Umbrella	19.7	21.4	41.0	24
[{Fe(salen)}$_2$S]			0.608	Umbrella	12.0	17.4	29.4	16

[a] Displacement of the metal from the N_2O_2 least-squares plane. [b] Dihedral angle between N_2O_2 co-ordination plane and least-squares planes of salicylaldiminato groups. [c] Dihedral angle between salicylaldiminato group planes ($\gamma \approx 0$ for the stepped arrangement).

Table 4. Comparison of bond distances (Å) within the co-ordination spheres of [Fe(acen)] derivatives

Complex	Fe–N(1)	Fe–N(2)	Fe–O(1)	Fe–O(2)
[{Fe(acen)}$_2$]	2.084(4)	2.105(3)	2.058(2)^a	1.976(3)
[{Fe(acen)}$_2$O]	2.044(18)	2.050(25)	1.775(13)^b	1.943(21)^b
[{Fe(acen)}$_2$S]	2.084(9)	2.076(6)	1.966(6)	1.932(6)

[a] This oxygen belongs to the other [Fe(acen)] unit in the dimer. [b] Distance within the [Fe(acen)] unit.

Table 5. Comparison of bond distances, angles, and magnetic moments in the μ-oxo and μ-sulphido derivatives of [Fe(acen)] and [Fe(salen)] (X = O or S)

Complex	Fe–X/Å	Fe–X–Fe/°	$\mu_{eff.}$	T/K	Ref.
[{Fe(acen)}$_2$O]	1.775	150.7	1.80	290	This work
[{Fe(acen)}$_2$S]	2.207	120.8	2.16	293	This work
[{Fe(salen)}$_2$O]	1.780	144.6	1.87	295	7
[{Fe(salen)}$_2$S]	2.170	121.8	2.06	290	16

spheres are reported in Table 2. The two compounds are not isostructural. The distorted square-pyramidal co-ordination around each iron of the dimeric unit is very similar in both complexes. Table 3 lists some conformational parameters of the structures reported together with those of some related salen complexes. The iron atoms are significantly out of the plane (0.584 Å) defined by the N_2O_2 donor atoms in the present complexes and the ligand exhibits the 'umbrella' conformation. Structure (**3**) is asymmetric, structure (**4**) approximately symmetrical with α = 22.3° and β = 22.7° (Table 3). The Fe–O and Fe–N bond distances within the Fe(acen) unit are very similar in complexes (**1**), (**3**), and (**4**), there being little effect of the oxidation state (Table 4). A rather interesting comparison concerns the triatomic skeletons, Fe–O–Fe and Fe–S–Fe; the bond distance and angle values support the existence of significant double-bond character in the oxo compound which decreases in the sulphido bridge (Table 5). A similar trend in structural parameters and magnetic properties is observed for the two series of iron–acen and iron–salen derivatives.

Conclusions

This paper reports the synthesis and structural characterization of three compounds (**1**), (**3**), and (**4**) which can serve as model compounds for further studies in iron–Schiff-base chemistry. Their good solubility in organic solvents, which is rather unusual for such base complexes, will allow the correlation of solid-state and solution properties and the study of the reactivity in homogeneous phases. This is the first report which correlates the structural properties of three complexes of iron(II) and iron(III) analogous to the corresponding [Fe(salen)] derivatives, which have become classic examples of the co-ordination chemistry of iron(II) and iron(III).

Acknowledgements

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