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A facile synthesis of [{Fe(salphen)}$_2$O] (salphenH$_2$=*N,N'-o*-phenylenebis(salicylidineimine)) and the X-ray crystal structure of [{Fe(salphen)}$_2$O]·DMSO

Fathy M. Ashmawy*, Abdullatif R. Ujaimi
Department of Chemistry, Faculty of Applied Sciences, University of Umm-Al-Qura, Mecca (Saudi Arabia)

Charles A. McAuliffe*, R. V. (Dick) Parish and Robin G. Pritchard
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD (U.K.)

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Abstract

Reaction of ferric perchlorate with the disodium salt of *N,N'-o*-phenylenebis(salicylideneimine) in ethanol produces the μ-oxo complex [{Fe(salphen)}$_2$O]. Recrystallization from dimethyl sulfoxide produces dark red [{Fe(salen)}$_2$O]·DMSO which single crystal X-ray studies show to be a square-based pyramid linked by Fe–O bonds; Fe–O 1.776(7) and 1.781(7) Å, Fe–O–Fe 146.7(4)°.

Introduction

The μ-oxo–diiron(III) complexes are of considerable interest to chemists and biologists. Two recent reviews have highlighted the importance of this type of coordination linkage with regard to the chemistry [1] and the role played by the oxo-bridged dinuclear iron centres in proteins [2].

A notable example of these complexes is [{Fe(salen)}$_2$O] [3–5] (salenH$_2$=*N,N'*-ethylenebis(salicylideneimine)), which has been studied by magnetic susceptibility measurements [6], electronic and Mössbauer spectroscopy [7–9], and by single crystal X-ray methods [3, 10–12].

Although the analogous complex formed from the sterically more rigid salphen ligand (salphenH$_2$=*N,N'-o*-phenylenebis(salicylideneimine)) is known, investigations of it are less common [6, 13–15]. We wish to report here a one-step synthesis of [{Fe(salphen)}$_2$O] and the single crystal X-ray structural determination, and the Mössbauer spectrum and magnetic susceptibility of its DMSO solvent adduct, [{Fe(salphen)}$_2$O]·DMSO.

Results and discussion

Previously reported preparations of [{Fe(salphen)}$_2$O] (**1**) have been from the reaction of [Fe(salphen)Cl] with potassium hydroxide in ethyl alcohol [6] or from reaction with potassium superoxide in dimethyl sulfoxide [14]. We have devised a one-step synthesis: direct reaction of ferric perchlorate with the disodium salt of the ligand in ethyl alcohol. Recrystallization of the product from DMSO yielded dark red crystals of [{Fe(salphen)}$_2$O]·DMSO (**2**) (see 'Experimental').

The IR spectrum of **2** shows bands expected for the salphen ligand and for lattice DMSO, but, in addition, a weak band is present at 870 cm^{-1}, assignable to the ν(Fe–O–Fe) frequency [1].

The room temperature magnetic moment, $\mu_{eff}=2.05_{\mu B}$/Fe atom is in good agreement with that obtained for the non-solvated complex [6, 13, 14], and reveals the presence of strong antiferromagnetic interactions in the complex. No ESR spectra were observed for **2** in the solid or in frozen DMF samples either at room or liquid nitrogen temperatures. A similar lack of an ESR spectrum was observed for the [{Fe(salen)$_2$}O]·CH_2Cl_2 complex [3]. It is not clear why an ESR spectrum for such complexes as these is not observed, although such factors as the effect of spin lattice splitting or intermolecular dipolar broadening on large zero-field splitting in the thermally populated spin states of the dimer have been proposed to explain this phenomenon [3].

The room temperature ^{57}Fe Mössbauer spectrum exhibits an isomer shift (*IS*) of 0.33 mm s^{-1} (with respect to Fe foil) and quadrupole splitting (*QS*) of

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*Authors to whom correspondence should be addressed.

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0.77 mm s^{-1}. These values are very similar to analogous salen complexes (*IS* range 0.31–0.39 mm s^{-1}, *QS* range 0.72–0.92 mm s^{-1}) [7, 9], indicating that a change in the ligand backbone has very little effect on the electronic environment of the iron atoms. Taken together with the magnetic susceptibility data, these results are consistent with an antiferromagnetic-coupling mechanism similar to that established for [{Fe(salen)}$_2$O] and other Fe–O–Fe systems [6].

Fractional atomic coordinates for non-hydrogen atoms are given in Table 1; selected bond lengths and angles in Table 2.

Crystal data

$C_{40}H_{28}Fe_2N_4O_5\cdot C_2H_6OS$, molecular weight = 834.5, monoclinic, $p2_1/C$, $a = 11.958(2)$, $b = 13.861(4)$, $c = 23.660(8)$ Å, $\beta = 101.86(4)°$ (by least-squares refinement of setting angles of 25 accurately centred reflection, $6.2 < \theta < 10.4°$) $U = 3837.9$ Å^3, $D_c = 1.444$ Mg m^{-3}, $Z = 4$, graphite monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, μ (Mo Kα) = 0.080 mm^{-1}.

Discussion of structure

The structure, which is shown in Fig. 1, is composed of μ-oxo-bridged ferric salphen dimers and dimethyl sulfoxide of crystallization. Each iron environment is that of a square-based pyramid linked by Fe–O bonds that are equal within experimental error, 1.776(7) and 1.781(7) Å. The Fe–O–Fe angle of 146.7(4)° falls in the middle of the established range [1] and is close to the value of 144.6(6)° reported for [{Fe(salen)}$_2$O] [12] and 142.4(5)° for [{Fe(salen)}$_2$O]·CH_2Cl_2 [3].

Experimental

Preparation of [{Fe(salphen)}O_2] (1)

A solution of hydrated ferric perchlorate (0.0125 mol) in ethanol (25 cm^3) was added to a stirred solution of Na_2salphen (0.0250 mol) in ethanol (50 cm^3) at room temperature. A red solid formed immediately. After 30 min stirring the red solid was filtered off and washed with warm (40 °C) ethanol (3×20 cm^3), then with dry diethyl ether (50 cm^3) and dried *in vacuo*. *Anal.* [{Fe(salphen)}$_2$O]: Found: C, 62.1; H, 3.7; N, 7.7; Fe, 15.0. Calc.: C, 63.5; H, 3.7; N, 7.4; Fe, 14.8%.

On recrystallization from dry dimethyl sulfoxide the solvate adduct [{Fe(salphen)}$_2$O]·DMSO (**2**) was obtained as dark red crystals. *Anal.* [{Fe(salphen)}$_2$O]·DMSO: Found: C, 60.9; H, 4.0; N, 6.8; S, 4.4. Calc.: C, 60.4; H, 4.1; N, 6.7; S, 3.9%.

TABLE 1. Fractional atomic coordinates (×10^4) for non-hydrogen atoms

	x/a	*y/b*	*z/c*
Fe(1)	4457(1)	2654(1)	3642(1)
C(2)	3825(10)	2290(7)	2380(5)
C(3)	2840(10)	1981(6)	2577(5)
C(4)	1835(11)	1777(8)	2186(5)
C(5)	1786(11)	1920(8)	1600(5)
C(6)	2744(13)	2245(8)	1408(5)
C(7)	3751(1)	2437(8)	1783(5)
N(8)	4809(8)	2404(6)	2815(3)
C(9)	5815(11)	2317(7)	2687(5)
C(10)	6868(10)	2338(7)	3105(5)
C(11)	6958(11)	2405(8)	3702(5)
C(12)	8053(11)	2356(9)	4048(5)
C(13)	9018(10)	2243(9)	3829(6)
C(14)	8922(11)	2197(9)	3234(7)
C(15)	7896(12)	2217(8)	2892(6)
O(16)	6059(6)	2509(6)	3937(3)
N(17)	3005(7)	1915(6)	3187(4)
C(18)	2325(9)	1407(7)	3408(5)
C(19)	2346(10)	1276(8)	4012(6)
C(20)	3223(11)	1639(8)	4449(5)
C(21)	3227(11)	1463(8)	5045(5)
C(22)	2348(13)	924(9)	5166(6)
C(23)	1473(11)	560(9)	4749(7)
C(24)	1488(10)	722(8)	4178(6)
O(25)	4101(6)	2138(5)	4337(3)
Fe(26)	4401(1)	5092(1)	3451(1)
C(27)	6783(9)	5023(8)	4096(5)
C(28)	6231(10)	5463(8)	4483(5)
C(29)	6750(11)	5558(8)	5063(5)
C(30)	7851(13)	5198(10)	5248(6)
C(31)	8396(12)	4765(11)	4871(7)
C(32)	7897(10)	4686(8)	4290(6)
N(33)	5104(8)	5796(6)	4228(4)
C(34)	4651(10)	6473(8)	4478(4)
C(35)	3526(11)	6873(8)	4273(5)
C(36)	2787(11)	6566(8)	3764(5)
C(37)	1697(10)	6978(9)	3607(5)
C(38)	1392(11)	7700(9)	3937(5)
C(39)	2099(13)	8015(9)	4435(6)
C(40)	3162(12)	7609(8)	4613(5)
O(41)	3073(6)	5901(5)	3424(3)
N(42)	6182(7)	4943(6)	3511(4)
C(43)	6685(9)	4729(7)	3091(5)
C(44)	6132(11)	4682(7)	2504(5)
C(45)	4968(10)	4968(8)	2291(5)
C(46)	4549(10)	4994(8)	1696(5)
C(47)	5242(14)	4702(8)	1321(5)
C(48)	6338(13)	4367(9)	1530(7)
C(49)	6756(12)	4381(8)	2102(7)
O(50)	4310(6)	5259(5)	2641(3)
O(51)	4045(5)	3887(5)	3608(3)
S(52)	9572(4)	5774(3)	7596(2)
O(53)	10353(8)	4987(7)	7692(4)
C(54)	8953(10)	5876(8)	6880(5)
C(55)	8345(9)	5447(8)	7879(5)

Structure determination and refinement

A rectangular, red–brown crystal 0.3×0.1×0.05 mm was mounted on a CAD-4 diffractometer. All measurements were performed at ambient temperature using $\omega/2°$ scan mode with ω scan width of $0.7 + 0.35 \tan\theta$ and scan speed varied according to

TABLE 2. Selected bond lengths (Å) and angles (°)

Fe(1)-N(8)	2.115(9)
Fe(1)-O(16)	1.911(7)
Fe(1)-N(17)	2.111(8)
Fe(1)-O(25)	1.919(7)
Fe(1)-Fe(26)	3.408(2)
Fe(1)-O(51)	1.776(7)
Fe(26)-N(33)	2.098(8)
Fe(26)-O(41)	1.934(7)
Fe(26)-N(42)	2.114(9)
Fe(26)-O(50)	1.911(7)
Fe(26)-O(51)	1.781(7)
O(16)-Fe(1)-N(8)	86.8(3)
N(17)-Fe(1)-N(8)	75.4(4)
N(17)-Fe(1)-O(16)	142.5(3)
O(25)-Fe(1)-N(8)	148.6(3)
O(25)-Fe(1)-O(16)	91.8(3)
O(25)-Fe(1)-N(17)	87.3(3)
O(51)-Fe(1)-N(8)	102.8(3)
O(51)-Fe(1)-O(16)	111.5(3)
O(51)-Fe(1)-N(17)	104.6(3)
O(51)-Fe(1)-O(25)	106.9(3)
O(41)-Fe(26)-N(33)	86.4(3)
N(42)-Fe(26)-N(33)	76.7(4)
N(42)-Fe(26)-O(41)	150.1(3)
O(50)-Fe(26)-Fe(1)	104.4(2)
O(50)-Fe(26)-N(33)	138.8(3)
O(50)-Fe(26)-O(41)	91.1(3)
O(50)-Fe(26)-N(42)	85.9(3)
O(51)-Fe(26)-N(33)	108.9(3)
O(51)-Fe(26)-O(41)	108.7(3)
O(51)-Fe(26)-N(42)	100.1(3)
O(51)-Fe(26)-O(50)	110.8(3)
Fe(26)-O(51)-Fe(1)	146.7(4)

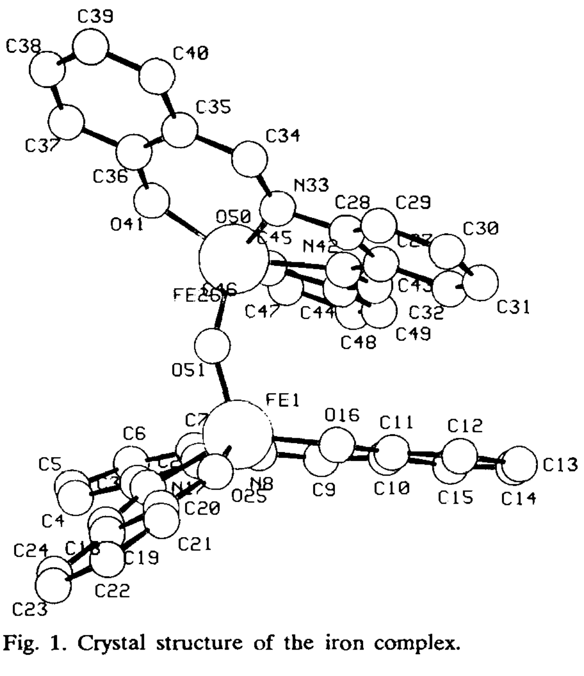

Fig. 1. Crystal structure of the iron complex.

the intensity gathered in a pre-scan (0.3–5° min^{-1}). A total of 6833 reflections was recorded ($1 \leq \theta \leq 25°$) yielding 2346 unique structure factors ($F \geq 3\sigma(F)$, $R_{\mathrm{int}} = 0.012$); negligible reduction in 3 intensity standards measured at 2 hourly intervals. Lp corrections were applied but absorption was ignored. Direct methods (MULTAN80) [16] were used to solve the phase problem. Hydrogen atoms were constrained to chemically reasonable positions during blocked-matrix least-squares refinement (SHELX76) [17]. All non-hydrogen atoms were treated anisotropically with hydrogen atoms subjected to overall isotropic refinement.

Final residuals were $R = 0.074$, $R_\omega = 0.054$ ($w = 1.8579/(\sigma^2(F) + 0.002\ F^2)$). Fluctuation in the final difference may work in the range −0.8 to 1.1 e $\mathrm{Å}^{-3}$. All calculations were performed on the Amdahl 470 computer of the Manchester Computing Centre.

Physical measurements

These were performed as previously reported [18].

Supplementary material

Atomic coordinates, bond lengths and angles and thermal parameters are available from the senior authors on request.

References

1 D. M. Kurtz, Jr., *Chem. Rev., 90* (1990) 585.

2 J. B. Vincent, G. L. Oliver-Lilley and B. A. Averill, *Chem. Rev., 90* (1990) 1447.

3 P. Coggan, A. T. McPhail, F. E. Mabbs and V. N. McLachlan, *J. Chem. Soc. A,* (1971) 1014.

4 P. C. H. Mitchell and D. A. Parker, *J. Inorg. Nucl. Chem., 35* (1973) 13.

5 R. G. Wollman and D. N. Hendrickson, *Inorg. Chem., 16* (1977) 72.

6 J. Lewis, F. E. Mabbs and A. Richards, *J. Chem. Soc. A,* (1967) 1014.

7 R. R. Berrett, B. W. Fitzsimmons and A. A. Owusu, *J. Chem. Soc. A,* (1968) 1575.

8 A. N. Buckly, I. R. Herbert, B. D. Rumbold, G. V. H. Geoffrey and K. S. Murray, *J. Phys. Chem. Solids, 31* (1970) 1423.

9 W. M. Reiff, *J. Chem. Phys., 54* (1971) 4718.

10 M. Gerloch, E. D. McKenzie and A. D. C. Towl, *J. Chem. Soc. A,* (1969) 2850.

11 R. N. Mukherjee, T. D. P. Stack and J. Holm, *J. Am. Chem. Soc., 110* (1988) 1850.

12 J. E. Davis and B. M. Gatehouse, *Acta Crystallogr., Sect. B, 29* (1973) 1934.

13 R. H. Heistand, A. L. Roe and L. Que, Jr., *Inorg. Chem., 21* (1982) 676.

14 T. Matsushito, H. Kono, M. Nishino and T. Shono, *Bull. Chem. Soc. Jpn.*, *55* (1982) 2581.

15 F. Lloret, M. Mollar, J. Morctal and J. Faus, *Inorg. Chim. Acta*, *124* (1986) 67.

16 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, *MULTAN-80*, a system of computer, programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York, U.K., and Louvain-la-Neuve, Belgium, 1980.

17 G. M. Sheldrick, *SHELX-76*, program for crystal structure determination, University of Cambridge, U.K., 1976.

18 F. M. Ashmawy, C. A. McAuliffe, R. V. Parish and J. Tames, *J. Chem. Soc., Dalton Trans.*, (1985) 1391.