Transition Metal Complexes with Thiosemicarbazide-based Ligands. Part 13.[1] Synthesis and Structure of μ-Oxo-bis-{[pentane-2,4-dione bis(*S*-methylisothiosemicarbazonato-κ²*N*,*N*")(3−)]iron(IV)}†

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Reaction of *S*-methylisothiosemicarbazide hydroiodide, pentane-2,4-dione and sodium carbonate with iron(III) nitrate in ethanol yielded paramagnetic (μ_{eff} = 3.00) [FeL(I)] [L = pentane-2,4-dione bis(*S*-methylisothiosemicarbazonato)(3−)]. When treated with ammonia a methanolic solution of [FeL(I)] yielded the diamagnetic complex [$(FeL)_2O$]. Its structure has been determined by X-ray crystallography, and characterized by spectroscopic measurements. The complex crystallizes in the monoclinic space group $P2_1/c$ with a = 11.542(1), b = 20.710(4), c = 13.232(2) Å, β = 113.12(1)° and Z = 4. The structure was solved by application of the heavy-atom method on the basis of 3362 reflections [$I > 3\sigma(I)$] and refined by full-matrix least squares to R 0.025. It consists of a binuclear complex molecule in which two iron atoms are bridged by oxygen. Both Fe atoms have approximate square-pyramidal co-ordination with the quadridentate ligand lying in the basal plane and the bridging oxygen occupying the apical position. The ligands in both halves of the molecule are saddle shaped, bent away from the apical oxygen atom and twisted around the Fe–O–Fe bridge. The Fe–O distances are 1.736(2) and 1.745(2) Å, Fe–N in the range 1.893(3)–1.917(2) Å. On the basis of the stoichiometry, crystal structure, electronic and NMR spectra, and magnetic measurements the formal oxidation state of +4 was assigned to iron in [$(FeL)_2O$].

A large number of metal complexes with ligands of semi-, thiosemi- and *S*-alkyl-isothiosemicarbazide types, having different structures, are known.[2–4] One of the common features of these complexes is that they contain metal atoms (including Fe) in their usual oxidation states. However, recent results[5–7] show that ligands derived from *S*-alkylisothiosemicarbazides are capable of stabilizing higher oxidation states for some metals. For example, [salicylaldehyde *S*-methylisothiosemicarbazonate(2−) forms a complex [$Mn^{IV}L_2$], and *S*-methyl-1,4-bis(salicylidene)isothiosemicarbazidate(2−) forms a μ-oxo tetranuclear mixed-valence complex [$(Fe_2L_2O)_2$][I_3]·I_2, containing both Fe^{III} and Fe^{IV} in a 3:1 ratio.[6] Another recent example of iron(IV) complexes is a series of monomeric square-pyramidal [FeL(I)][7] with L = pentane-2,4-dione bis(*S*-alkylisothiosemicarbazonate)(3−) where alkyl = Me, Et, Pr^n or Bu^n. It is not surprising that among iron(IV) complexes there are few examples of the structures which are fully characterized by X-ray diffraction.[7–10]

In this paper we describe the synthesis, crystal and molecular structure and spectral characterization of a square-pyramidal μ-oxo complex, [$(FeL)_2O$] with L = pentane-2,4-dione bis(*S*-methylisothiosemicarbazonate)(3−), which represents one of the rare examples of a binuclear complex of Fe^{IV}.

Experimental

Syntheses.—A mixture of *S*-methylisothiosemicarbazide hydroiodide[11] (1.85 g, 8 mmol), pentane-2,4-dione (0.5 cm^3, 5 mmol), and Na_2CO_3·$10H_2O$ (1.00 g, 3.5 mmol) was dissolved in ethanol (10 cm^3) and heated for about 10 min. After removal of the insoluble material by filtration, an ethanolic solution (5 cm^3) of $Fe(NO_3)_2$·$9H_2O$ (1.62 g, 4 mmol) was added to the reaction mixture. It was heated for another 10 min, whereupon $NaNO_3$ started to crystallize, followed by black needle-like crystals the elemental analysis of which corresponded to the complex [FeL(I)] [L = pentane-2,4-dione bis(*S*-methylisothiosemicarbazonate)(3−)]. Crystallization of [FeL(I)] was complete after 10 h at room temperature. The crystals were separated by filtration, washed with water and dried in air. Yield: 0.30 g. The required complex, [$(FeL)_2O$], was obtained by mild heating (for about 5 min) of a solution of [FeL(I)] (0.30 g) in methanol (15 cm^3) to which aqueous ammonia (1 cm^3) was added. The colour changed from dark brown to green. The product crystallized within 2 h, was separated by filtration and washed with methanol and diethyl ether. Yield: 0.15 g. The elemental analysis (Fe, C, H, N, S) of both compounds was satisfactory.

Crystal-structure Determination.—*Crystal data.* $C_{18}H_{30}Fe_2N_{12}OS_4$, M = 670.47, monoclinic, a = 11.542(1), b = 20.710(4), c = 13.232(2) Å, β = 113.12(1)°, U = 2908.6 $Å^3$, Z = 4, D_c = 1.54 g cm^{-3}, $F(000)$ = 1392, μ(Mo-Kα) = 13.1 cm^{-1}. The space group was determined uniquely from the systematic absences as $P2_1/c$.

Data collection and processing. The intensity data were collected from a crystal with dimensions 0.2 × 0.2 × 0.3 mm on a

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Final atomic coordinates for $[(FeL)_2O]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	0.194 50(3)	0.474 94(2)	0.499 95(3)	C(1)	0.064 1(3)	0.472 4(1)	0.280 5(2)
Fe(2)	0.142 67(3)	0.348 22(2)	0.639 01(3)	C(2)	0.351 0(3)	0.401 9(2)	0.414 7(2)
S(1)	−0.060 4(1)	0.485 42(5)	0.153 06(7)	C(3)	0.450 1(3)	0.406 7(2)	0.516 6(3)
S(2)	0.301 4(1)	0.613 96(5)	0.774 49(8)	C(4)	0.461 9(2)	0.445 1(2)	0.605 4(3)
S(3)	0.463 72(7)	0.400 48(4)	0.948 25(7)	C(5)	0.283 0(3)	0.557 8(1)	0.670 4(2)
S(4)	−0.255 18(6)	0.301 14(4)	0.562 32(7)	C(6)	−0.033 3(5)	0.424 8(2)	0.066 8(3)
O	0.132 3(1)	0.411 63(8)	0.550 0(1)	C(7)	0.363 3(3)	0.360 1(2)	0.326 0(3)
N(1)	0.061 7(2)	0.502 4(1)	0.368 1(2)	C(8)	0.584 5(3)	0.448 3(2)	0.704 5(3)
N(2)	0.158 8(2)	0.435 3(1)	0.285 9(2)	C(9)	0.154 5(4)	0.656 1(2)	0.723 3(3)
N(3)	0.245 5(2)	0.435 9(1)	0.393 3(2)	C(10)	0.351 0(2)	0.371 9(1)	0.823 0(2)
N(4)	0.363 3(2)	0.481 9(1)	0.602 5(2)	C(11)	0.342 2(2)	0.272 6(1)	0.613 6(2)
N(5)	0.386 7(2)	0.523 3(1)	0.689 2(2)	C(12)	0.252 0(2)	0.242 9(1)	0.522 7(2)
N(6)	0.181 7(2)	0.548 6(1)	0.580 4(2)	C(13)	0.122 2(2)	0.240 6(1)	0.493 6(2)
N(7)	0.229 4(2)	0.384 1(1)	0.782 8(2)	C(14)	−0.096 6(2)	0.304 3(1)	0.578 6(2)
N(8)	0.400 9(2)	0.333 4(1)	0.771 4(2)	C(15)	0.371 8(3)	0.440 6(2)	1.010 4(3)
N(9)	0.306 2(2)	0.312 5(1)	0.676 5(2)	C(16)	0.478 9(2)	0.257 2(2)	0.646 0(3)
N(10)	0.069 1(2)	0.275 2(1)	0.549 3(2)	C(17)	0.042 1(3)	0.197 2(2)	0.402 3(2)
N(11)	−0.057 0(2)	0.263 3(1)	0.523 0(2)	C(18)	−0.317 0(3)	0.238 9(2)	0.461 8(3)
N(12)	−0.019 2(2)	0.346 1(1)	0.647 0(2)				

CAD-4 diffractometer, in ω-2θ mode with ω scan width of $0.7 + 0.35 \tan\theta$ and scan rate varying from 1 to 7° min^{-1}. Graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) was used. Data were collected to a maximum 2θ of 48°. The range of indices was *h*, *k*, ±*l*. A total of 4921 reflections were measured, of which 4703 were unique. Periodic remeasurement of two standard reflections revealed a loss in intensity of 5.7% during the data collection. A linear decay correction was applied. The correction factors on *I* ranged from 1.000 to 1.030, with an average value of 1.015. Correction for Lorentz and polarization effects was applied, but not for absorption.

Structure analysis and refinement. The structure was solved using the Patterson heavy-atom method which revealed the positions of the Fe atoms. The remaining atoms were located in successive Fourier difference syntheses. Refinement was first by block-diagonal and finally by full-matrix least-squares calculations with all non-hydrogen atoms allowed anisotropic motion. Hydrogen atoms were initially located by Fourier difference synthesis. Using as trial coordinates the peaks associated with the methyl carbons, the positions of the hydrogen atoms were calculated with the assumption of standard tetrahedral geometry and C–H distances of 0.95 Å. For the methyne hydrogen and hydrogens attached to nitrogen the positions obtained from Fourier difference syntheses were retained. All the hydrogen atoms were then allowed to ride on the corresponding C or N atoms [$B(H) = 1.3B_{eq}(C,N)$]. The function minimized was $w(\|F_o\| - \|F_c\|)$ using unit weights for all observed reflections. Anomalous dispersion effects were included in F_c. Only the 3362 reflections having intensities greater than $3.0\sigma(I)$ were used in refinement. The final cycle of refinement included 334 variable parameters and converged at $R = 0.025$ and $R' = 0.036$, where $R = \Sigma|\Delta F|/\sigma|F_o|$, and $R' = |w(\Delta F)^2/\Sigma w F_o^2|^{\frac{1}{2}}$. The standard deviation of an observation of unit weight was 0.87, and the highest peak in the final Fourier difference map had a height of 0.28 e $Å^{-3}$. Crystallographic computations were performed on a PDP-11/73 computer using the SDP/PDP package and the physical constants tabulated therein.[12] Final atomic parameters are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Spectroscopic Characterization.—Electronic absorption spectra were recorded in the visible and near-UV region, in acetone solutions, at room temperature, on a Beckman DU-5 spectrophotometer. $\lambda_{max}(CH_3COCH_3)$ = 557, 471 and 360 nm. The ^1H NMR spectrum was recorded in $CDCl_3$ solution on a Varian FT-80A spectrometer at 80 MHz. Chemical shifts relative to $SiMe_4$ are: $\delta_H(CDCl_3)$ 2.5 (6 H, s, SCH_3), 3.0 (6 H, s, terminal CH_3 of pentanedione), 6.8 [1 H, s, CH on C(3)] and 7.65 (2 H, br, NH).

Magnetic susceptibilities were measured by the Faraday method at room temperature.

Results and Discussion

Crystal and Molecular Structure.—The structure consists of neutral binuclear complex units in which two iron atoms are bridged by an oxygen atom. All intermolecular contacts between non-hydrogen atoms are greater than the sums of the corresponding van der Waals radii. An ORTEP[13] drawing of the molecule is shown in Fig. 1 together with the atom labelling. Interatomic distances and bond angles are presented in Table 2, and two characteristic elevations of the molecule in Fig. 2.

The Fe–O bonds of 1.736(2) and 1.745(2) Å in the structure of $[(FeL)_2O]$ are among the shortest observed in μ-oxo complexes. According to the Cambridge Structural Database (CSD),[14] most of the distances lie in the range from 1.76 to 1.80 Å. However, the Fe–O–Fe angle of 153.7(1)° and the Fe ··· Fe distance [3.390(1) Å] are unremarkable. Both iron atoms have distorted square-pyramidal co-ordination. The basal plane comprises four nitrogen donors from the quadridentate ligand, whereas the apical position is occupied by the bridging oxygen. The iron atoms are displaced towards the apical oxygen atoms by 0.4881(4) and 0.4987(4) Å from the mean basal planes of the respective four nitrogen-donor atoms. This displacement is typical for five-co-ordinated μ-oxo iron complexes.[14] The Fe–N distances, ranging from 1.893(3) to 1.917(2) Å, are significantly shorter than in any μ-oxo or thiosemicarbazonato iron complexes described so far.[14–19] The quadridentate ligand L forms two five- and one six-membered chelate ring in co-ordination with Fe. The five-membered thiosemicarbazide chelate rings are approximately planar, but the whole ligand is of a saddle shape. The angles between the mean planes of the five-membered rings belonging to the same ligand are 27.6 and 31.8°, respectively. Both ligands are bent away from the oxygen bridge. They are also twisted with respect to the Fe–O–Fe axis by an angle of 36.5° (*cf.* Fig. 2). Bond distances in the thiosemicarbazide fragments of the ligand (Table 2) indicate a pronounced delocalization of electron density in the chelate rings. The two C–N distances are practically equal (Table 2). In the vicinity of the amino nitrogen atoms in the Fourier difference maps only one hydrogen atom was located, the configuration of the nitrogen atoms being nearly trigonal. Also,

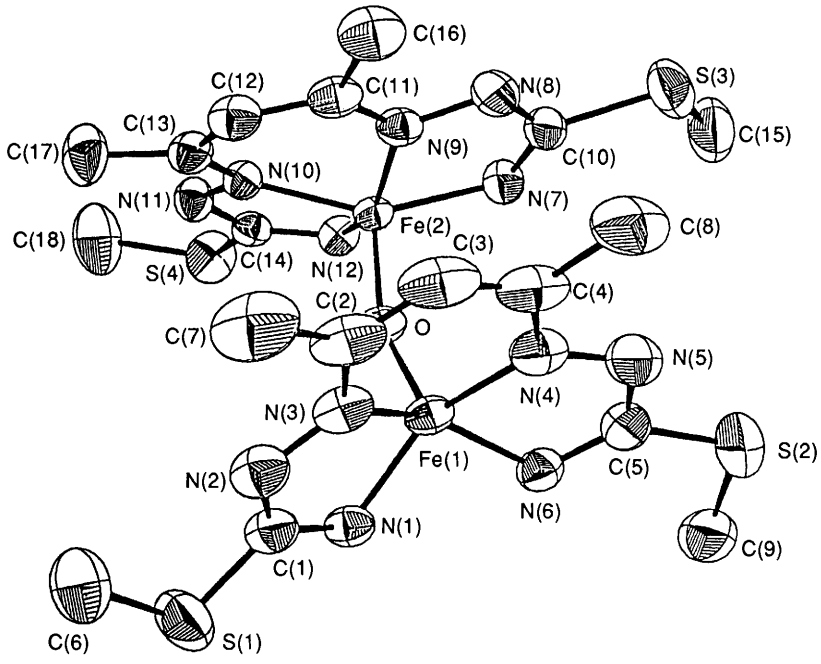

Fig. 1 ORTEP[13] view of the molecular structure of $[(FeL)_2O]$ showing the numbering scheme. The thermal ellipsoids enclose 25% probability. Hydrogen atoms are omitted for clarity

Table 2 Bond distances (Å) and angles (°) for $[(FeL)_2O]$

Fe(1)–O	1.745(2)	N(3)–C(2)	1.337(4)	S(1)–C(6)	1.805(5)	N(11)–C(14)	1.318(4)
Fe(1)–N(1)	1.901(3)	N(4)–N(5)	1.371(4)	S(2)–C(5)	1.750(4)	N(12)–C(14)	1.316(4)
Fe(1)–N(3)	1.909(3)	N(4)–C(4)	1.358(4)	S(2)–C(9)	1.787(4)	C(2)–C(3)	1.389(6)
Fe(1)–N(4)	1.893(3)	N(5)–C(5)	1.332(4)	S(3)–C(10)	1.760(4)	C(2)–C(7)	1.510(6)
Fe(1)–N(6)	1.900(3)	N(6)–C(5)	1.314(4)	S(3)–C(15)	1.782(4)	C(3)–C(4)	1.381(6)
Fe(2)–O	1.736(2)	N(7)–C(10)	1.315(4)	S(4)–C(14)	1.758(3)	C(4)–C(8)	1.505(5)
Fe(2)–N(7)	1.917(2)	N(8)–N(9)	1.373(3)	S(4)–C(18)	1.787(4)	C(11)–C(12)	1.388(5)
Fe(2)–N(9)	1.902(2)	N(8)–C(10)	1.320(5)	N(1)–C(1)	1.326(5)	C(11)–C(16)	1.499(4)
Fe(2)–N(10)	1.904(2)	N(9)–C(11)	1.349(4)	N(2)–N(3)	1.379(5)	C(12)–C(13)	1.394(4)
Fe(2)–N(12)	1.913(2)	N(10)–N(11)	1.380(3)	N(2)–C(1)	1.314(4)	C(13)–C(17)	1.498(4)
S(1)–C(1)	1.754(4)	N(10)–C(13)	1.336(4)				
N(1)–Fe(1)–N(3)	79.6(1)	N(7)–Fe(2)–N(9)	79.3(2)	N(4)–N(5)–C(5)	108.3(3)	N(10)–N(11)–C(14)	107.8(2)
N(1)–Fe(1)–N(4)	150.2(1)	N(7)–Fe(2)–N(10)	149.0(2)	Fe(1)–N(6)–C(5)	112.8(2)	Fe(2)–N(12)–C(14)	113.1(2)
N(1)–Fe(1)–N(6)	93.5(2)	N(7)–Fe(2)–N(12)	95.5(2)	N(1)–C(1)–N(2)	122.0(3)	N(7)–C(10)–N(8)	121.3(3)
N(3)–Fe(1)–N(4)	91.9(1)	N(9)–Fe(2)–N(10)	90.4(2)	C(3)–C(2)–C(7)	120.1(4)	C(12)–C(11)–C(16)	120.1(3)
N(3)–Fe(1)–N(6)	150.3(1)	N(9)–Fe(2)–N(12)	150.1(2)	N(3)–C(2)–C(3)	120.2(4)	N(9)–C(11)–C(12)	119.9(3)
N(4)–Fe(1)–N(6)	79.7(1)	N(10)–Fe(2)–N(12)	79.1(1)	N(3)–C(2)–C(7)	119.6(5)	N(9)–C(11)–C(16)	119.9(3)
O–Fe(1)–N(1)	105.6(2)	O–Fe(2)–N(7)	104.5(2)	C(2)–C(3)–C(4)	129.5(3)	C(11)–C(12)–C(13)	127.8(3)
O–Fe(1)–N(3)	104.7(2)	O–Fe(2)–N(9)	105.5(1)	C(3)–C(4)–C(8)	120.7(4)	C(12)–C(13)–C(17)	119.9(3)
O–Fe(1)–N(4)	104.2(2)	O–Fe(2)–N(10)	106.4(1)	N(4)–C(4)–C(3)	119.8(4)	N(10)–C(13)–C(12)	120.4(3)
O–Fe(1)–N(6)	104.9(1)	O–Fe(2)–N(12)	104.2(1)	N(4)–C(4)–C(8)	119.4(5)	N(10)–C(13)–C(17)	119.7(3)
Fe(1)–N(1)–C(1)	112.1(2)	Fe(2)–N(7)–C(10)	112.7(3)	N(5)–C(5)–N(6)	120.4(3)	N(11)–C(14)–C(12)	121.3(3)
N(3)–N(2)–C(1)	107.6(3)	N(9)–N(8)–C(10)	108.1(2)	S(1)–C(1)–N(1)	118.7(3)	S(3)–C(10)–N(7)	126.4(2)
Fe(1)–N(3)–C(2)	125.8(3)	Fe(2)–N(9)–C(11)	126.3(3)	S(1)–C(1)–N(2)	119.4(3)	S(3)–C(10)–N(8)	112.2(2)
Fe(1)–N(3)–N(2)	117.1(2)	Fe(2)–N(9)–N(8)	117.9(2)	S(2)–C(5)–N(5)	112.8(3)	S(4)–C(14)–N(11)	118.7(2)
N(2)–N(3)–C(2)	116.6(4)	N(8)–N(9)–C(11)	115.5(2)	S(2)–C(5)–N(6)	126.9(3)	S(4)–C(14)–N(12)	120.1(2)
Fe(1)–N(4)–C(4)	126.4(3)	Fe(2)–N(10)–C(13)	125.5(3)	C(1)–S(1)–C(6)	102.9(2)	C(10)–S(3)–C(15)	103.7(2)
Fe(1)–N(4)–N(5)	117.2(3)	Fe(2)–N(10)–N(11)	117.9(2)	C(5)–S(2)–C(9)	102.8(2)	C(14)–S(4)–C(18)	102.1(2)
N(5)–N(4)–C(4)	116.1(4)	N(11)–N(10)–C(13)	115.5(2)	Fe(1)–O–Fe(2)	153.7(1)		

in these maps no hydrogen atom bonded to hydrazinic nitrogen was found. The delocalization is therefore caused by deprotonation of the terminal NH_2 groups. The geometry of the six-membered pentane-2,4-diiminato chelate ring is in accordance with the expected charge delocalization for a deprotonated species.

^1H *NMR Spectrum.*—The observation of sharp signals in the ^1H NMR spectrum of the binuclear complex supports the formulation of the compound as a diamagnetic (or effectively diamagnetic) species not only in the solid state but also in $CDCl_3$ solution. The room-temperature spectrum of the complex dissolved in $CDCl_3$ (Fig. 3) exhibits all expected signals and is in complete agreement both with the structure in the solid state and with the expected high symmetry of the complex molecule in solution. The interesting feature is the position of the signal at δ 6.8, assigned to the central methyne proton of the pentane-2,4-diimine fragment, which indicates the strong aromatic character of this six-membered chelate ring.

Electronic Spectrum.—The spectrum of the binuclear complex is shown in Fig. 4. In the visible and near-UV region it

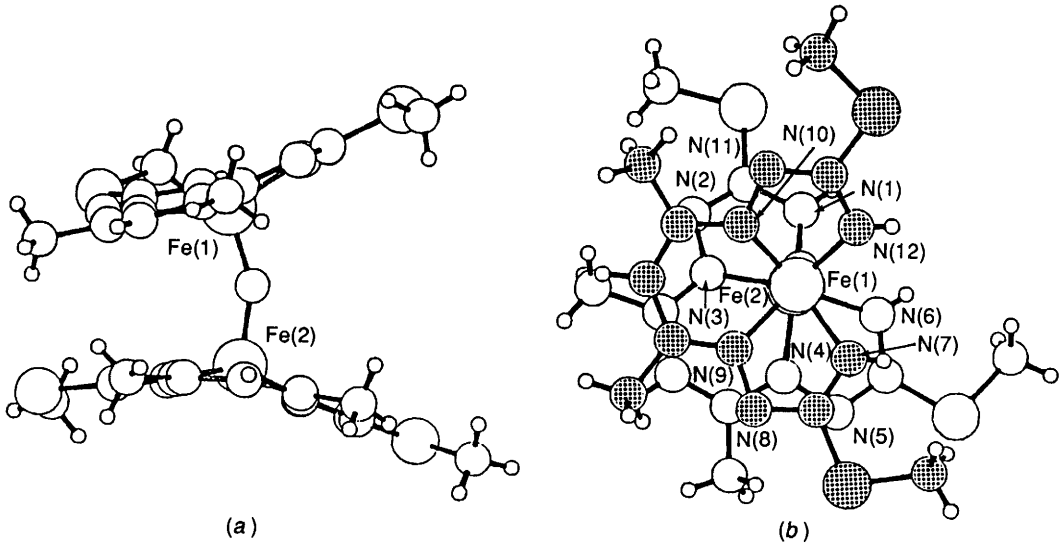

Fig. 2 Structure of $[(FeL)_2O]$ projected onto the Fe–O–Fe plane (*a*) showing the puckering mode of the chelates with respect to each other, and onto the plane approximately perpendicular to the Fe ··· Fe axis, (*b*) showing the torsional disposition of the upper chelate (shaded circles) with respect to the lower one (open circles)

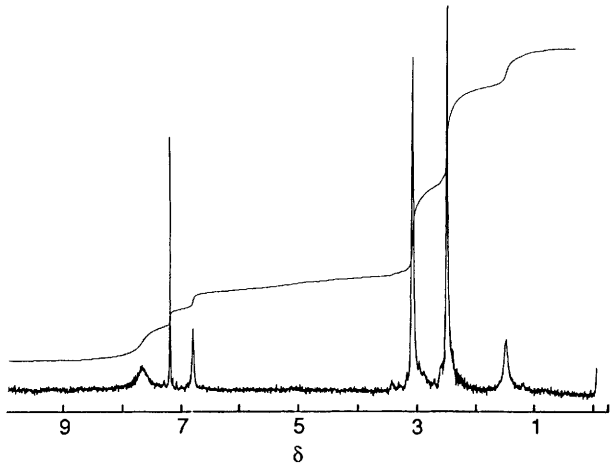

Fig. 3 80 MHz Proton NMR spectrum of $[(FeL)_2O]$ in $CDCl_3$

exhibits three well resolved broad maxima of medium intensities, at 557, 471 and 360 nm. The absorption features (energies and intensities) of these bands are characteristic of crystal-field transitions. Their assignment is discussed below in connection with the examination of the oxidation state of iron in the binuclear complex.

Oxidation State and Electronic Configuration of Iron.—In the majority of μ-oxo binuclear complexes iron is in the +3 formal oxidation state. However, all the foregoing structural and spectroscopic results lead to a conclusion that $[(FeL)_2O]$ is a diamagnetic, low-spin complex of iron(IV). This formulation is consistent with the stoichiometry deduced from the crystal-structure determination, and confirmed by elemental analysis, and by the number of protons observed in the ^1H NMR spectrum. Further evidence for this comes from the exceptionally short Fe–N distances (mean 1.905 Å) which, together with diamagnetism as evident from the NMR spectrum, removes any doubt that the iron must be in a low-spin state. On this basis it is possible to assign the electronic spectrum as follows. In C_{4v} symmetry one would predict the d-orbital ordering to be d_{xz},d_{yz} (e) < d_{xy} (b_2) < d_{z^2} (a_1) < $d_{x^2-y^2}$ (b^1). Therefore, the ground state of low-spin Fe^{IV} would be ^1E corresponding to the $(e)^4$ configuration. The observed bands at

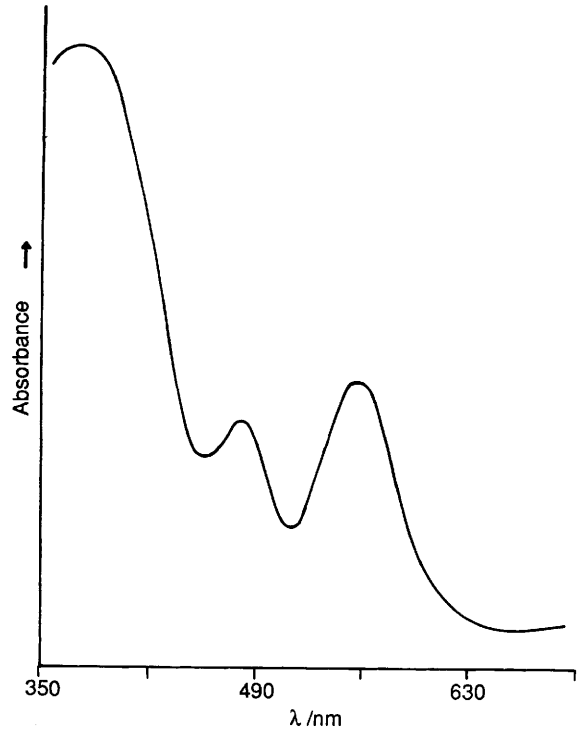

Fig. 4 Electronic spectrum of $[(FeL)_2O]$ in acetone

17 950, 20 880 and 27 780 cm^{-1} may then be assigned to $^1E(B_2)$, $^1E(A_1)$ and $^1E(B_1)$ transitions, respectively.

Acknowledgements

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