A Low-spin Iron Nitrosyl Complex from the Reaction of NO with (5*H*,14*H*-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecinato)iron(II), and its Crystal Structure†

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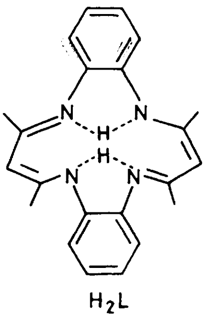
The reaction of NO with [FeL]·thf, (**1**) (H_2L = 5*H*,14*H*-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetra-azacyclotetradecine, thf = tetrahydrofuran) in thf led to a deep green cyrstalline solid [FeL(NO)]·thf, (**2**). The N–O stretching vibration at 1 636 cm^{-1} (Nujol) is quite low, if compared to the other nitrosyl derivatives of iron chelate complexes. The low-spin state revealed by the magnetic moment [$\mu_{eff.}$ = 1.91 at 292 K] is confirmed by the structural parameters of (**2**). The square-pyramidal geometry and bond parameters indicate low-spin Fe^{III}: the displacement of iron(III) from the N_4 donor plane is 0.386(1) Å, while the average Fe–N distance is 1.944(7) Å. The NO group displays a bent bonding mode [Fe–N–O, 144.1(9)°; Fe–N, 1.716(11) and N–O, 1.17(2) Å] in agreement with the low stretching frequency. Complex (**2**) crystallized in the monoclinic space group $P2_1/c$ with a = 11.397(2), b = 13.767(3), c = 16.080(2) Å, β = 105.67(1)°, Z = 4, R = 0.063.

Nitrosyl derivatives of macrocyclic and polydentate metal complexes are a class of compounds of interest for a variety of reasons.[1] Among these the most relevant is the use of NO as a mediator for oxygen transfer to organic substrates.[2,3] In particular the iron derivatives have received a lot of attention for their peculiar magnetic properties and structural features.[1,4] Their synthesis is quite straightforward and requires the reaction of NO with the iron(II) complex. Two main classes of such iron compounds have received the most attention, those containing the porphyrinato ion[1a,b] or a tetradentate Schiff-base dianion.[1c,3,4b] Significant structural and magnetic differences exist between the two classes.

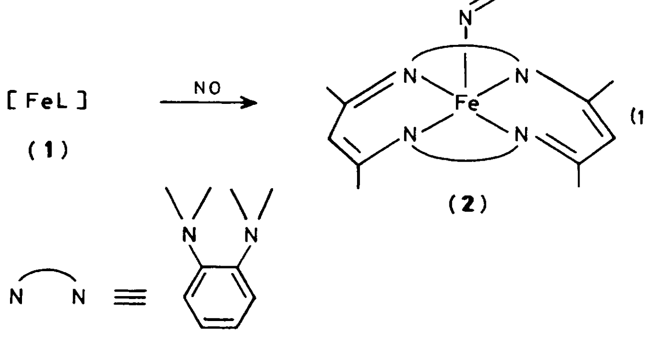
We report here the synthesis and *X*-ray structure of [FeL(NO)]·thf (5*H*,14*H*-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetra-azacyclotetradecine,[5] thf = tetrahydrofuran) containing a macrocyclic ligand having intermediate properties between porphyrins and tetradentate Schiff bases.

Results and Discussion

The reaction of [FeL]·thf, (**1**), with NO was carried out at room temperature in thf and led quantitatively to the corresponding mononitrosyl derivative (**2**), equation (1). Complex (**2**) crystallized from thf with a molecule of solvent as deep green crystals. The NO stretching vibration is relatively low (1 636 cm^{-1}), similar to that in porphyrinato complexes,[1a,b] and is significantly lower than those found in nitrosyl derivatives of tetradentate Schiff-base complexes (*ca.* 1 700 cm^{-1}).[4b,6] The two classes of compounds differ greatly regarding their magnetic properties. Porphyrinato complexes are normally in a spin equilibrium between $S = \frac{3}{2}$ and $S = \frac{1}{2}$ states,[4a,b] while Schiff-base complexes are normally in a low-spin state.[1a,b] Complex (**2**) has a magnetic moment of 1.91 at 292 K, as expected for a low-spin state. This is further supported by the structural parameters (see later).



H_2L



A view of complex (**2**) is reported in the Figure. The structure reveals that the iron atom is five-co-ordinate in a square-pyramidal co-ordination geometry, while the ligand L has the usual saddle shape exhibited in other complexes[5,7–10] and the NO group is in a bent arrangement. Bond distances and angles (Table 1) of the macrocyclic ligand are essentially identical with chemically equivalent parameters in other complexes of the same ligand.[5,7–10] There is no asymmetry in the two halves of the ligand as revealed by some characteristic structural parameters: (*i*) both five-membered chelate rings have an envelope conformation with the iron atom diplaced by 0.776(2) and

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

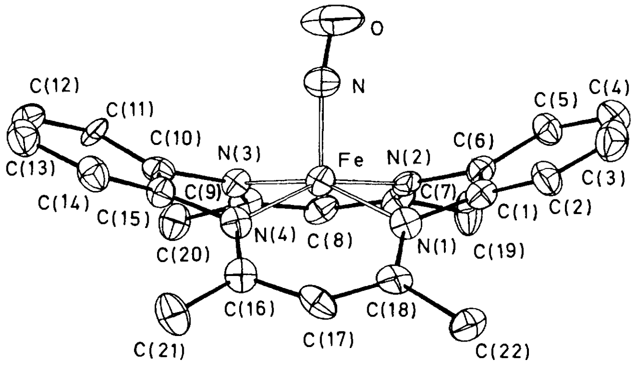

Figure. An ORTEP drawing of complex (**2**) (30% probability ellipsoids)

0.772(1) Å respectively from the N(1), C(1), C(6), N(2) and N(3), C(10), C(15), N(4) planes. Such planes form a dihedral angle of 33.4(5)° and angles of 16.7(4) and 16.6(4)° with the N_4 plane; (*ii*) the six-membered chelate rings are puckered having the iron displaced by 0.288(2) and 0.265(1) Å from the N(1), C(18), C(17), C(16), N(4) and N(2), C(7), C(8), C(9), N(3) planes. Such planes form a dihedral angle of 57.3(4)° and angles of 28.9(3) and 28.4(3)° respectively with the N_4 plane.

Bonding patterns describing the 16 π-electron ring system, which is not delocalized, are maintained. The N–C(aromatic) distances have a single bond character [av. 1.43(1) Å], N–C(aliphatic) bond lengths have a double bond character [av. 1.34(1) Å]. Table 2 lists structural and magnetic parameters for some Fe^{III}–L complexes [(**2**)—(**7**)]. Some parameters of the iron co-ordination sphere are diagnostic for the low-spin state. The Fe–N bond distances in (**2**) are comparable to those in the low-spin systems (**3**) and (**4**) while they are significantly shorter than those in the high-spin systems (**5**), (**6**), and (**7**). The displacement of iron from the N_4 plane parallels the trend observed in the Fe–N distances, the value observed for (**2**) being close to those in (**3**) and (**4**) and significantly shorter than those in (**5**), (**6**), and (**7**). In addition the N–C_t distance (N–C_t = N to centre of macrocycle bond distance) agrees well with those of the low-spin systems (**3**) and (**4**). The formal iron(III) complex [FeLPh], (**4**),[8] has a magnetic moment of 2.21 close to that of (**2**).

A comparison of the co-ordination geometry of the Fe–NO group with the same group present in tpp[1a,b] (tpp = 5,10,15,20-tetraphenylporphyrinate) and Schiff-base complexes[4,6] is stressed because of the similar bonding mode of the NO group, and the same co-ordination number of the iron atoms. The Fe–N bond distance in (**2**) [1.716(11) Å] is very similar to that found in [Fe(tpp)(NO)], (**8**), [1.171(7) Å][1a] and in [Fe(salen)(NO)], (**9**), [1.81(11) Å] [salen = *NN'*-ethylenebis(salicylideneiminate)(2 –)],[4c] while the N–O bond distance, which reveals a sort of reduction of NO to NO^-, is significantly longer in (**2**) [1.17(2) Å] *vs.* 1.122(12) in (**8**), 1.10 in (**9**), and 1.121(8) Å in [Fe(tpp)(NO)(mim)], (**10**) (mim = *N*-methylimidazole),[1b] and only close to the value found in a polynuclear Fe–NO complex [N–O_{av} = 1.20(2) Å].[6] One of the more interesting features of nitrosyl complexes is the variation in the geometry of the M–N–O moiety. The Fe–N–O angle varies from 144.1(9)° in (**2**) to 149.2(6)° in (**8**),[1a] 127(2)° in (**9**),[4c] 142.1(6)° and 138.3(11)° in (**10**).[1b] Several theoretical studies have attempted to predict the geometry of square-pyramidal nitrosyl complexes.[11,12] All studies emphasize the importance of the number of electrons (*n*) in the M–N–O group. For instance, for the fragment denoted by $\{MNO\}^n$ the theories[11] suggest a linear M–N–O group when $n = 6$, and a strongly bent M–N–O moiety, with the M–N–O angle approaching 120°, when $n = 8$. The Fe–NO fragment[12] in complexes (**2**), (**8**), and (**9**) is a $\{FeNO\}^n$ ($n = 7$) and thus has only one electron in an orbital which favours the bending. This may be the reason why the Fe–N–O angle in these complexes is substantially larger than 120°. The assumptions above, however, consider only a small contribution of the orbitals of the other ligands to the Fe–NO moiety. This is probably not correct in the case of delocalized electronic structures like those of tpp, Schiff bases, and L, but in the case of L we have only a very limited delocalization. In a polynuclear complex containing a N_4Fe–NO moiety, the Fe–NO fragment has a linear arrangement.[6]

Table 1. Selected bond distances (Å) and angles (°) for complex (**2**)

Fe–N	1.716(11)	N(1)–C(18)	1.34(1)
Fe–N(1)	1.948(7)	N(2)–C(6)	1.42(1)
Fe–N(2)	1.931(8)	N(2)–C(7)	1.35(1)
Fe–N(3)	1.945(7)	N(3)–C(9)	1.34(1)
Fe–N(4)	1.951(7)	N(3)–C(10)	1.44(1)
O–N	1.17(2)	N(4)–C(15)	1.42(1)
N(1)–C(1)	1.42(1)	N(4)–C(16)	1.32(2)
N(3)–Fe–N(4)	83.1(3)	Fe–N(1)–C(1)	108.9(7)
N(2)–Fe–N(4)	157.2(4)	C(1)–N(1)–C(18)	126.1(9)
N(2)–Fe–N(3)	93.5(3)	Fe–N(2)–C(7)	126.1(8)
N(1)–Fe–N(4)	92.4(3)	Fe–N(2)–C(6)	109.0(7)
N(1)–Fe–N(3)	157.0(4)	C(6)–N(2)–C(7)	124.9(9)
N(1)–Fe–N(2)	82.0(3)	Fe–N(3)–C(10)	109.6(6)
N–Fe–N(4)	105.4(4)	Fe–N(3)–C(9)	125.8(7)
N–Fe–N(3)	98.8(4)	C(9)–N(3)–C(10)	124.2(9)
N–Fe–N(2)	97.4(4)	Fe–N(4)–C(16)	129.4(8)
N–Fe–N(1)	104.1(4)	Fe–N(4)–C(15)	107.6(6)
Fe–N–O	144.1(9)	C(15)–N(4)–C(16)	122.8(9)
Fe–N(1)–C(18)	124.3(8)		

Table 2. Structural and magnetic parameters for some related Fe^{III}–L complexes

Compound	Fe–N[a]	Fe–N_4[b]	N–C_t[c]	$\mu_{eff.}$	Ref.
(**3**) [{FeL(CO)}$_2$]	1.927	0.29	1.905	diamagnetic	7
(**4**) [FeLPh]	1.908(3)	0.23	1.895	2.21	8
(**5**) [FeLCl]·MeCN	2.003(2)	0.600	1.910	5.95	9
(**6**) [(FeL)$_2$(μ-O)]·MeCN	2.053(5)	0.698(2)	1.931	1.96	10
(**7**) [(FeL)$_2$(μ-S)]·thf	2.055(10)	0.698	1.934	2.17	*d*
(**2**) [FeL(NO)]·thf	1.944(7)	0.386(1)	1.905	1.91	This work

[a] Fe–N(equatorial) average distance. [b] Distance of Fe from the equatorial plane defined by N_4 donor atoms. [c] Distances of N to centre of macrocyclic core. [d] P. Berno, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, submitted for publication.

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The synthesis of [FeL]·thf was carried out by a modification of the reported procedure.[5,7] Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer. Magnetic susceptibilities were measured using a Faraday balance.

Synthesis of [FeL(NO)]·thf.—A toluene (105 cm^3) suspension of [FeL]·thf (3.25 g, 6.92 mmol) was treated with NO at room temperature. The red colour of the suspension turned to red-maroon, then a dark green solid crystallized out. The absorption of NO lasted for 2 h. The solid recrystallized from

Table 3. Fractional atomic co-ordinates (× 10^4) for complex (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe	3 718(1)	1 373(1)	991(1)
O	2 047(11)	954(8)	1 891(7)
N	2 745(8)	1 407(7)	1 640(6)
N(1)	3 074(7)	2 351(5)	111(5)
N(2)	2 756(7)	522(6)	114(5)
N(3)	4 786(7)	333(5)	1 569(5)
N(4)	5 096(7)	2 192(5)	1 565(5)
C(1)	1 910(12)	2 044(9)	−399(8)
C(2)	957(11)	2 668(10)	−776(8)
C(3)	−170(15)	2 279(13)	−1 148(9)
C(4)	−389(11)	1 303(13)	−1 131(9)
C(5)	551(12)	654(9)	−729(8)
C(6)	1 719(12)	1 034(9)	−371(8)
C(7)	3 042(12)	−398(8)	−44(8)
C(8)	4 073(12)	−870(8)	491(8)
C(9)	4 895(11)	−541(8)	1 236(8)
C(10)	5 564(10)	686(8)	2 374(8)
C(11)	5 981(11)	143(9)	3 106(8)
C(12)	6 612(12)	647(12)	3 840(8)
C(13)	6 827(12)	1 655(10)	3 890(9)
C(14)	6 323(11)	2 184(9)	3 119(9)
C(15)	5 711(11)	1 729(8)	2 348(8)
C(16)	5 505(11)	2 992(9)	1 286(8)
C(17)	4 829(12)	3 401(8)	496(10)
C(18)	3 716(12)	3 106(8)	−58(8)
C(19)	2 359(12)	−970(10)	−816(9)
C(20)	5 945(11)	−1 190(8)	1 640(7)
C(21)	6 669(11)	3 465(9)	1 685(9)
C(22)	3 254(11)	3 689(9)	−913(8)
O(1S)	−749(13)	4 631(13)	1 015(11)
C(1S)	−501(26)	3 781(23)	711(17)
C(2S)	602(32)	3 365(29)	1 238(19)
C(3S)	894(20)	3 960(35)	1 960(19)
C(4S)	−12(37)	4 731(18)	1 836(13)

boiling thf gave crystals suitable for *X*-ray analysis (yield, *ca.* 85%) (Found: C, 63.00; H, 6.65; N, 14.40. Calc. for [FeL(NO)]·thf, $C_{26}H_{30}FeN_5O_2$: C, 62.90; H, 6.00; N, 14.00%). The i.r. spectrum shows a strong band (Nujol) at 1 636 cm^{-1}; $\mu_{eff.}$ = 1.91 at 292 K.

Crystal-structure Determination of Complex (**2**).—*Crystal data.* $C_{22}H_{22}FeN_5O{\cdot}C_4H_8O$, $M = 500.4$, monoclinic, $a = 11.397(2)$, $b = 13.767(3)$, $c = 16.080(2)$ Å, $\beta = 105.67(1)°$, $U = 2\,429.2(8)$ Å^3, $Z = 4$, $D_c = 1.368$ g cm^{-3}, $F(000) = 1\,052$, Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 6.50 cm^{-1}, space group $P2_1/c$, crystal dimensions: 0.25 × 0.50 × 0.53.

The crystal selected for study was mounted in a glass capillary and sealed under nitrogen. The reduced cell was obtained with use of TRACER.[13] The intensities of 3 915 reflections were collected at room temperature on a Philips PW 1100 diffractometer (graphite-monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å, 2θ range 6—48°) using the 'three-point' technique; 1 320 of these were considered observed [$I > 3\sigma(I)$] and used in the structure solution and refinement. Data reduction, structure solution, and refinement were performed on a GOULD 32/77 computer using SHELX 76.[14] The structure amplitudes were obtained after the usual Lorentz and polarization corrections [14] and the absolute scale was established by the Wilson method.[15] The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected. The function minimized during the least-squares refinement was $\Sigma w|\Delta F|^2$. A weighting scheme based on counting statistics was applied. Anomalous scattering corrections were included in all structure factor calculations.[16b] Scattering factors for neutral atoms were taken from ref. 16*a* for non-hydrogen atoms and from ref. 17 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first performed isotropically, then anisotropically for non-hydrogen atoms, by blocked full-matrix least squares down to $R = 0.063$ ($R' = 0.065$). The *X*-ray analysis revealed the presence of a thf molecule of crystallization, which was found to be affected by high thermal motion as often happens in situations like this. All hydrogen atoms except those of thf were located in difference maps and introduced in the subsequent refinement as fixed contributors with isotropic thermal parameters fixed at 0.10 Å^2. The final difference map showed no unusual feature, with no significant peak above the general background.

Final atomic co-ordinates are listed in Table 3 for non-hydrogen atoms and bond distances and angles in Table 1. Additional material available from the Cambridge Crystallographic Data Centre comprises the H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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