Preparation and Magnetism of the Binuclear Iron(II) Complexes [{$Fe(C_9H_{21}N_3)X_2$}$_2$] (X = NCS, NCO, or N_3) and their Reaction with NO. Crystal Structures of [{$Fe(C_9H_{21}N_3)(NCS)_2$}$_2$] and [$Fe(C_9H_{21}N_3)(NO)(N_3)_2$]†

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Reaction of $Fe(ClO_4)_2{\cdot}6H_2O$ with *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L) in methanol and addition of solid NaSCN, NaOCN, or NaN_3 gave yellow compounds of the type [{$FeLX_2$}$_2$] (X = NCS, NCO, or N_3). [{$FeL(NCS)_2$}$_2$] is a binuclear, neutral complex in the solid state containing two bridging and two terminal thiocyanato ligands as has been shown by *X*-ray crystallography. Variable-temperature magnetic susceptibility measurements indicate negligible intramolecular spin coupling in [{$FeL(NCS)_2$}$_2$] and [{$FeL(NCO)_2$}$_2$] [$\mu_{eff.}$(298 K) = 5.4 and 5.35 μ_B per Fe^{II}, respectively]. In [{$FeL(N_3)_2$}$_2$] intramolecular antiferromagnetic exchange coupling of high-spin configurated Fe^{II} centres is observed ($J = -11$ cm^{-1}, $g = 2.2$). [{$FeL(NCS)_2$}$_2$] and [{$FeL(N_3)_2$}$_2$] reacted with NO to yield [$FeL(NO)(NCS)_2$] and [$FeL(NO)(N_3)_2$], respectively. [$FeL(NO)(N_3)_2$] is a six-co-ordinate neutral complex with a bent Fe–NO group [155.5(10)°]. The structure for [$FeL(NO)(N_3)_2$] has been determined. [$FeL(NO)(NCS)_2$] and [$FeL(NO)(N_3)_2$] are paramagnetic with magnetic moments of 4.20 and 4.06 μ_B between 100 and 293 K indicating three unpaired electrons, respectively. Reaction of [$FeL'Cl_3$] (L′ = 1,4,7-triazacyclononane) with $NaNO_2$ in 0.1 dm^{-3} mol HCl and addition of $NaClO_4$ afforded yellow-brown [$FeL'(NO)(NO_2)_2$][ClO_4]$\cdot 2H_2O$. The cyclic voltammogram of [$FeL'(NO)(NO_2)_2$][ClO_4]$\cdot 2H_2O$ in acetonitrile revealed a reversible one-electron transfer ($E_{\frac{1}{2}} = -0.29$ V *vs.* ferrocenium–ferrocene) corresponding to the couple '{Fe–NO}^{6}–{Fe–NO}^{7}' and an irreversible reduction wave ($E = -1.18$ V *vs.* ferrocenium–ferrocene).

We are currently investigating the ligating properties of the small tridentate macrocycles *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L) and 1,4,7-triazacyclononane (L′) towards substitution-labile transition metal(II) ions. Nickel(II),[1] copper(II),[2,3] and cobalt(II)[4] form stable 1:1 complexes in methanolic solution; in the presence of azide binuclear complexes containing bridging and terminal azido ligands form readily. These materials are ideally suited for the study of intramolecular magneto-structural correlations.

Here we report our results of a similar investigation with iron(II). We have recently shown[5] that L reacts with $Fe(ClO_4)_2{\cdot}6H_2O$ in methanol in the presence of acetate ions to yield the binuclear complex [$Fe_2L_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2$][$ClO_4$]$\cdot H_2O$, which serves as a model compound for the di-iron centres in deoxyhaemerythrin. If this reaction is carried out in the presence of thiocyanate, isocyanate, or azide complexes of composition [$FeLX_2$] (X = NCS, NCO, or N_3) formed, which are dimers in the solid state as we will show here. Their magnetic properties have been investigated.

[{$FeL(NCS)_2$}$_2$] and [{$FeL(N_3)_2$}$_2$] react in methanolic solution with NO to form monomeric six-co-ordinate nitrosyl complexes [$FeL(NO)X_2$] (X = NCS or N_3), which are of the type '{Fe–NO}^{7}' according to the nomenclature of Enemark and Feltham.[6] Variable-temperature magnetic measurements indicate that these complexes are high-spin complexes with three unpaired electrons per iron centre.

The reaction of [$FeL'Cl_3$][7] with HNO_2 yields [$FeL'(NO)(NO_2)_2$]$^+$ a '{Fe–NO}^{6}' species, which is electrochemically reduced to the corresponding '{Fe–NO}^{7}' species.[6]

Experimental

Instruments used in the preparative part of this work were a Perkin-Elmer Lambda 9 spectrophotometer for electronic spectra and a Beckmann Acculab 10 spectrophotometer for i.r. spectra (400—4 000 cm^{-1}; samples measured as KBr discs). Magnetic moments of powdered samples were measured by the Faraday method (Sartorius microbalance, Bruker research magnet B-E 100088 and Bruker B-VT 1000 automatic temperature control) between 100 and 298 K. Diamagnetic corrections were applied using Pascal's constants.[8] The apparatus used for cyclic voltammetric measurements has been described previously.[9] Cyclic voltammograms of [$FeL'(NO)(NO_2)_2$][ClO_4]$\cdot 2H_2O$ were measured in acetonitrile with 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate as supporting electrolyte at a gold electrode at 25 °C. Measurements were made under an argon atmosphere using an Ag–AgCl reference electrode. At the beginning of each experiment a cyclic voltammogram of the solution containing only the supporting electrolyte was measured. To this solution solid samples were added and dissolved with stirring to yield a concentration of *ca.* 10^{-3} mol dm^{-3} of the respective material. Cyclic voltammograms were recorded at scan rates of 50—200 mV s^{-1}. An approximately equimolar amount of ferrocene was then added as internal standard. Redox potentials (V) are given *versus* the reference system ferrocenium–ferrocene.

The ligands *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L) and 1,4,7-triazacyclononane (L′) were prepared as described in the literature.[10] All other chemicals were of reagent grade.

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† Di-μ-[thiocyanato-*NS*]-bis[(thiocyanato-*N*)(*N,N′,N″*-trimethyl-1,4,7-triazacyclononane)iron(II)] and diazidonitrosyl(*N,N′,N″*-trimethyl-1,4,7-triazacyclononane)iron respectively.

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

Preparation of Complexes [$FeLX_2$] (X = NCS, NCO, *or* N_3).—To a stirred solution of L (0.36 g) in methanol (30 cm^3) under an argon atmosphere was added solid $Fe(ClO_4)_2 \cdot 6H_2O$ (0.32 g), resulting in a bluish green colouration. After stirring for 2 h at room temperature, solid NaSCN (0.12 g), NaOCN (0.12 g), or NaN_3 (0.14 g) was added, respectively. The colour of the solution changed immediately to yellow. The solution was allowed to stand at room temperature for 2—3 d, after which time yellow crystals of the desired product [$\{FeL(NCS)_2\}_2$] (yield 0.22 g, 64%), [$\{FeL(NCO)_2\}_2$] (yield 0.18 g, 58%), or [$\{FeL(N_3)_2\}_2$] (yield 0.22 g, 70%) precipitated, which was filtered off and dried under argon.

[$\{FeL(NCS)_2\}_2$] (Found: C, 38.6; H, 6.3; Fe, 16.0; N, 20.5. Calc. for $C_{11}H_{21}FeN_5S_2$: C, 38.5; H, 6.10; Fe, 16.3; N, 20.4%). The complex is paramagnetic with a magnetic moment of μ = 5.4 μ_B per Fe between 100 and 298 K and with $\lambda_{max.}$ = 378 nm ($\varepsilon = 2.5 \times 10^3$ dm^3 mol^{-1} cm^{-1}) in the electronic spectrum (CH_3OH solution) and with ν(NCS) at 2 070 and 2 020 cm^{-1} in the i.r. spectrum (KBr disc).

[$\{FeL(NCO)_2\}_2$] (Found: C, 42.2; H, 6.9; Fe, 17.6; N, 22.3. Calc. for $C_{11}H_{21}FeN_5O_2$: C, 42.45; H, 6.75; Fe, 17.95; N, 22.5%). The complex is paramagnetic with a magnetic moment of μ = 5.35 μ_B per Fe between 100 and 298 K and with ν(OCN) at 2 140 and 2 190 cm^{-1} in the i.r. spectrum (KBr disc).

[$\{FeL(N_3)_2\}_2$] (Found: C, 34.6; H, 6.5; Fe, 17.8; N, 39.2. Calc. for $C_9H_{21}FeN_9$: C, 34.7; H, 6.75; Fe, 18.0; N, 40.5%). The complex exhibits antiferromagnetic behaviour with effective magnetic moments of $\mu_{eff.}$ (103 K) = 3.80 μ_B and $\mu_{eff.}$ (293 K) = 4.91 μ_B per Fe centre. For further details see the Results and Discussion section. In the i.r. spectrum (KBr disc) $\nu(N_3)$ bands were observed at 2 080 and 2 020 cm^{-1}.

Preparation of Nitrosyldithiocyanato(N,N′,N″-*trimethyl*-1,4,7-*triazacyclononane*)*iron and Diazidonitrosyl*(N,N′,N″-*trimethyl*-1,4,7-*triazacyclononane*)*iron*.—Through a stirred solution of [$\{FeL(NCS)_2\}_2$] (or [$\{FeL(N_3)_2\}_2$]) (0.20 g) in methanol (40 cm^3) under an argon atmosphere a stream of NO gas was passed for 15 min at 25 °C. The colour of the solution changed from yellow to brown. The solution was allowed to stand at 6 °C for 3 d, after which time brown crystals of [$FeL(NO)(NCS)_2$] (yield 0.14 g, 64%) and [$FeL(NO)(N_3)_2$] (yield 0.11 g, 50%), respectively, precipitated. These were filtered off and dried under argon.

[$FeL(NO)(NCS)_2$] (Found: C, 35.5; H, 5.7; Fe, 14.6; N, 22.0. Calc. for $C_{11}H_{21}FeN_6OS_2$: C, 35.4; H, 5.60; Fe, 14.95; N, 22.5%). The complex is paramagnetic with a magnetic moment of μ = 4.20 μ_B between 100 and 293 K with ν(NO) at 1 735 cm^{-1} and ν(NCS) at 2 020 cm^{-1} in the i.r. spectrum (KBr disc).

[$FeL(NO)(N_3)_2$] (Found: C, 31.6; H, 6.1; Fe, 16.2; N, 41.3. Calc. for $C_9H_{21}FeN_{10}O$: C, 31.65; H, 6.15; Fe, 16.4; N, 41.0%). The complex is paramagnetic with a magnetic moment of μ = 4.06 μ_B between 100 and 293 K with $\lambda_{max.}$ = 434 nm ($\varepsilon = 2.7 \times 10^3$ dm^3 mol^{-1} cm^{-1}) in the electronic spectrum (CH_3CN solution) and with ν(NO) at 1 690 cm^{-1} and $\nu(N_3)$ at 1 995 and 2 020 cm^{-1} in the i.r. spectrum (KBr disc).

Dinitronitrosyl(1,4,7-*triazacyclononane*)*iron Perchlorate Dihydrate*.—Trichloro(1,4,7-triazacyclononane)iron(III)[7] (0.16 g) and $NaNO_2$ (1.5 g) were dissolved in 0.1 mol dm^{-3} hydrochloric acid at room temperature with stirring. After 2 h sodium perchlorate (0.5 g) was added to the brown solution. Upon standing at 6 °C in the refrigerator brown microcrystals precipitated overnight, which were filtered off and air dried (yield 0.12 g) (Found: C, 16.5; H, 4.6; Fe, 12.1; N, 18.9; ClO_4, 23.1. Calc. for $C_9H_{21}ClFeN_6O_9 \cdot 2H_2O$: C, 16.3; H, 4.3; Fe, 12.6; N, 18.9; ClO_4, 22.45%). The compound is diamagnetic with $\lambda_{max.}$ = 362 nm ($\varepsilon = 3.2 \times 10^3$ dm^3 mol^{-1} cm^{-1}) in the electronic spectrum (CH_3CN solution), and with ν(NO) at 1 890 cm^{-1}, $\nu_{asym}(NO_2)$ at 1 430 cm^{-1}, $\nu_{sym}(NO_2)$ at 1 310 cm^{-1}, and ν(NH) at 3 200 cm^{-1} in the i.r. spectrum (KBr disc).

Table 1. Data for crystal structure analyses *

Compound	[$\{FeL(NCS)_2\}_2$]	[$FeL(NO)(N_3)_2$]
Formula	$C_{22}H_{42}Fe_2N_{10}S_4$	$C_9H_{21}FeN_{10}O$
M	686.6	341.2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	8.93(2)	13.465(3)
b/Å	15.52(2)	8.102(2)
c/Å	11.47(2)	14.174(2)
β/°	92.6(2)	91.23(1)
U/Å^3	1 586.5	1 546.0
Z	2	4
D_c/g cm^{-3}	1.44	1.47
μ(Mo-K_α)/cm^{-1}	11.4	9.32
2θ range/°	$2.5 \leqslant 2\theta \leqslant 50$	$2.5 \leqslant 2\theta \leqslant 70$
Transmission coefficient	0.71—0.36	0.66—0.55
Approx. crystal size (mm)	0.2 × 0.2 × 0.15	0.27 × 0.42 × 0.61
No. of unique reflections	1 255	3 067
No. of observed data	1 129	2 654
Criterion for observed $I \geqslant n\sigma(I)$	n = 2.0	n = 2.5
No. of parameters refined	157	190
R	0.094	0.055
R'	0.084	0.050
Shift/e.s.d. in last cycles of refinement		
maximum	0.61	0.01
average	0.10	0.01

* Parameters common to both determinations: λ(Mo-K_α) = 0.710 69 Å; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(I)$; T = 293 K.

Crystal Structure Determinations and Refinements.—Details of the data collection procedures (Siemens AED II diffractometer; ω scan), structure solution, and refinement are given in Table 1. In each case corrections were made for Lorentz, polarisation and empirical *X*-ray absorption effects. Computations were carried out on an ECLIPSE computer using the program STRUCSY.[11] The structures were solved by Patterson and Fourier syntheses with refinement by full-matrix least-squares methods. Methylene hydrogen atoms were incorporated into the final model at idealised geometries with C–H 0.96 Å and tetrahedral geometry for carbon atoms and were refined with isotropic thermal parameters. Scattering factors were from ref. 12. Atomic co-ordinates are given in Tables 2 and 3. Single crystals of [$\{FeL(NCS)_2\}_2$] were not ideally suited for *X*-ray crystallography which is reflected by the rather high final R value and the fact that only few reflections at $\theta > 20°$ were observed. Thus the precision of the structure determination is not as good as would be desirable, but it does unambiguously establish the overall geometry of the binuclear complex [$\{FeL(NCS)_2\}_2$].

Results and Discussion

Yellow crystals of composition [$FeLX_2$] (X = NCS, NCO, or N_3) precipitated in good yields under strictly anaerobic conditions from methanolic solutions containing the tridentate macrocycle, $Fe(ClO_4)_2 \cdot 6H_2O$ (1:1), and excess of NaSCN, NaOCN, or NaN_3, respectively.

Crystals of the thiocyanato complex consist of binuclear, neutral species, [$\{FeL(NCS)_2\}_2$]. The molecular structure in the solid state, as determined by *X*-ray crystallography, is shown

Table 2. Atomic co-ordinates(× 10^4) for the non-hydrogen atoms in [{FeL(NCS)$_2$}$_2$] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	1 889(3)	1 329(2)	924(3)	C(3)	4 035(23)	2 803(13)	1 349(22)
N(1)	2 588(16)	1 450(11)	−732(13)	C(4)	4 693(20)	2 174(11)	2 080(21)
N(2)	1 674(17)	−42(11)	800(16)	C(5)	3 884(20)	792(13)	2 946(17)
N(3)	2 219(16)	2 738(10)	1 344(14)	C(6)	2 622(22)	1 199(16)	3 620(17)
N(4)	4 161(15)	1 259(11)	1 858(15)	C(7)	652(22)	2 263(14)	2 938(20)
N(5)	1 254(16)	1 363(11)	2 818(14)	C(8)	1 726(21)	2 968(13)	2 509(18)
S(1)	2 726(6)	1 053(4)	−3 131(6)	C(9)	1 573(20)	3 323(12)	424(17)
S(2)	883(6)	−1 606(3)	−213(6)	C(10)	5 265(24)	752(14)	1 153(19)
C(1)	2 660(19)	1 281(14)	−1 745(20)	C(11)	21(25)	696(14)	3 050(20)
C(2)	1 323(19)	−685(14)	378(18)				

Table 3. Atomic co-ordinates (× 10^4) for the non-hydrogen atoms in [FeL(NO)(N$_3$)$_2$] with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	−2 351.0(5)	1 195.7(8)	2 356.9(4)	O(4)	−1 644(4)	−1 860(6)	3 041(4)
N(1)	−3 492(3)	417(5)	1 238(2)	C(1)	−4 277(4)	1 691(6)	1 319(4)
N(3)	−1 530(3)	1 666(5)	1 029(2)	C(2)	−3 868(4)	3 422(6)	1 277(3)
N(4)	−1 858(3)	−751(6)	2 583(3)	C(3)	−2 162(4)	4 456(6)	1 419(3)
N(11)	−3 447(3)	984(5)	3 357(3)	C(4)	−1 763(4)	3 367(6)	674(3)
N(12)	−3 485(3)	−203(6)	3 855(3)	C(5)	−1 926(4)	396(6)	367(3)
N(13)	−3 539(4)	−1 348(6)	4 350(3)	C(6)	−3 053(4)	400(7)	286(3)
N(21)	−1 368(3)	2 497(6)	3 170(3)	C(7)	−3 915(4)	−1 251(6)	1 436(4)
N(22)	−602(4)	2 011(6)	3 506(3)	C(8)	−3 259(4)	4 648(6)	2 764(3)
N(23)	147(4)	1 655(8)	3 852(4)	C(9)	−440(4)	1 410(8)	1 195(4)

Table 4. Important distances (Å) and angles (°) in [{FeL(NCS)$_2$}$_2$]

Fe–N(1)	2.03(2)	N(1)–C(1)	1.19(3)
Fe–N(2)	2.14(2)	C(1)–S(1)	1.64(2)
Fe–N(3)	2.25(1)	N(2)–C(2)	1.15(3)
Fe–N(4)	2.25(1)	C(2)–S(2)	1.62(2)
Fe–N(5)	2.27(2)		
Fe–S(2)	2.61(1)	Fe ··· Fe′	5.678(8)
N(1)–Fe–N(2)	93.5(10)	N(1)–Fe–S(2)	91.1(6)
N(1)–Fe–N(5)	172.5(10)	N(2)–Fe–S(2)	93.6(6)
N(2)–Fe–N(5)	93.5(9)	S(2)–Fe–N(3)	91.2(5)
N(3)–Fe–N(4)	80.8(7)	N(3)–Fe–N(5)	79.0(7)
N(1)–Fe–N(3)	93.8(9)	N(1)–Fe–N(4)	98.1(9)
N(2)–Fe–N(3)	171.1(8)	N(2)–Fe–N(4)	93.4(9)
S(2)–Fe–N(4)	168.2(4)	S(2)–Fe–N(5)	91.2(6)
N(4)–Fe–N(5)	78.7(7)	Fe–N(1)–C(1)	156.6(5)
N(1)–C(1)–S(1)	178(1)	Fe–N(2)–C(2)	156.1(5)
N(2)–C(2)–S(2)	178(1)	Fe′–S(2)–C(2)	101.2(9)

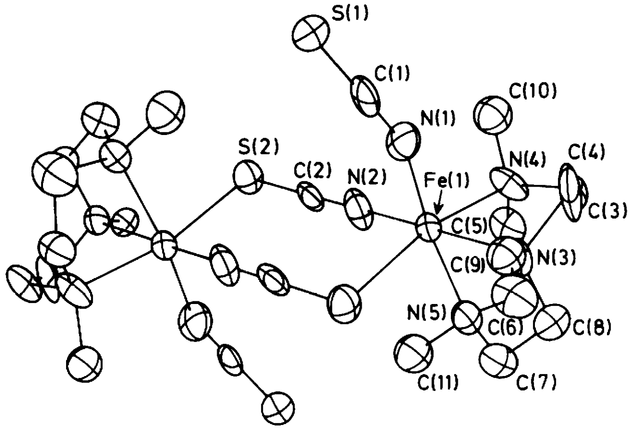

Figure 1. Molecular structure of [{FeL(NCS)$_2$}$_2$] and atomic numbering scheme

in Figure 1. Selected bond distances and angles are summarised in Table 4. The geometry around the iron(II) centres is distorted octahedral. Each iron is bound facially to a cyclic triamine, a terminal N-co-ordinated thiocyanato ligand, and two end-to-end bound μ-thiocyanato bridges *via* one nitrogen atom and one sulphur atom, respectively. The halves of the molecule are related by a crystallographic centre of symmetry. Di-μ-thiocyanato-bridged complexes of the present structure have been characterised previously for dimers of Ni$^{\text{II}}$ [13] and Pt$^{\text{II}}$ [14] by *X*-ray crystallography. The three Fe–N bond lengths of the co-ordinated macrocycle are equidistant within experimental error [average 2.26(2) Å] and agree well with those found in [Fe$_2$L$_2$(μ-OH)(μ-CH$_3$CO$_2$)$_2$][ClO$_4$]·H$_2$O.[5]

The two Fe–N bonds of the terminal and bridging thiocyanato ligand are not equivalent [2.14(2) and 2.03(2) Å respectively], which is in accord with the observation of two ν(NCS) bands in the i.r. spectrum at 2 070 and 2 020 cm^{-1}. The magnetic moment of 5.4 μ_B per iron(II) is independent of the temperature between 100 and 293 K and indicates four unpaired electrons (*d*^{6} high-spin configuration). No or negligible intradimer exchange coupling is observed in contrast to the [Ni$_2$(en)$_4$(μ-NCS)$_2$][NCS]$_2$ (en = ethylenediamine) and [Ni$_2$(tren)$_2$(μ-NCS)$_2$][NCS]$_2$ (tren = 2,2′,2″-triaminotriethylamine) complexes, where weak ferromagnetic intradimer coupling has been reported.[15,16]

For [{FeL(NCO)$_2$}$_2$] a similar binuclear structure containing two end-to-end co-ordinated isocyanato bridging ligands and two terminal N-co-ordinated OCN$^-$ ligands is proposed. In the i.r. spectrum of [{FeL(NCO)$_2$}$_2$] two ν(NCO) bands at 2 190 and 2 140 cm^{-1} are observed; the former may be assigned tentatively to the bridging μ-isocyanate, ν_{asym}(OCN), whereas the latter may be the ν_{asym}(OCN) mode of a terminal N-co-ordinated OCN$^-$ ligand.[17] The magnetic moment of 5.35 μ_B per Fe$^{\text{II}}$ is again temperature independent between 100 and 298 K, indicating high-spin electron configurations of both Fe$^{\text{II}}$ centres in the dimer with negligible intramolecular exchange coupling. The magnetic susceptibility data in this temperature range adhere closely to the Curie–Weiss law; θ was found to be +4.2

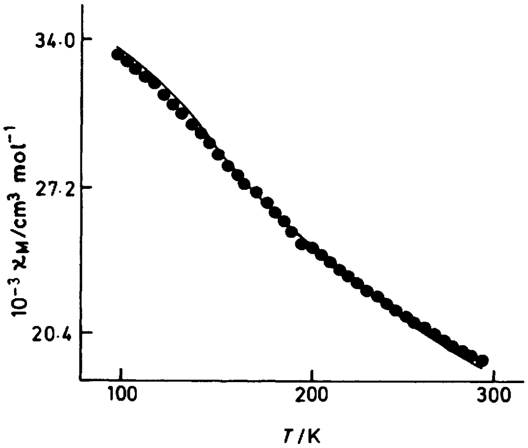

Figure 2. Molar magnetic susceptibility of $[\{FeL(N_3)_2\}_2]$ as a function of temperature: (——) calculated, (●) experimental

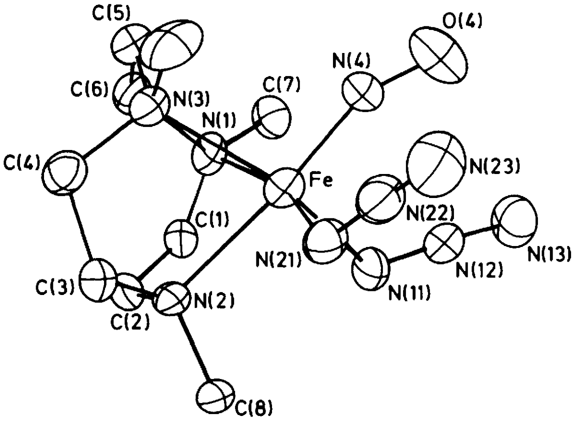

Figure 3. Molecular structure of $[FeL(NO)(N_3)_2]$ and atomic numbering scheme

K, which may indicate a very weak ferromagnetic coupling. The corresponding complexes $[Ni_2(tren)_2(OCN)_2][BPh_4]_2$ and $[Cu(tren)_2(OCN)_2][BPh_4]_2$ display a weak antiferromagnetic exchange interaction ($J = -4.4$ cm^{-1}) for the former and no coupling for the latter.[16]

It is noted that Little and Long[18] have reported a series of high-spin pseudo octahedral $[Fe(py)_2X_2]$ (py = pyridine) complexes (X = NCO, NCS, Cl, or Br), which have polymeric chain structures with bridging end-to-end co-ordinated NCS^- or NCO^- ligands. These materials also display normal Curie–Weiss behaviour above 100 K (high-spin Fe^{II}) with no spin-exchange coupling.

Interestingly, and in contrast to the complexes $[\{FeL(NCS)_2\}_2]$ and $[\{FeL(NCO)_2\}_2]$, the variable-temperature magnetic susceptibility data (100—298 K) of $[\{FeL(N_3)_2\}_2]$ provide evidence for a binuclear structure of this species. The molar magnetic susceptibility as a function of temperature is shown in Figure 2. The magnetic data were found to be reproducible between different preparations. The data were readily fitted using an isotropic Heisenberg model, $H = -2J\, S_1 \cdot S_2$ with $S_1 = S_2 = 2$ and $g = 2.2$.[19] The spin-exchange coupling constant, J, was calculated to be -11 cm^{-1}. Thus $[\{FeL(N_3)_2\}_2]$ displays weak intramolecular antiferromagnetic coupling, which is thought to be propagated by two end-to-end µ-azido bridges.[20] A similar structure has been established by X-ray crystallography for $[Ni_2(L'')_2(N_3)_2(\mu\text{-}N_3)_2]$,[1] where L″ is the tridentate macrocycle 1,5,9-triazacyclododecane. This complex shows strong intradimer antiferromagnetic coupling.[1] In the i.r. spectrum of $[\{FeL(N_3)_2\}_2]$, two $\nu(N_3)$ frequencies at 2 080 and 2 020 cm^{-1} are observed. We have as yet not been able to grow single crystals of $[\{FeL(N_3)_2\}_2]$ suitable for an X-ray structure determination.

Duggan and Hendrickson[16] have analysed the variability of exchange coupling in end-to-end co-ordinated bridging NCS^-, OCN^-, and N_3^- nickel(II) dimers in terms of the symmetry and energies of the bridge molecular orbitals. For a symmetric bridging situation, *e.g.* in the µ-azido-bridged Fe^{II} dimer, there are no first-order ferromagnetic exchange pathways, whereas in the µ-cyanato- and µ-thiocyanato-bridged complexes, where the bridge is no longer symmetric [in the sense that no mirror plane exists perpendicular to the Fe $\cdots$ Fe vector of the planar $Fe_2(\mu\text{-}NCS)_2$ or $Fe_2(\mu\text{-}NCO)_2$ unit], ferromagnetic and antiferromagnetic exchange pathways are possible, which may effectively cancel each other at temperatures > 100 K. Thus the present series of complexes may be another illustration of the situation described for the analogous Ni^{II} dimers.

Table 5. Important distances (Å) and angles (°) in $[FeL(NO)(N_3)_2]$

Fe–N(1)	2.273(4)	Fe–N(21)	2.032(4)
Fe–N(2)	2.246(4)	N(11)–N(12)	1.196(6)
Fe–N(3)	2.236(3)	N(12)–N(13)	1.167(7)
Fe–N(4)	1.738(5)	N(21)–N(22)	1.193(7)
Fe–N(11)	2.075(4)	N(22)–N(23)	1.149(7)
		N(4)–O(4)	1.142(7)
Fe–N(4)–O(4)	155.5(10)	Fe–N(11)–N(12)	120.7(3)
Fe–N(21)–N(22)	127.0(4)	N(11)–N(12)–N(13)	176.6(9)
N(21)–N(22)–N(23)	174.7(7)	N(11)–Fe–N(21)	96.9(3)
N(11)–Fe–N(3)	163.9(10)	N(1)–Fe–N(2)	78.4(2)
N(21)–Fe–N(3)	93.5(2)	N(11)–Fe–N(4)	94.2(3)
N(21)–Fe–N(4)	97.2(3)	N(4)–Fe–N(1)	97.3(3)
N(1)–Fe–N(3)	78.4(2)	N(11)–Fe–N(1)	88.5(2)
N(21)–Fe–N(1)	164.1(11)	N(4)–Fe–N(2)	174.3(9)
N(2)–Fe–N(3)	79.1(2)	N(11)–Fe–N(2)	89.2(2)
N(21)–Fe–N(2)	86.7(2)	N(4)–Fe–N(3)	96.6(3)

$[\{FeL(NCS)_2\}_2]$ and $[\{FeL(N_3)_2\}_2]$ reacted readily under anaerobic conditions in methanolic solution with NO yielding brown crystalline solids of $[FeL(NO)(NCS)_2]$ and $[FeL(NO)(N_3)_2]$, respectively. Both complexes are soluble in a variety of polar organic solvents such as acetonitrile, dichloromethane, and methanol. The i.r. spectra exhibit intense bands at 1 735 cm^{-1} for $[FeL(NO)(NCS)_2]$ and at 1 690 cm^{-1} for $[FeL(NO)(N_3)_2]$, which are assigned to the N–O stretching frequency.

Crystals of $[FeL(NO)(N_3)_2]$ were suitable for X-ray crystallography; they consist of monomeric, six-co-ordinate iron nitrosyl complexes of the type '$\{Fe\text{–}NO\}^7$' according to the nomenclature of Enemark and Feltham.[6] The molecular structure and the atomic labelling scheme are shown in Figure 3. Selected bond distances and angles of the $FeN_5(NO)$ core are given in Table 5. The geometry around the iron centre is distorted octahedral. The tridentate macrocycle is again facially co-ordinated. Two terminal azido ligands are *cis* with respect to each other. The Fe–NO moiety is bent; the Fe–N–O bond angle is 155.5(10)°. The co-ordinated NO is not disordered. The Fe–N distance of the Fe–NO group is short [1.738(5) Å] indicating considerable double-bond character. Interestingly, the Fe–NO moiety does not cause a significant lengthening of the *trans* Fe–N bond. No significant *trans* influence of the nitrosyl group was detected. For $[FeL(NO)(NCS)_2]$ we propose a similar structure containing two N-co-ordinated, terminal NCS ligands.

The compounds $[\mathrm{FeL(NO)(NCS)_2}]$ and $[\mathrm{FeL(NO)(N_3)_2}]$ are paramagnetic having a quartet ground state. The effective room-temperature magnetic moments are 4.20 and 4.06 μ_B, respectively. The temperature dependence of the magnetic susceptibilities were measured between 100 and 298 K. Both complexes obey Curie–Weiss law $[\chi_M = C/(T - \theta)]$ with $\theta = -2.9$ K for $[\mathrm{FeL(NO)(NCS)_2}]$ and $\theta = +1.4$ K for $[\mathrm{FeL(NO)(N_3)_2}]$. Thus both complexes are six-co-ordinate, high-spin species of the type $\{\mathrm{Fe{-}NO}\}^7$ containing three unpaired electrons. The fact that $[\mathrm{FeL(NO)(N_3)_2}]$ has a strongly bent FeNO group indicates that one component of π^*(NO) is occupied. Based on the molecular orbital scheme of Mingos[21] we propose the electronic configuration $[d_{yz}, \pi^*(\mathrm{NO})]^2$, $[d_{xz}, \pi^*(\mathrm{NO})]^2$, $(d_{xy})^1$, $[\pi^*(\mathrm{NO}), d_{z^2}]^1$, $[\pi^*(\mathrm{NO}), d_{yz}]^1$.

To our knowledge $[\mathrm{FeL(NO)(NCS)_2}]$ and $[\mathrm{FeL(NO)(N_3)_2}]$ represent the first case of well characterised octahedral $\{\mathrm{Fe{-}NO}\}^7$ complexes with a quartet ground state. There are a number of well characterised low-spin, six-co-ordinate iron nitrosyl complexes known;[22–24] they all contain bent Fe–N–O groups. The well known $[\mathrm{Fe(NO)(H_2O)_5}][\mathrm{SO_4}]$ is reported to be high spin but no structure determination appears to have been carried out.[25] A number of five-co-ordinate $\{\mathrm{Fe{-}NO}\}^7$ complexes are known to display spin-crossover phenomena ($S = \frac{3}{2} \longleftrightarrow S = \frac{1}{2}$), and crystal structures of [Fe(salen)(NO)] [salen = *N,N'*-ethylenebis(salicylideniminate)] at 98 ($S = \frac{1}{2}$) and 296 K ($S = \frac{3}{2}$) have been reported.[26–29] Only marginally significantly structural changes above and below the transition temperature were detected. The average Fe–N–O angle is 147° for the high-spin complex {comparable to the present structure of $[\mathrm{FeL(NO)(N_3)_2}]$} and 127° for the low-spin form. High- and low-spin forms of the also five-co-ordinate $[\mathrm{Fe(NO)(tmtactd)}]^{2+}$ (tmtactd = *N,N',N'',N'''*-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) have linear Fe–NO groups.[30]

The reaction of $[\mathrm{FeL'Cl_3}]^7$ in 0.1 mol dm^{-3} hydrochloric acid with sodium nitrite at room temperature afforded a clear brown solution, from which upon addition of sodium perchlorate brown crystals of $[\mathrm{FeL'(NO)(NO_2)_2}][\mathrm{ClO_4}]\cdot 2\mathrm{H_2O}$ precipitated. In the i.r. spectrum (KBr disc) a strong ν(NO) band was observed at 1 890 cm^{-1} which is characteristic for iron nitrosyl complexes of the type '$\{\mathrm{Fe{-}NO}\}^6$'; $\nu_{\mathrm{asym}}(\mathrm{NO_2})$ and $\nu_{\mathrm{sym}}(\mathrm{NO_2})$ stretching frequencies at 1 430 and 1 310 cm^{-1} are indicative of N-co-ordinated nitro groups. A six-co-ordinate, octahedral monocation containing a facially co-ordinated cyclic triamine, one nitrosyl, and two nitro ligands is formed by the above reaction. Variable-temperature magnetic susceptibility measurements (100—298 K) of a powdered sample indicate a small temperature-independent magnetic moment of 1.2 μ_B. Low-spin $\{\mathrm{Fe{-}NO}\}^6$ complexes are known to show in some instances a small temperature-independent paramagnetism; *e.g.* for $[\mathrm{Fe(S_2CNR_2)_2(NO)X}]$ (X = Br or I) complexes effective magnetic moments at room temperature of 0.44—1.12 μ_B have been reported.[31] On the other hand, it is also conceivable that contamination by small amounts of the reduced form $[\mathrm{FeL'(NO)(NO_2)_2}]$, a paramagnetic $\{\mathrm{Fe{-}NO}\}^7$ species (see below) is responsible for the observed magnetic moment. Nitrosyl nitro iron complexes of the type $\{\mathrm{Fe{-}NO}\}^6$ and low-spin $\{\mathrm{Fe{-}NO}\}^7$ have been extensively studied by Ileperuma and Feltham.[32]

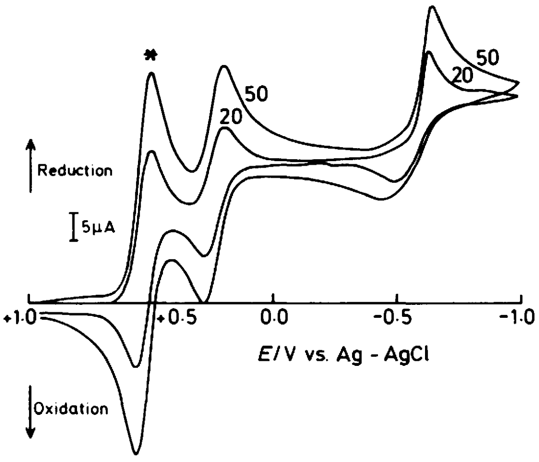

Figure 4. Cyclic voltammogram of $[\mathrm{FeL'(NO)(NO_2)_2}][\mathrm{ClO_4}]\cdot 2\mathrm{H_2O}$ (*ca.* 10^{-3} mol dm^{-3}) in acetonitrile {0.1 mol dm^{-3} $[\mathrm{NBu_4}][\mathrm{PF_6}]$ supporting electrolyte, ferrocenium–ferrocene internal standard(*), 25 °C, Au electrode}

The cyclic voltammogram of $[\mathrm{FeL'(NO)(NO_2)_2}][\mathrm{ClO_4}]\cdot 2\mathrm{H_2O}$ in acetonitrile containing tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) as supporting electrolyte is shown in Figure 4. In the potential range +1.0 to −1.0 V (*vs.* Ag–AgCl) a reversible one-electron-transfer process at $E_{\frac{1}{2}} = -0.29$ V *vs.* ferrocenium–ferrocene and an irreversible one-electron reduction at −1.18 V *vs.* ferrocenium–ferrocene are observed (Figure 4; see below). The ratio $I_p^{\mathrm{ox}}/I_p^{\mathrm{red}}$ for the former

$$\underset{\{\mathrm{Fe{-}NO}\}^6}{[\mathrm{FeL'(NO)(NO_2)_2}]^+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \underset{\{\mathrm{Fe{-}NO}\}^7}{[\mathrm{FeL'(NO)(NO_2)_2}]}$$

process of unity and $\Delta E_p = 85$ mV are independent of the scan rate (50—200 mV s^{-1}). Coulometric measurements at a potential of −0.4 V *vs.* Ag–AgCl indicate the transfer of 0.9 ± 0.2 electrons per iron centre.

Thus it is possible to reduce the $\{\mathrm{Fe{-}NO}\}^6$ complex reversibly yielding a $\{\mathrm{Fe{-}NO}\}^7$ species. We have as yet not been able to reduce $[\mathrm{FeL'(NO)(NO_2)_2}]^+$ chemically and isolate the proposed neutral complex $[\mathrm{FeL'(NO)(NO_2)_2}]$.

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