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Transition Metal Complexes with Sulfur Ligands. XXXVIII*. 18 and 19 Electron Iron(II) Nitrosyl Complexes with Thiolato Thioether Ligands Including Nitrogen and Oxygen Donators in S_5, OS_4, NS_4, S_4 and S_3 Donator Sets: Synthesis and Reactions of $[Fe(NO)('S_5')]^{n+}$, $[Fe(NO)('N_HS_4')]^{n+}$ ($n = 0, 1$) and $[Fe(NO)_2(L)]$ and X-ray Structure Analysis of $[Fe(NO)('N_HS_4')]$**

DIETER SELLMAN†, HERBERT KUNSTMANN, MATTHIAS MOLL and FALK KNOCH

Institut für anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstr. 1, D-8520 Erlangen, F.R.G.

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Abstract

In order to investigate the coordination and activation of nitrogen monoxide by iron centers in a coordination sphere dominated by sulfur, a series of new iron nitrosyl complexes has been synthesized. The mononitrosyl Fe^{II} complexes $[Fe(NO)('S_5')]BF_4$ and $[Fe(NO)('N_HS_4')]BF_4$ with the pentadentate ligands $'S_5'^{2-}$ = 1,5-bis-(2-mercaptophenylthio)-3-thiapentane(2–) or $'N_HS_4'^{2-}$ = 1,5-bis-(2-(2-mercaptophenylthio)ethyl)amine(2–) are obtained from $NOBF_4$ and $[Fe(CO)('XS_4')]$ (X = S, NH). If these and related carbonyl complexes are reacted with gaseous nitrogen monoxide the dinitrosyl complexes $[Fe(NO)_2(L)]$ are isolated with L = $'S_5'^{2-}$, $'OS_4'^{2-}$ = 1,5-bis(2-(2-mercaptophenylthio)ethyl)ether(2–), $'S_4'^{2-}$ = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2–) and $'S_3'^{2-}$ = 1,4,7-trithiaheptane(2–). Reacting $[Fe(NO)('XS_4')]BF_4$ with N_2H_4 or N_3^- does not lead to a nucleophilic attack at NO, but to a reduction yielding the neutral 19 electron species $[Fe(NO)('XS_4')]$ (X = NH, S); the reaction between $[Fe(NO)('S_5')]BF_4$ and hydroxylamine gives the dinitrosyl species $[Fe(NO)_2('S_5')]$ again. The formation of the different products is explained by a primary reaction resulting in the 19 electron complexes $[Fe(NO)('XS_4')]^{\bullet}$, (X = S, NH); they are either isolated or react with another NO (e.g. from gaseous NO or NH_2OH) yielding the dinitrosyl species in which S or X donators are decoordinated. This is supported by the reaction of $[Fe(NO)('S_5')]BF_4$ with sodium borohydride resulting again in $[Fe(NO)('S_5')]$. A 19 electron intermediate forms also in the reaction between $[Fe(NO)('XS_4')]BF_4$, X = S, NH and PMe_3 leading to a substitution-reduction product $[Fe(PMe_3)('XS_4')]$ under smooth conditions. The $[Fe(NO)('XS_4')]$ species (X = S, NH) are paramagnetic (μ_{eff} = 2.36 and 2.13 BM respectively); all other complexes are diamagnetic and were characterized by spectroscopic means and elemental analyses.

$[Fe(NO)('N_HS_4')]$ crystallizes in space group $P2_1/c$ with $a = 1262.7(6)$, $b = 744.9(7)$, $c = 1988.6(9)$ pm, $\beta = 106.45(4)°$, $Z = 4$ and $D_{calc} = 1.60$ g/cm^3; $R = 0.067$, $R_w = 0.058$. The iron center is pseudo-octahedrally coordinated by four S atoms in a plane and two *trans* N atoms; the FeNO group is strongly bent (147.2(7)°). Bond distances and angles of the $[FeN_2S_4]$ core indicate that the odd electron occupies a molecular orbital of $\pi^*(NO)$ as well as $[FeN_HS_4]$ character.

Introduction

Activation of molecular nitrogen by coordination to iron and/or molybdenum sulfur centers is considered to be one of the key steps in nitrogen fixation by nitrogenases. All attempts, however, to substantiate this by synthesizing a transition metal sulfur ligand complex which coordinates molecular nitrogen, have proved unsuccessful so far. Rather, the search for such a species has turned into the investigation of the fundamental and characteristic properties which are shown by metal sulfur ligand complexes. These properties are of significance for many oxidoreductases as well [2], but in the context of nitrogenase the coordination of CO or NO^+, which are isoelectronic to N_2, is of special interest. Here we report the syntheses and properties of nitrosyl complexes with the fragments $[Fe('S_5')]$ (I), $[Fe('N_HS_4')]$ (II) and $[Fe('OS_4')]$ (III) respectively, as well as closely related compounds.

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*Dedicated to Professor Ernst Otto Fischer on the occasion of his 70th birthday. For Part XXXVII see ref. 1.

**$'S_5'^{2-}$ = 1,5-bis-(2-mercaptophenylthio)-3-thiapentane-(2–), $'N_HS_4'^{2-}$ = 1,5-bis(2-(2-mercaptophenylthio)ethyl)-amine(2–); L = $'S_5'^{2-}$, $'S_4'^{2-}$ = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2–), $'S_3'^{2-}$ = 1,4,7-Trithiaheptane(2–) and $'OS_4'^{2-}$ = 1,5-bis(2-(2-mercaptophenylthio)ethyl)ether(2–).

†Author to whom correspondence should be addressed.

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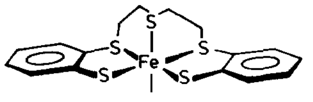

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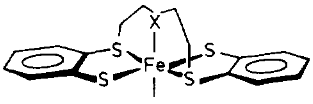


II: X = NH, III: X = O

Experimental

General

All reactions were carried out under nitrogen using the Schlenk technique. Solvents were dried and distilled under nitrogen before use. IR spectra (CaF_2 cuvettes or KBr disks) were recorded on a Zeiss IMR 16 infrared spectrometer; the solvent bands were compensated. Mass spectra were recorded on a Varian MAT 212 mass spectrometer and NMR spectra on a Jeol PMX 60 (^1H) and a Jeol FT-JNM-GX 270 spectrometer (^1H, ^{13}C). Magnetic moments were determined with a Johnson Matthey magnetic susceptibility balance. N_2H_4 was obtained by distilling N_2H_5OH (Fluka) from KOH at reduced pressure. The other reagents were purchased from the following companies: $NaBH_4$, $NOBF_4$, n-butyllithium: Merck, $NH_2OH{\cdot}HCl$: Fluka, $'S_3'{-}H_2$: EGA. $[Fe(CO)('S_5')]$ [3], $[Fe(CO)('XS_4')]$ (X = NH, O) [1], $[Fe('S_4')(CO)_2]$ [4] and PMe_3 [5] were prepared as described in the literature.

X-ray Structure Determination of $[Fe(NO)('N_HS_4')]$

Single crystals (*ca.* $0.4 \times 0.4 \times 0.15$ mm^3) were grown by slow condensation of methanol into a DMF solution of $[Fe(NO)('N_HS_4')]$ and sealed in a glass capillary. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically, the aromatic hydrogen atoms were calculated for ideal geometry and restricted during refinement; the methylene hydrogen atoms were calculated for ideal tetrahedra and rotated around the central carbon atom during refinement. The isotropic hydrogen atoms were refined with a common temperature factor. The amine hydrogen atom was determined by difference Fourier synthesis and refined as a rigid group. Table I contains crystal data and data collection procedures, Table II the final atomic coordinates.

Synthesis of Complexes

$[Fe('S_5')(NO)]BF_4$

58 mg (0.5 mmol) of $NOBF_4$ in solid form were added to a suspension of 225 mg (0.5 mmol) of $[Fe(CO)('S_5')]$ in 25 ml of CH_2Cl_2. After stirring for

TABLE I. Summary of Crystallographic Data and Data Collection Procedures of $[Fe(NO)('N_HS_4')]$

M_r	437.4
Space group	$P2_1/c$
Crystal system	monoclinic
Cell dimensions	
a (pm)	1262.7(6)
b (pm)	744.9(7)
c (pm)	1988.6(9)
β (°)	106.45(4)
Molecules/unit cell	4
Cell volume (pm^3)	$1794(2) \times 10^6$
D_{calc} (g/cm^3)	1.60
Diffractometer	Nicolet-3m/V
Radiation	Mo Kα/graphite monochromator
Scan technique	ω
Scan speed (°/min)	$3.0 < \theta < 15$
$2\theta_{max}$ (°)	54
Independent reflections	3018
Reflections collected	4383
σ-criterion	$F_o > 5.0\sigma(F)$
Program	SHELXTL-PLUS
R	0.067
R_w	0.058
Temperature of measurement	211 K

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (pm$^2 \times 10^{-1}$) of the Non-hydrogen Atoms of $[Fe(NO)('N_HS_4')]$

	x	y	z	U(eq)
Fe(1)	2656(1)	81(2)	291(1)	16(1)
N(1)	3697(7)	−1434(10)	257(4)	24(3)
O(1)	3968(7)	−2614(10)	−37(4)	48(3)
N(2)	1388(6)	2263(10)	221(3)	18(2)
S(1)	2175(2)	−1008(3)	1244(1)	23(1)
S(2)	3843(2)	2120(3)	1032(1)	21(1)
S(3)	2812(2)	1369(3)	−731(1)	19(1)
S(4)	1276(2)	−1714(3)	−342(1)	21(1)
C(15)	3802(7)	1476(12)	1893(4)	21(3)
C(14)	4524(8)	2303(12)	2470(4)	25(3)
C(13)	4502(8)	1813(13)	3137(4)	26(3)
C(12)	3815(7)	497(12)	3228(4)	24(3)
C(11)	3086(8)	−357(12)	2660(4)	22(3)
C(10)	3066(7)	129(12)	1972(4)	18(3)
C(16)	2969(9)	4124(12)	915(5)	29(4)
C(17)	1763(8)	3621(13)	790(5)	27(3)
C(25)	1947(7)	−34(12)	−1399(4)	19(3)
C(24)	1977(8)	198(12)	−2099(4)	23(3)
C(23)	1288(8)	−874(12)	−2618(4)	26(3)
C(22)	602(8)	−2131(12)	−2450(4)	24(3)
C(21)	571(8)	−2366(13)	−1759(4)	26(3)
C(20)	1263(8)	−1347(11)	−1215(4)	19(3)
C(26)	1924(9)	3347(11)	−816(4)	23(3)
C(27)	978(8)	3021(12)	−495(5)	22(3)

14 h the brown suspension had turned to a green solution. It was concentrated to about one third of its original volume and filtered through filter pulp. Addition of 25 ml of pentane yielded brown needles after two days, which were collected, washed with 3 X 10 ml of diethylether and dried in high vacuum for 8 h. Yield: 190 mg (70%).

Anal. Calc. for $C_{16}H_{16}BF_4FeNOS_5$ (541.3): C, 35.50; H, 2.97; N, 2.58. Found: C, 35.38; H, 3.01; N, 2.54%.

$[Fe(NO)('N_HS_4')]BF_4$

54 mg (0.46 mmol) of $NOBF_4$ in solid form were added to a red solution of 200 mg (0.46 mmol) of $[Fe(CO)('N_HS_4')]$ in 20 ml of CH_2Cl_2. The mixture was stirred for 15 h during which time the colour turned to dirty green. After filtration 25 ml of diethylether were added. The resulting dark green crystals were collected and dried in high vacuum for 10 h. Yield: 150 mg (60%).

Anal. Calc. for $C_{16}H_{17}BF_4FeN_2OS_4$ (524.2): C, 36.65; H, 3.27; N, 5.34. Found: C, 36.55; H, 3.35; N, 5.33%.

$[Fe(NO)_2('S_5')]$

Through a red brown suspension of 400 mg (0.89 mmol) of $[Fe(CO)('S_5')]$ in 50 ml of methanol gaseous NO was bubbled for 2 h. After stirring the reaction mixture for 2 d NO was bubbled again through the reaction mixture which had turned to brown. After another 2 d of stirring a brown solid was collected, washed with 10 ml of methanol, dried in vacuum and extracted with 10 ml of 1,2-dichloroethane. The extract was filtered and 10 ml of ethanol were added to the brown filtrate yielding a highly viscous precipitate. It solidified when drying in high vacuum for 8 h. Yield: 80 mg (19%).

Anal. Calc. for $C_{16}H_{16}FeN_2O_2S_5$ (484.5): C, 39.66; H, 3.33; N, 5.78. Found: C, 39.83; H, 3.43; N, 5.76%.

$[Fe(NO)_2('OS_4')]$

Through a suspension of 180 mg (0.41 mmol) of $[Fe(CO)('OS_4')]$ in 25 ml of methanol gaseous NO was bubbled for 1.5 h, leading to a colour change from violet to brown. After stirring for 15 h the brown precipitate which formed was collected, washed with methanol and diethylether and dried in vacuum. The precipitate was redissolved in 10 ml of 1,2-dichloroethane. Addition of 10 ml of ethanol yielded again a brown precipitate which was collected and dried in high vacuum for 10 h. Yield: 52 mg (27%).

Anal. Calc. for $C_{16}H_{16}FeN_2O_3S_4$ (468.4): C, 41.03; H, 3.44; N, 5.98. Found: C, 41.03; H, 3.50; N, 5.98%.

$[Fe(NO)_2('S_4')]$

A solution of 420 mg (1 mmol) of $[Fe(CO)_2('S_4')]$ in 30 ml of chloroform was heated to 60 °C. Bubbling NO through the red solution for 3 h led to a colour change to brown. After addition of 25 ml of ethanol the mixture was kept at −78 °C for 5 d yielding a brown precipitate which was collected and dried in high vacuum for 6 h. Yield: 70 mg (16%).

Anal. Calc. for $C_{14}H_{12}FeN_2O_2S_4$ (424.7): C, 39.68; H, 2.84; N, 6.60. Found: C, 39.67; H, 2.84; N, 6.42%.

$[Fe(NO)_2('S_3')]$

2 mmol of n-butyllithium (1.27 ml of a 1.6 molar solution of n-butyllithium in n-hexane) were added to 0.13 ml (155 mg, 1 mmol) of $'S_3'$-H_2 in 30 ml of THF at −78 °C. After warming up to room temperature 200 mg (1 mmol) of $FeCl_2 \cdot 4H_2O$ were added and NO was bubbled through the mixture, which was stirred for another 48 h under NO. The mixture was evaporated to dryness and the residue was stirred with 20 ml of methanol yielding an orange precipitate. It was collected, washed with 2 X 10 ml of methanol and 2 X 10 ml of diethylether and dried in high vacuum for 8 h. Yield: 130 mg (48%).

Anal. Calc. for $C_4H_8FeN_2O_2S_3$ (269.13): C, 17.92; H, 3.03; N, 10.44. Found: C, 17.97; H, 3.13; N, 10.40%.

$[Fe(NO)('N_HS_4')]$

A solution of 65 mg (0.38 mmol) of NEt_4N_3 in 10 ml of CH_2Cl_2 was added dropwise to 100 mg (0.19 mmol) of $[Fe(NO)('N_HS_4')]BF_4$ in 15 ml of CH_2Cl_2 at −20 °C. After stirring for 1 h the red–brown mixture was evaporated to dryness and the residue stirred with 20 ml of methanol for 15 h. The green precipitate which had formed was collected, washed with 2 X 10 ml of methanol and dried in high vacuum for 6 h. Yield: 40 mg (48%).

Anal. Calc. for $C_{16}H_{17}FeN_2OS_4$ (437.4): C, 43.94; H, 3.91; N, 6.41. Found: C, 44.17; H, 3.94; N, 5.92%.

$[Fe(NO)('S_5')]$

0.1 ml (*ca.* 3 mmol) of N_2H_4 were added to 175 mg (0.32 mmol) of $[Fe(NO)('S_5')]BF_4$ in 25 ml of methanol yielding a green voluminous precipitate. After stirring the mixture for another 15 h the green precipitate was collected, washed with 3 X 10 ml of methanol and 10 ml of chloroform and dried in high vacuum for 6 h. Yield: 90 mg (65%).

Anal. Calc. for $C_{16}H_{16}FeNOS_5$ (454.4): C, 42.29; H, 3.55; N, 3.08. Found: C, 42.57; H, 3.58; N, 2.65%.

$[Fe(NO)('S_5')]$ *by reaction of* $[Fe(NO)('S_5')]BF_4$ *with* NEt_4N_3

55 mg (0.32 mmol) of NEt_4N_3 were added to 175 mg (0.32 mmol) of $[Fe(NO)('S_5')]BF_4$ in 20 ml of methanol at −30 °C. During 15 h of stirring the mixture was warmed up to 10 °C yielding a green

precipitate which was collected, dried in vacuum and digested with 20 ml of acetone by stirring for 15 h. The green precipitate was collected and dried in high vacuum for 10 h. Yield: 70 mg (48%).

Anal. Calc. for $C_{16}H_{16}FeNOS_5$ (454.4): C, 42.29; H, 3.55; N, 3.08. Found: C, 42.42; H, 3.54; N, 2.21%.

$[Fe(NO)_2('S_5')]$ by reaction of $[Fe(NO)('S_5')]BF_4$ with $NH_2OH \cdot HCl$

175 mg (0.32 mmol) of $[Fe(NO)('S_5')]BF_4$ in 20 ml of methanol were stirred with 22 mg (0.32 mmol) of $NH_2OH \cdot HCl$ for 5 d. A brown precipitate formed which was collected, dried in vacuum and redissolved in CH_2Cl_2. The brown solution was filtered over SiO_2, evaporated to dryness and the resulting brown powder was dried in high vacuum for 6 h. Yield: 70 mg (45%).

Anal. Calc. for $C_{16}H_{16}FeN_2O_2S_5$ (484.5): C, 39.66; H, 3.33; N, 5.78. Found: C, 45.52; H, 3.83; N, 2.92%.

$[Fe(NO)('S_5')]$ by reaction of $[Fe(NO)('S_5')]BF_4$ with $NaBH_4$

10 mg (0.24 mmol) of $NaBH_4$ were added at −78 °C to 130 mg (0.24 mmol) of $[Fe(NO)('S_5')]BF_4$ in 15 ml of methanol. While stirring for 15 h the temperature was increased to 10 °C and a green precipitate formed. It was collected, washed with 3 × 10 ml of methanol and dried in vacuum for 30 min. Subsequently it was washed with 5 ml of $CHCl_3$ and dried in high vacuum for 20 h. Yield: 60 mg (55%).

Anal. Calc. for $C_{16}H_{16}FeNOS_5$ (454.4): C, 42.29; H, 3.55; N, 3.08. Found: C, 40.43; H, 3.30; N, 2.59%.

$[Fe(PMe_3)('S_5')]$ by reaction of $[Fe(NO)('S_5')]BF_4$ with PMe_3

0.3 ml (*ca.* 3 mmol) of PMe_3 were added to 130 mg (0.24 mmol) of $[Fe(NO)('S_5')]BF_4$ in 15 ml of methanol at −20 °C. The mixture was stirred for 15 h yielding a brown precipitate. It was collected, washed with 2 × 5 ml of methanol, dried in high vacuum for 8 h and analyzed as $[Fe(NO)(PMe_3)('S_5')]$. Yield 65 mg (51%).

Anal. Calc. for $C_{19}H_{25}FeNOPS_5$ (530.5): C, 43.02; H, 4.75; N, 2.64. Found: C, 43.63; H, 5.36; N, 1.52%.

The brown material was dissolved in 20 ml of CH_2Cl_2, filtered over filter pulp and 25 ml of pentane were added to the brown filtrate yielding brown microcrystals after 2 d. They were collected, washed with diethylether, dried in vacuum for 10 h and analyzed as $[Fe(PMe_3)('S_5')]$. Yield 30 mg (25% relative to $[Fe(NO)('S_5')]BF_4$).

Anal. Calc. for $C_{19}H_{25}FePS_5$ (500.2): C, 45.57; H, 4.99; N, 0.00. Found: C, 44.85; H, 4.97; N, 0.09%.

$[Fe(PMe_3)('N_HS_4')]$ by reaction of $[Fe(NO)('N_HS_4')]BF_4$ with PMe_3

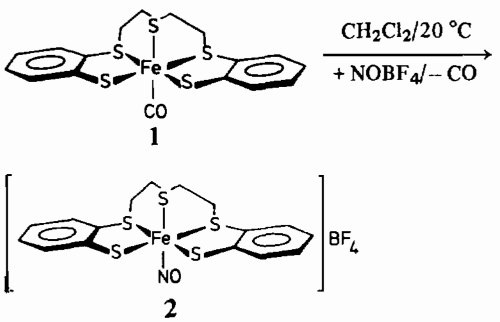
0.3 ml (*ca.* 3 mmol) of PMe_3 in 10 ml of methanol were added dropwise to 100 mg (0.19 mmol) of $[Fe(NO)('N_HS_4')]BF_4$ in 20 ml of methanol at −20 °C. After warming up to room temperature the green precipitate which formed was collected, washed with methanol and dried in high vacuum for 6 h. Yield: 50 mg (54%).

Anal. Calc. for $C_{19}H_{26}FeNPS_4$ (483.1): C, 47.24; H, 5.42; N, 2.90%. Found: C, 46.29; H, 5.35; N, 2.55%.

Results and Discussion

Synthesis of Mononitrosyl Complexes

The thermally very stable carbonyl complex **1** reacts with $NOBF_4$ under smooth conditions according to eqn. (1).



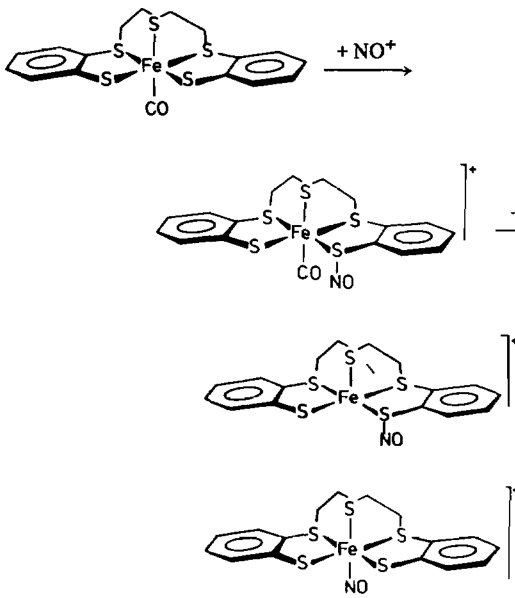
1

2

(1)

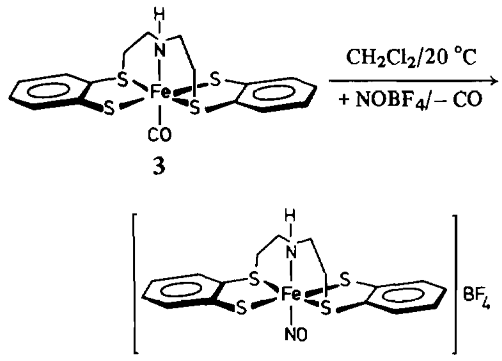
The red–brown CH_2Cl_2 solution of **1**, which contains also undissolved **1**, turns into a clear green solution upon the addition of solid $NOBF_4$ under simultaneous evolution of carbon monoxide; monitoring the reaction by solution IR spectroscopy shows the decrease of the ν(CO) band of **1** at 1960 cm^{-1} and the concomitant increase of the ν(NO) band of **2** at 1880 cm^{-1}; after *ca.* 14 h the reaction is finished and only the ν(NO) band of **2** can be observed. Filtration and addition of pentane precipitates brown needles of **2**, which are soluble in CH_2Cl_2, THF, acetone or methanol giving green to blue–green solutions. Analogously $[Fe(NO)('S_5')]PF_6$ is obtained with $NOPF_6$. In KBr the characteristic ν(NO) band of **2** appears slightly shifted at 1870 cm^{-1}. The ^{13}C NMR spectrum of **2** shows two signals for the C_2H_4 groups at 52.15 and 46.15 ppm and only six C_6H_4 signals between 152.40 and 127.13 ppm (see Table V). The number of signals proves, that the benzorings are in plane and **2** possesses the same configuration as **1**, whose structure has been determined by X-ray structure analysis; it proved to be the *meso* form of all isomers which are possible for $[Fe(CO)('S_5')]$ [6a].

1 is a thermally very stable carbonyl complex and heating it in DMF solution up to 140 °C for several hours causes no noticeable decarbonylation [3]. The facile CO substitution by NO^+ under retention of configuration points to an indirect substitution mechanism. As suggested for complexes with the tertiary butyl derivative of $'S_5'^{2-}$ we assume that the CO substitution takes place via a thionitrosylation [6a] of the thiolato S atom (eqn. (2))



(2)

The positive charge induced by nitrosylating the thiolato S atom labilizes the Fe–CO bond in the same way as if the Fe(II) centers were oxidized; after removal of the CO ligand the free site of coordination is occupied by the NO ligand via a 1,2 (S–Fe) shift. In quite the same way **3** yields the corresponding **4**.



3

(3)

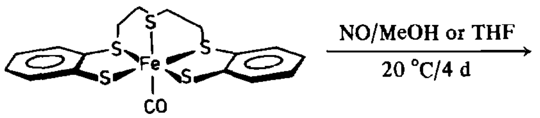
4

The fact, that **3** contains a fragment with thioether atoms occupying *trans* positions as well as an N donator atom *trans* to the CO ligand seems to have no influence on the reaction; here again the comparison of the ^{13}C NMR spectra of **3** and **4**, respectively, indicates that the $[Fe('N_HS_4')]$ fragments have identical configurations.

In the series of CO complexes with the fragments **I**, **II** or **III** respectively, $[Fe(CO)('OS_4')]$ is the most labile one and loses CO easily, e.g. upon heating in boiling CH_2Cl_2 [1]. This may be the reason that reacting $[Fe(CO)('OS_4')]$ with $NOBF_4$ in CH_2Cl_2 at room temperature does not give the expected $[Fe(NO)('OS_4')]BF_4$; other reactions take place rapidly leading to, among other products, a species showing two ν(NO) bands at 1760 and 1730 cm^{-1}. Even at temperatures as low as −78 °C $[Fe(NO)('OS_4')]BF_4$ could not be obtained.

Synthesis of Dinitrosyl Complexes

Another general method of synthesis of nitrosyl complexes is the reaction of carbonyl complexes with gaseous nitrogen monoxide exemplified by the conversion of $[Cr(CO)_6]$ into $[Cr(NO)_4]$ [7]. Substituting the 2 electron donator CO by the 3 electron donator NO in monocarbonyl complexes like $[Fe(CO)('S_5')]$ or $[Fe(CO)('OS_4')]$ should give 19 electron species which might be highly reactive, and because usually the 18 electron rule is obeyed by the complexes discussed here, consecutive reactions are to be expected. Indeed the reaction according to eqn. (4) does not lead to a mononitrosyl species, but to the dinitrosyl complex **5**. Carrying out the reaction in THF the decrease of the ν(CO) band at 1960 cm^{-1} and the increase of the ν(NO) bands at 1780 and 1750 cm^{-1} can be monitored by IR spectroscopy (Fig. 1). Isolation of the pure complex, however, is easier by carrying out reaction (4) in methanol; **5** is then obtained as a brown precipitate, which is soluble in THF, CH_2Cl_2, $CHCl_3$ or $1,2\text{-}C_2H_4Cl_2$.

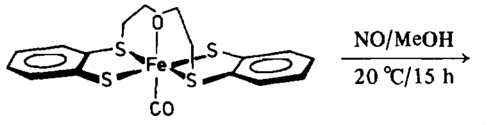


1

$[Fe(NO)_2('S_5')]$ (4)

5

The analogous reaction occurs with $[Fe(CO)('OS_4')]$ (eqn. (5)). Again a dinitrosyl complex is isolated as brown powder and analyzed as **6**. In the case of $[Fe(CO)('N_HS_4')]$ a dinitrosyl complex forms as well, here however, a pure compound could not be isolated.



$[Fe(NO)_2('OS_4')]$ (5)

6

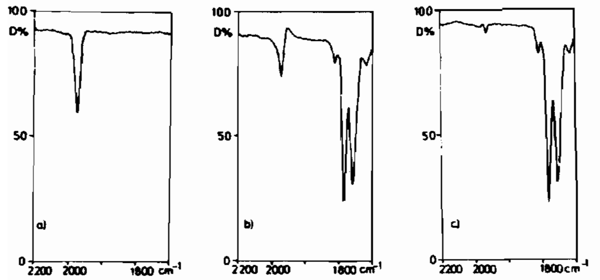


Fig. 1. ν(CO)/ν(NO) IR spectra in THF of (a) [Fe(CO)('S_5')], (b) after 2 d under gaseous NO and (c) after 3 d under NO.

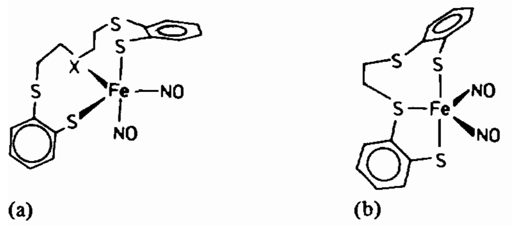


Fig. 2. Proposed structures of (a) [$Fe(NO)_2$('XS_4')] (X = S, O) and (b) [$Fe(NO)_2$('S_4')].

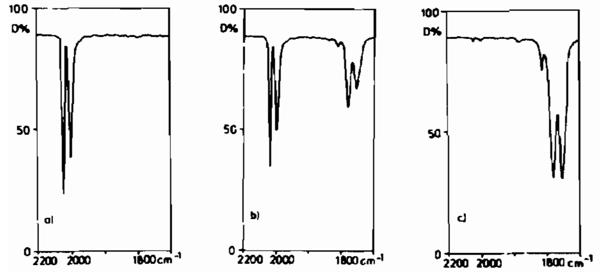
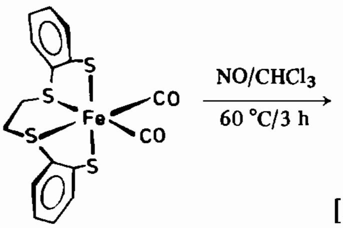


Fig. 3. ν(NO)/ν(CO) IR spectra in $CHCl_3$ of (a) [$Fe(CO)_2$('S_4')], (b) after 30 min of reaction with NO, (c) after 3 h of reaction with NO.

It has not been possible as yet to grow single crystals of these complexes, but their IR spectra with relatively high ν(NO) frequencies point to a *cis* dinitrosyl complex with linear NO bonds. According to the ^1H and ^{13}C NMR spectra the compounds are diamagnetic; if the 18 electron rule is not violated, a structure in which the ligands act in a tridentate manner only according to Fig. 2a is consistent with these data.

The decoordination of donator atoms of the 'S_5' ligand in [$Fe(NO)_2$('S_5')] also follows from the ^{13}C NMR spectrum (see Table III); it shows a larger number of signals than the starting complex [Fe(CO)('S_5')] indicating a lowering of symmetry in the iron ligand core.



[$Fe(NO)_2$('S_4')] (6)
7

The same principles obviously rule the reaction between [$Fe(CO)_2$('S_4')] and NO ('S_4'$^{2-}$ = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(−2)) according to eqn. (6). Bubbling NO through a $CHCl_3$ solution of [$Fe(CO)_2$('S_4')] leads to a rapid colour change from red to brown. Monitoring the reaction by solution IR spectra shows the decrease of the ν(CO) bands at 2040 and 1990 cm^{-1} of [$Fe(CO)_2$('S_4')] and the increase of ν(NO) bands at 1770 and 1750 cm^{-1} of [$Fe(NO)_2$('S_4')] (Fig. 3); a mixed carbonyl nitrosyl species cannot be observed. From the solution a brown powder is isolated, which analyzes as 7.

In accordance with the discussion above also in 7 the tetradentate 'S_4'$^{2-}$ ligand probably acts tridentately only (Fig. 2b); the similar ν(NO) frequencies suggest an identical set of donator atoms for 5, 6 and 7. Again a comparison of the ^{13}C NMR spectra of [$Fe(CO)_2$('S_4')] and [$Fe(NO)_2$('S_4')] indicates a lower symmetry of the latter one.

In order to confirm the assumption that the tetra- and pentadentate ligands act tridentately only [$Fe(NO)_2$('S_3')], 'S_3'$^{2-}$ = 1,4,7-tetrathiaheptane(2−), was also synthesized, which should show similar ν(NO) frequencies (eqn. (7)). [$Fe(NO)_2$('S_3')] was obtained as an orange powder, showing two ν(NO) bands at 1760 and 1725 cm^{-1}; the marginally lower ν(NO) frequencies might be attributed to the aliphatic thiolato donator S atoms.

$$FeCl_2{\cdot}4H_2O + \text{'}S_3\text{'}{-}Li_2 \xrightarrow[20\,°C/48\,h]{NO/THF}$$

$$[Fe(NO)_2(\text{'}S_3\text{'})] + 2LiCl + 4H_2O \qquad (7)$$

Even in this relatively simple case, a definite description of the structure on the basis of the spectroscopic data is not possible. The ^{13}C NMR spectrum shows four signals between 39.17 and 32.35 ppm, the two ν(NO) bands point to a *cis* position of the NO ligands, the 'S_3'$^{2-}$ ligand, however, can coordinate in two different ways, as shown by IV and V in Fig. 4; IV as well as V should give rise to two ^{13}C signals each.

IV V

Fig. 4. Proposed structures of [Fe(NO)$_2$('S$_3$')].

Because of the stereochemical non-rigidity, which is usually observed for five coordinate complexes, the individual configurations might easily interconvert explaining the appearance of four signals in the ^{13}C NMR spectrum.

In **5**, **6**, **7** and [Fe(NO)$_2$('S$_3$')] the iron centers are formally Fe^{II} (with neutral NO); they differ in this respect from the usual Fe(NO)$_2$ complexes with sulfur ligands, e.g. Roussin's ester [Fe(NO)$_2$(SR)]$_2$, which contains iron in the oxidation state +1 (neutral NO, thiolate −1) [8]. Furthermore the substitution of CO by two NO ligands leads obviously to the simultaneous cleavage of Fe–S bonds in order not to exceed a 18 electron configuration. Table III summarizes selected spectroscopic data of the iron dinitrosyl complexes.

Reactions of [Fe(NO)('XS$_4$')]BF$_4$ (X = S, NH) with Nucleophiles; Synthesis and Structure of the 19 Electron Complex [Fe(NO)('N$_H$S$_4$')]

The NO ligands in nitrosyl complexes with high ν(NO) frequencies usually can undergo nucleophilic addition reactions [9a, b]; accordingly we have attempted to react [Fe(NO)('XS$_4$')]BF$_4$ (X = S, NH) with nitrogen nucleophiles in order to convert the NO ligand into other nitrogen species. In no case could such a conversion be observed, but neutral 19 electron mononitrosyl or 18 electron dinitrosyl complexes formed.

Reacting [Fe(NO)('N$_H$S$_4$')]BF$_4$ according to eqn. (8) the green CH$_2$Cl$_2$ solution turns red–brown upon addition of the azide and working up yields green [Fe(NO)('N$_H$S$_4$')] (**8**). **8** is paramagnetic in the solid state (μ_{eff} = 2.13 BM, 295 K), but yields a relatively well resolved ^{1}H NMR spectrum in CD$_2$Cl$_2$. It shows the M^+ ion at m/e = 437 in the field desorption mass spectrum and a low frequency ν(NO) band at 1620 cm^{-1} in the IR spectrum. These data suggested the formation of one of the rare 19 electron complexes and in order to determine its molecular structure, an X-ray structure analysis was carried out. Figure 5 shows the view of one molecule, Table IV contains relevant distances and angles.

$$\underset{\mathbf{4}}{[Fe(NO)('N_HS_4')]BF_4} \xrightarrow[-20\,°C/1\,h]{NEt_4N_3/CH_2Cl_2}$$

$$\underset{\mathbf{8}}{[Fe(NO)('N_HS_4')]} + \text{other products} \qquad (8)$$

The Fe center of **8** is pseudooctahedrally surrounded by four sulfur atoms in a plane and two N atoms in the remaining *trans* positions. Noticeably the complex shows the *meso* configuration whereas

TABLE III. Selected Spectroscopic Data of the Iron Dinitrosyl Complexes[a]

Compound	IR in KBr (cm^{-1})		^{1}H NMR (ppm)	^{13}C NMR (pm)	MS (m/e)
[Fe(NO)$_2$('S$_3$')]	1795(sh) 1760 1725	ν(NO) ν(NO) ν(NO)	2.6–3.3m (C$_2$H$_4$)	39.17; 37.10; 32.50; 32.35; (C$_2$H$_4$)	EI 208 (M^+ – 2NO)
[Fe(NO)$_2$('S$_4$')]	1805(sh) 1770 1740	ν(NO) ν(NO) ν(NO)	6.7–7.9m (C$_6$H$_4$) 3.1–3.7m (C$_2$H$_4$)	141.07; 140.67; 134.76; 134.25; 132.74; 132.39; 129.76; 129.56; 127.74; 127.34; (C$_6$H$_4$) 35.32; (C$_2$H$_4$)	FD 396 (M^+ – C$_2$H$_4$)
[Fe(NO)$_2$('S$_5$')]	1810(sh) 1770 1740	ν(NO) ν(NO) ν(NO)	6.7–7.9m (C$_6$H$_4$) 2.8–3.6m (C$_2$H$_4$)	132.55; 130.93; 128.16; 127.83; 127.10; 126.06; 125.43; (C$_6$H$_4$) 34.27; 32.94; 30.71; 30.56; 30.31; (C$_2$H$_4$)	FD 484 (M^+)
[Fe(NO)$_2$('OS$_4$')]	1800(sh) 1765 1730	ν(NO) ν(NO) ν(NO)	6.3–7.6m (C$_6$H$_4$) 2.6–3.6m (C$_2$H$_4$)		FD 408 (M^+ – 2NO)

[a] sh: shoulder; m: multiplet; FD: field desorption; EI: electron impact ionisation; all NMR spectra were recorded in CDCl$_3$, relative to TMS.

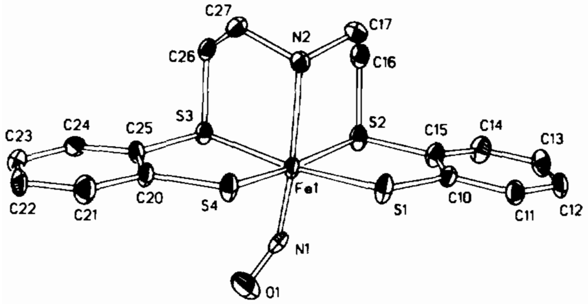


Fig. 5. Molecular structure of [Fe(NO)('N_HS_4')] (H atoms omitted).

TABLE IV. Selected Distances (pm) and Angles (°) of [Fe(NO)('N_HS_4')]

Fe(1)–N(1)	174.8(8)	N(2)–Fe(1)–N(1)	171.9(3)
Fe(1)–N(2)	225.8(7)	S(1)–Fe(1)–N(1)	100.5(2)
Fe(1)–S(1)	229.7(3)	S(1)–Fe(1)–N(2)	87.5(2)
Fe(1)–S(2)	234.1(3)	S(2)–Fe(1)–N(1)	95.1(3)
Fe(1)–S(3)	230.5(2)	S(2)–Fe(1)–N(2)	83.5(2)
Fe(1)–S(4)	227.2(3)	S(2)–Fe(1)–S(1)	88.9(1)
N(1)–O(1)	116.0(9)	S(3)–Fe(1)–N(1)	89.0(2)
N(2)–C(17)	149.1(11)	S(3)–Fe(1)–S(1)	169.5(1)
N(2)–C(27)	148.3(11)	S(4)–Fe(1)–N(1)	93.8(3)
S(1)–C(10)	177.7(8)	S(4)–Fe(1)–S(1)	84.7(1)
S(2)–C(15)	179.3(8)	S(4)–Fe(1)–S(2)	169.9(1)
S(2)–C(16)	183.1(10)	S(4)–Fe(1)–S(3)	90.1(1)
S(3)–C(25)	179.6(8)	O(1)–N(1)–Fe(1)	147.2(7)
S(3)–C(26)	183.0(9)	C(17)–N(2)–Fe(1)	112.0(5)
S(4)–C(20)	175.5(8)	C(10)–S(1)–Fe(1)	104.5(3)
C(15)–C(10)	140.6(12)	C(15)–S(2)–Fe(1)	104.0(3)
C(16)–C(17)	151.9(14)	C(16)–S(2)–Fe(1)	101.2(3)
C(26)–C(27)	152.4(13)	C(16)–S(2)–C(15)	99.3(4)

the starting complex **4** had the '*trans*' configuration and therefore a rearrangement must have occurred by the reduction of **4**.

A comparison of the bond distances in the carbonyl complex [Fe(CO)('N_HS_4')] (**3**), which is isoelectronic to **4**, and **8** shows a dramatic lengthening of the Fe–S(thioether) and Fe–N(amine) distances; they increase from 222.5(3) and 225.1(3) pm in **3** [1] to 230.5(4) and 234.5(3) pm in **8**, and from 207.2(8) pm more than 18 pm up to 225.8(7) pm in **8**. In contrast to these increases, the Fe–S(thiolato) distances cover in both complexes the same range of 227–230 pm, which is typical for these Fe(II)–thiolato complexes [ref. 6a and refs. therein]. The most remarkable property of **8**, however, is undoubtedly the Fe–N–O angle of 147.2(7)°; it characterizes the Fe–NO group in a position halfway between the linear arrangement for the 18 electron [Fe^{II}–NO^+] situation and the 120° angle which is expected for the 20 electron case [Fe^{II}–NO^-] [9]. The NO group is located in the plane going through Fe1 and N2 and bisecting the [S3–Fe1–S4] angle. Interestingly, also the [N2–Fe1–N1] angle is already slightly bent (171.9(3)°). Tentatively, this might be traced back to repulsion between 'lone-pair' electrons at N1 and S2, respectively.

The conversion of linear into bent M–N–O groups has often been invoked for explaining important aspects of metal nitrosyl chemistry as for example the associative (instead of dissociative) substitution of coligands by other Lewis bases [10]. The bending of linear NO groups is probably also one of the elementary steps when ligating NO is reduced to hydroxylamine and finally to ammonia or nitride in the nitrogen cycle [11]. It is generally assumed that in six coordinate 18 electron complexes the basic reason for this bending is the validity of the '18 electron rule' [9b]*. It causes the nineteenth electron to become localized mainly in the lowest unoccupied π^*(NO) orbital, when the 18 electron complex is reduced, e.g. by single electron transfer; this leads to a reduction in the NO bond order which is deduced from the ν(NO) frequency shift of ~300 cm^{-1} and ν(NO) bands of ~1600 cm^{-1} in the reduced species.

19 electron nitrosyl complexes are often too unstable to be isolated** and there are only a very few fully characterized examples as for example [$CpW(NO)_2(PPh_3)$] [13], [$Ru(NO)(bipy)_2Cl$]I [14], [$Ru(NO)(py)_4Cl$]PF_6 [15], [Fe(NO)(*o*-phenylenbisdimethylarsine)Cl]PF_6 [16] and [Fe(NO)(TPP)(4-methylpiperidine)], TPP = tetraphenylporphinato(2–) [17]; only the first and the last one have been structurally characterized showing MNO angles of 168.4(8)° [13] and 143.7° [17], respectively. With respect to the FeNO angles [Fe(NO)(TPP)(4-methylpiperidine)] and **8** compare well and even the Fe–N(O) distances of 174.0(7) and 174.8(8) pm are practically identical. These similarities could signal an equal bonding situation in the Fe–NO entity, but the N–O distances of 111.2(9) pm in the first one and 116.0(9) pm in **8** show that differences exist. Though in both complexes the odd electron might preferably occupy a π^*(NO) orbital, by comparing the 18 electron CO complex **3** and the 19 electron complex **8** it is possible to detect further effects. Thus especially the large increase of the *trans*-Fe–N(H) distance as well as the Fe–S(thioether) distances indicate that the odd electron must reside in an orbital which has also antibonding [Fe'N_HS_4'] character. Moreover, the [S1–Fe–S3] and [S2–Fe–S4] angles of 169.5(1)° and 169.9(1)° show that the Fe atom has moved out of the S_4 plane *ca.* 18 pm in the direction of the NO ligand, *i.e.* the same distance by which the Fe–N(H) distance has in-

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*The situation is different in five coordinate metal nitrosyl complexes with bent MNO groups and formal 16 electron configuration, see ref. 9c.

**Unstable examples are the [$Fe(NO)(CN)_5$]$^{3-}$ [12a] and [$Mo(NO)_2(Me_2dtc)_2$]$^-$ [12b] species.

creased. Pictorially speaking the iron center looks as if it is inflated by the odd electron and since it cannot push away the tightly bound NH donator it must move itself out of the $'N_HS_4'$ cavity.

Further Reactions with Nucleophiles

The formation of the isolable $[Fe(NO)('N_HS_4')]$ suggests that the reduction of 18 electron nitrosyl iron complexes is favoured if sulfur dominates the coordination sphere. Indeed such an easy reduction is also observed with the $[Fe(NO)('S_5')]^+$ complex. Upon addition of N_2H_4 to a blue–green methanol solution of 2, which contains also undissolved 2, $[Fe(NO)('S_5')]$ (9) precipitates immediately as a green voluminous solid.

$$\underset{\mathbf{2}}{[Fe(NO)('S_5')]BF_4} \xrightarrow[20\ ^\circ C/15\ h]{N_2H_4/MeOH} \underset{\mathbf{9}}{[Fe(NO)('S_5')]} + \text{other products} \qquad (9)$$

9 too is paramagnetic ($\mu_{eff} = 2.36$ BM, 295 K), but like 8 it yields a fairly well resolved ^1H NMR spectrum in CD_2Cl_2. Interestingly, in the field desorption mass spectrum not only the M^+ ion at $m/e = 454$, but also ions at 908, 878 and 848, respectively, are observed indicating that the mononuclear 9 possibly dimerizes under certain conditions.

9 forms also by reduction of 2 with azide ions

$$\underset{\mathbf{2}}{[Fe(NO)('S_5')]BF_4} \xrightarrow[15\ h/-30\ ^\circ C]{NEt_4N_3/MeOH} \underset{\mathbf{9}}{[Fe(NO)('S_5')]} + \text{other products} \qquad (10)$$

If 2 is reacted with $NH_2OH{\cdot}HCl$, however, according to eqn. (11) the dinitrosyl species 5 forms

$$\underset{\mathbf{2}}{[Fe(NO)('S_5')]BF_4} \xrightarrow[20\ ^\circ C/3\ d]{NH_2OH\cdot HCl/MeOH} \underset{\mathbf{5}}{[Fe(NO)_2('S_5')]} \qquad (11)$$

These reactions are most plausibly explained by assuming a reduction of $[Fe(NO)('S_5')]BF_4$ as a primary step resulting in the 19 electron species $[Fe(NO)('S_5')]^{\bullet}$. The reducing electrons stem from either reaction (12a), (12b) or (12c).

$$N_2H_4 \longrightarrow N_2 + 4H^+ + 4e^- \qquad (12a)$$

$$N_3^- \longrightarrow 3/2N_2 + e^- \qquad (12b)$$

$$NH_2OH \longrightarrow NO + 3H^+ + 3e^- \qquad (12c)$$

The $[Fe(NO)('S_5')]$ complex can be isolated if no other reactive species are present; in the presence of NO, however, it adds another NO ligand forming the dinitrosyl complex $[Fe(NO)_2('S_5')]$ with $'S_5'^{2-}$ acting as tridentate ligand (Fig. 2). In order to confirm this assumption, 2 was reacted with a typical reducing agent such as $NaBH_4$ (eqn. (13)). As expected a green solid was isolated, which was characterised by its KBr IR spectrum and elemental analysis to be 9.

$$\underset{\mathbf{2}}{[Fe(NO)('S_5')]BF_4} \xrightarrow[-78\ ^\circ C/15\ h]{MeOH/NaBH_4} \underset{\mathbf{9}}{[Fe(NO)('S_5')]} \qquad (13)$$

An unexpected reaction of the nitrosyl complex 2 takes place with PMe_3. While the substitution of CO by PMe_3 in the carbonyl complex 1 needs heating in boiling THF [3], substitution of NO by PMe_3 in 2 occurs at temperatures as low as -20 °C.

$$\underset{\mathbf{2}}{[Fe(NO)('S_5')]BF_4} \xrightarrow[-20\ ^\circ C/15\ h]{MeOH/PMe_3} \underset{\mathbf{10}}{[Fe(NO)(PMe_3)('S_5')]} + \text{other products} \xrightarrow[-NO]{CH_2Cl_2/\text{pentane}} \underset{\mathbf{11}}{[Fe(PMe_3)('S_5')]} \qquad (14)$$

Upon addition of PMe_3 to a blue–green solution of 2 in methanol, which also contains undissolved 2, a brown solid rapidly precipitates; one ν(NO) band at 1710 cm^{-1} and elemental analyses characterize it as the neutral intermediate 10. With respect to 2 the neutral 10 is a reduced species; PMe_3 which was added in excess might have supplied the reducing electrons. Recrystallizing 10 from CH_2Cl_2/pentane leads to brown microcrystals, whose KBr IR spectrum and elemental analysis are compatible with 11 [3].

If PMe_3 is added to a blue–green methanol suspension of 4, the analogous 12 forms

$$\underset{\mathbf{4}}{[\mathrm{Fe(NO)('N_HS_4')]BF_4}} \xrightarrow[-20\ ^\circ\mathrm{C}/5\ \mathrm{h}]{\mathrm{MeOH/PMe_3}}$$

$$\underset{\mathbf{12}}{[\mathrm{Fe(PMe_3)('N_HS_4')}]} + \text{other products} \tag{15}$$

It had been synthesized before by the reaction according to eqn. (16) [1].

$$[\mathrm{Fe(CO)('N_HS_4')}] + \mathrm{PMe_3} \xrightarrow[\text{reflux}]{\mathrm{THF}} \mathbf{12} + \mathrm{CO} \tag{16}$$

The NO ligand, which is usually relatively inert towards substitution is obviously easily substituted in $[\mathrm{Fe(NO)('XS_4')]BF_4}$, (X = S, NH) by the 2 electron donator PMe_3. In order to find a common nominator for all these reactions the surprisingly mild conditions of reactions (14) and (15), respectively, might yield the clue. Taken into consideration that many substitution reactions at carbonyl complexes occur via odd electron, paramagnetic 17 electron or 19 electron species as was shown especially by the studies of J. K. Kochi and coworkers [18], the primary formation of the 19 electron species $[\mathrm{Fe(NO)('XS_4')}]^{\bullet}$ by reduction would plausibly explain the different reaction products. These 19 electron complexes are expected to be labile towards substitution including the X and S donator atoms (which, however, cannot leave the molecule being part of the chelate ligand).

If no other reactive species is present in solution, the 19 electron species can be isolated, as has been proved by the isolation of **8** and **9**; if, however, odd electron molecules such as NO or powerful nucleophiles such as PMe_3 are available, the 19 electron complexes stabilize either by decoordination of X and S donator atoms and addition of another NO giving $[\mathrm{Fe(NO)_2('XS_4')}]$ or by loss of volatile ligands as NO and coordination of PMe_3 giving $[\mathrm{Fe(PMe_3)('XS_4')}]$.

In Table V selected spectroscopic data of the $[\mathrm{Fe(NO)('XS_4')}]^{n+}$ ($n = 0, 1$) complexes are summarized.

Conclusions

The results show that six coordinate Fe^{II} centers surrounded by S_5 or NS_4 donator sets coordinate nitrogen monoxide yielding $[\mathrm{Fe(NO)('XS_4')}]^+$ complexes, X = S, NH. Despite their high ν(NO) frequencies, the NO ligands are not reactive towards nucleophilic attack, neither by N_2H_4, N_3^- or NH_2OH nor PMe_3. It is proved that primary reactions give 19 electron species which can be isolated or lose NO yielding $[\mathrm{Fe(PMe_3)('XS_4')}]$. 19 electron intermediates and the well known lability of 19 electron complexes towards substitution would also explain why the reaction of $[\mathrm{Fe(CO)('XS_4')}]$ or related complexes such as $[\mathrm{Fe(CO)_2('S_4')}]$ with an excess of gaseous nitrogen monoxide results in dinitrosyl species such as $[\mathrm{Fe(NO)_2('XS_4')}]$ or $[\mathrm{Fe(NO)_2('S_4')}]$. If in a primary step NO reduces the 18 electron carbonyl complex to a 19 electron species, decoordination of CO and/or one of the sulfur or X donator atoms

TABLE V. Selected Spectroscopic Data of the Iron Mononitrosyl Complexes[a]

Compound	IR in KBr (cm^{-1})	^1H NMR (ppm)	^{13}C NMR (ppm)	FD-MS [*m*/*e*]
$[\mathrm{Fe(NO)('S_5')]BF_4}$	1870 ν(NO)	7.3–7.6m (C_6H_4) 3.3–4.1m (C_2H_4)	152.40; 132.48; 132.23; 129.48; 128.42; 127.13; (C_6H_4) 52.15; 46.15; (C_2H_4)	454 ($M^+ - BF_4$)
$[\mathrm{Fe(NO)('N_HS_4')]BF_4}$	3160 ν(NH) 1880 ν(NO)	7.1–7.9m (C_6H_4) 6.65 s (NH) 3.0–4.0m (C_2H_4)		407 ($M^+ - BF_4, -NO$)
$[\mathrm{Fe(NO)('S_5')}]$	1645 ν(NO)	7.1–7.6m (C_6H_4) 2.7–3.5m (C_2H_4)		454 (M^+)
$[\mathrm{Fe(NO)('N_HS_4')}]$	3240 ν(NH) 1620 ν(NO)	7.2–7.7m (C_6H_4) 6.88s (NH) 2.8–3.6m (C_2H_4)		437 (M^+)

[a] FD: field desorption; s: singlet; m: multiplet; all NMR spectra were recorded in CD_2Cl_2, relative to TMS.

would be facilitated opening up coordination sites for the ligation of NO and resulting finally again in a 18 electron species. In this respect, these nitrosyl complexes with predominantly thioether and thiolato sulfur atoms in the coordination sphere of the metal show unprecedented reactivity patterns.

Supplementary Material

Further details of the X-ray crystal structure analysis have been deposited and can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2 by citing the deposition no. CSD 53040, the authors and the reference.

Acknowledgements

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