Transition metal complexes with sulfur ligands
Part CII*. Changes in configuration and reactivity caused by alkyl substituents R in [Fe(L)('N$_R$S$_4$')] complexes** (L=CO, NO$^+$, NO, PMe$_3$, N$_2$H$_4$; R=CH$_3$, CH$_2$CH$_2$CO$_2$CH$_3$, CH$_2$CH$_2$CO$_2^-$)†

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Abstract

In search for complexes revealing functional and structural characteristics of the active sites of nitrogenases the iron(II) complexes [Fe(L)('N$_E$S$_4$')] (E=CH$_2$CH$_2$COOCH$_3$; L=CO (**2**), PMe$_3$ (**11**), N$_2$H$_4$ (**9**)) and [Fe('N$_E$S$_4$')]$_x$ (**7**), [Fe(L)('N$_{Me}$S$_4$')] (L=CO (**1**), PMe$_3$ (**10**), N$_2$H$_4$ (**8**), NO (**13**), NO$^+$ (**12**)) and [Fe('N$_{Me}$S$_4$')]$_x$ (**6**), Na[Fe(CO)('N$_A$S$_4$')] (**16**) (A=CH$_2$CH$_2$COO$^-$) and {Na[Fe('N$_A$S$_4$')]}$_x$ (**15**) as well as the free ligands 'N$_E$S$_4$'-H$_2$·HCl (**5**), 'N$_{Me}$S$_4$'-H$_2$·HCl (**4**) and Na$_3$-'N$_A$S$_4$' (**14**) were synthesized. **1** was characterized by X-ray structure analysis. It crystallizes in the space group $P2_1/c$ with $a=753.9(4)$, $b=1283.7(8)$, $c=1931.9(10)$ pm, $\beta=95.86(4)°$, $Z=4$. Unexpectedly, the [Fe(L)('N$_R$S$_4$')] complexes (R=CH$_3$, CH$_2$CH$_2$CO$_2$CH$_3$, CH$_2$CH$_2$CO$_2$Na) show different co-ordination geometries and considerably higher reactivities in comparison to the corresponding [Fe(L)('N$_H$S$_4$')] complexes with the parent ligand 'N$_H$S$_4$'$^{2-}$ (2,2'-bis(2-mercapto-phenylthio)diethylamine(2−)). These differences can be traced back to the fact that the N atom is a tertiary amine in 'N$_R$S$_4$'$^{2-}$ and a secondary amine in the 'N$_H$S$_4$'$^{2-}$ ligand. Repulsive interactions among the three N substituents in the 'N$_R$S$_4$'$^{2-}$ ligands lead to a weakening of the Fe–N bond, to a *meso* configuration of the [Fe('NS$_4$')] core and ultimately to higher reactivities of the [Fe(L)('N$_R$S$_4$')] complexes in comparison to the [Fe(L)('N$_H$S$_4$')] parent compounds. The low-spin complexes [Fe(CO)('N$_{Me}$S$_4$')] (**1**) and [Fe(CO)('N$_H$S$_4$')] (**3**) may serve as examples: [Fe(CO)('N$_H$S$_4$')] (**3**) has C_1 symmetry and a short Fe–N distance (207.2(8) pm), whereas [Fe(CO)('N$_{Me}$S$_4$')] (**1**) reveals C_s symmetry and a long Fe–N bond (218.7(4) pm). Such long Fe–N bonds can only be observed in the parent [Fe(L)('N$_H$S$_4$')] complexes with σ ligands when electrons occupy antibonding σ^* molecular orbitals.

Key words: Crystal structures; Iron complexes; Carbonyl complexes; Nitrosyl complexes; Amine complexes

Introduction

Iron is the dominating metal in the active sites of the three types of nitrogenases known so far, the Fe/Mo [2], Fe/V [3] and Fe/Fe nitrogenases [4]. Analytical and spectroscopic results [5] as well as the X-ray structure analysis of the Fe/Mo nitrogenase of *Azotobacter vinelandii* [6] indicate that the Fe centers in the active sites are surrounded by sulfur donors. There-fore iron complexes which have sulfur coordination spheres and can bind key intermediates of the N$_2$ fixation such as N$_2$, N$_2$H$_2$, N$_2$H$_4$ and NH$_3$ are of interest not only as model compounds for nitrogenases, but also as potential catalysts for a reduction of N$_2$ under mild conditions.

Recently we described a series of complexes containing the [Fe('N$_H$S$_4$')] fragment and ligands such as N$_2$H$_2$, N$_2$H$_4$ and NH$_3$. These complexes demonstrate that key intermediates of the N$_2$ fixation can be co-ordinated to [FeS] centers [7]. The [Fe('N$_H$S$_4$')] fragment exists in the two diastereomeric forms I and II.
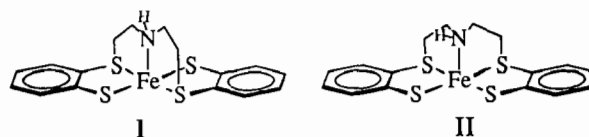
Diastereomeric forms of the [Fe('N$_H$S$_4$')] fragment.

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*For Part CI see ref. 1.

**R=CH$_3$: 'N$_{Me}$S$_4$'$^{2-}$ = 2,2'-bis(2-mercaptophenylthio)diethyl-methylamine(2−); R=CH$_2$CH$_2$CO$_2$CH$_3$: 'N$_E$S$_4$'$^{2-}$ = 3-(N,N-bis-2-(2-mercaptophenylthio)ethylamino)propionicacidmethylester-(2−); R=CH$_2$CH$_2$CO$_2^-$: 'N$_A$S$_4$'$^{3-}$ = 3-(N,N-bis-2-(2-mercapto-phenylthio)ethylamino)propionate(3−).

†Dedicated to Professor Helmut Werner on the occasion of his 60th birthday.

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Coordination of the σ–π ligand N_2H_2 leads to the dinuclear complex [μ-$N_2H_2\{Fe('N_HS_4')\}_2$] containing the enantiomers of the chiral fragment I and diamagnetic low-spin Fe(II) centers. On the contrary, the σ ligands N_2H_4 and NH_3 yield mononuclear complexes with the achiral fragment II and paramagnetic high-spin Fe(II) centers. Coordination of N_2 could not be achieved so far neither with fragment I nor with fragment II.

Therefore, we tried to modify the [Fe('NS$_4$')] core expecting a change in electronic properties of the Fe center by alkyl and alkyl carboxylate substituents being introduced at the amine donor of the 'NS$_4$' ligand so that the coordination of N_2 would become possible. Alkyl carboxylate substituents were expected to lead to water soluble complexes with the ability to form micelles in aqueous solution. Such complexes might also disfavor dimerization of [Fe('N$_R$S$_4$')] fragments and favor coordination of the non-polar N_2 molecules over competing solvent molecules.

Experimental

General

Unless otherwise noted, all synthetic procedures were carried out at ambient temperature under nitrogen atmosphere using Schlenk techniques. Solvents were dried and distilled before use. As far as possible the reactions were monitored by IR spectroscopy. Spectra were recorded on the following instruments. IR (CaF$_2$ cuvettes or KBr discs): Perkin Elmer 983 or Perkin Elmer 1620 FT IR; solvent bands were compensated. NMR: JEOL JNM-PX 60, JNM-GX 270 and JNM-EX 270. Mass spectra: Varian MAT 212. Magnetic susceptibility: Johnson Matthey susceptibility balance. 'S$_2$'-H$_2$ = 1,2-benzenedithiol [8], [Fe(CO)('N$_E$S$_4$')] (E = CH$_2$CH$_2$COOCH$_3$) [9] and PMe$_3$ [10] were prepared by literature methods. NEt$_4$N$_3$ was obtained by reaction of NEt$_4$Cl and NaN$_3$ in MeOH and subsequent recrystallization from acetone, hydrazine by two-fold distillation of $N_2H_4 \cdot H_2O$ from solid KOH [11].

X-ray structure analysis of [Fe(CO)('N$_{Me}$S$_4$')] (1)

Single crystals of [Fe(CO)('N$_{Me}$S$_4$')] (1) were obtained by layering a saturated THF solution with Et$_2$O. A single crystal was sealed in a glass capillary and measured on a Siemens P4 diffractometer. The structure was solved by direct methods (SHELXTL-PLUS). Non-hydrogen atoms were refined with anisotropic, hydrogen atoms with common isotropic temperature factors. The aromatic H atoms were calculated for ideal geometries and restricted during refinement. The aliphatic hydrogen atoms were calculated for ideal tetrahedra and allowed to rotate around the central carbon atom during refinement.

Table 1 summarizes crystallographic data for 1 and Table 2 the fractional atomic coordinates.

Syntheses

[Fe(CO)('N$_{Me}$S$_4$')] (1)

(a) MeN(C$_2$H$_4$Br)$_2 \cdot$ HBr. N-Methyldiethanolamine (28.7 ml, 0.25 mol) and PBr$_3$ (26.2 ml, 0.28 mol) in 80 ml of concentrated hydrobromic acid were heated in a sealed tube for 8 h. The clear brown reaction mixture was evaporated to dryness, the remaining brown oil was dissolved in 100 ml of EtOH, and layered with 100 ml of Et$_2$O. The precipitating white product was filtered off and dried *in vacuo*. Yield 54 g (67%).

(b) [Fe(CO)('N$_{Me}$S$_4$')] (1). 1,2-Benzenedithiol (2.4 ml, 20 mmol) and FeCl$_2 \cdot$ 4H$_2$O (2.0 g, 10 mmol) were added to a solution of sodium (1.6 g, 50 mmol) in 150 ml of MeOH. The resulting black–red solution was saturated with CO. Addition of MeN(C$_2$H$_4$Br)$_2 \cdot$ HBr (3.26 g, 10 mmol) yielded a red–brown solid, which was filtered off after 12 h and washed with MeOH and Et$_2$O. The product was recrystallized at -20 °C from a saturated CH$_2$Cl$_2$ solution layered with Et$_2$O. Yield 3.46 g (77%).

Anal. Calc. for C$_{18}$H$_{19}$FeNOS$_4$ (449.5) = [Fe(CO)-('N$_{Me}$S$_4$')]: C, 48.10; H, 4.26; N, 3.12. Found: C, 48.06; H, 4.26; N, 2.88%.

IR (KBr): ν(CO) = 1937 cm^{-1}. NMR (CD$_2$Cl$_2$, δ (ppm)): ^{1}H NMR (270 MHz): 7.6–6.8 (m, 8H, C$_6$H$_4$),

TABLE 1. Selected crystallographic data of [Fe(CO)('N$_{Me}$S$_4$')] (1)

Formula	C$_{18}$H$_{19}$NS$_4$FeO
Molecular weight	449.4
Crystal size (mm)	$0.4 \times 0.3 \times 0.2$
Crystal system	monoclinic
Space group	$P2_1/c$
Cell dimensions	
a (pm)	753.9(4)
b (pm)	1283.7(8)
c (pm)	1931.9(10)
β (°)	95.86(4)
V (pm^3)	$1859(2) \times 10^6$
Z	4
D_{calc} (g/cm^3)	1.61
μ (cm^{-1})	12.5
Temperature of measurement (K)	293
Diffractometer	Siemens P4
Radiation (Å)	Mo Kα (0.71073)
Scan technique	ω scan
$2\theta_{max}$ (°)	54
Scan speed (°/min)	3–29
Reflections measured	4764
Independent reflections	4088
Observed reflections	2523
σ Criterion	$F > 4\sigma(F)$
Parameters refined	227
R/R_w	0.045/0.036

TABLE 2. Fractional atomic coordinates ($\times 10^2$) and isotropic thermal parameters ($pm^2 \times 10^{-1}$) of the non-hydrogen atoms of [Fe(CO)('$N_{Me}S_4$')] (1)

	x	y	z	U_{eq}[a]
Fe(1)	942(1)	1164(1)	2210(1)	26(1)
C(1)	−1088(6)	1533(3)	1780(2)	32(1)
O(1)	−2405(4)	1780(3)	1479(2)	54(1)
S(1)	2295(2)	2400(1)	1595(1)	40(1)
S(2)	1306(2)	−8(1)	1374(1)	33(1)
S(3)	−302(2)	−16(1)	2871(1)	31(1)
S(4)	649(2)	2401(1)	3043(1)	35(1)
C(15)	2220(6)	713(4)	705(2)	34(2)
C(14)	2425(6)	239(4)	78(2)	42(2)
C(13)	3142(6)	781(5)	−446(3)	51(2)
C(12)	3688(7)	1799(5)	−322(3)	52(2)
C(11)	3455(6)	2284(4)	295(3)	47(2)
C(10)	2690(6)	1761(3)	829(2)	35(2)
C(25)	−803(5)	683(3)	3625(2)	29(1)
C(24)	−1679(6)	169(4)	4129(2)	39(2)
C(23)	−2135(7)	698(4)	4693(3)	47(2)
C(22)	−1695(7)	1750(4)	4781(3)	47(2)
C(21)	−834(6)	2255(4)	4279(2)	42(2)
C(20)	−374(6)	1744(3)	3687(2)	30(1)
C(16)	3274(6)	−700(3)	1745(2)	38(2)
C(17)	4442(6)	16(4)	2198(2)	41(2)
C(26)	1657(6)	−718(3)	3244(2)	38(2)
C(27)	3215(6)	12(4)	3341(2)	44(2)
N(1)	3517(4)	630(3)	2710(2)	33(1)
C(2)	4767(6)	1500(4)	2953(3)	51(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.9–2.3 (m, 8H, C_2H_4), 2.8 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (67.94 MHz): 218 (CO), 158, 134, 132, 130, 129, 122 (C_6H_4), 60, 43 (C_2H_4), 50 (CH_3). FD mass spectrum (THF, m/z): 449 ([Fe(CO)('$N_{Me}S_4$')]$^+$).

'$N_{Me}S_4$'-H_2·HCl (4)

A deep red solution of [Fe(CO)('$N_{Me}S_4$')] (1) (900 mg, 2.0 mmol) in 50 ml of CH_2Cl_2 was refluxed with concentrated hydrochloric acid (0.6 ml, 7.2 mmol) for 2 h. The resulting clear yellowish solution was stirred with anhydrous Na_2SO_4 for 2 h. The Na_2SO_4 was filtered off and the filtrate was evaporated to dryness in vacuo yielding the product as a pink, highly viscous oil, which was not purified further. Yield 670 mg (83%).

Anal. Calc. for $C_{17}H_{22}ClNS_4$ (404.1) = '$N_{Me}S_4$'-H_2·HCl: C, 50.53; H, 5.49; N, 3.47. Found: C, 49.11; H, 5.70; N, 3.16%.

^1H NMR (CDCl$_3$, δ (ppm), 270 MHz): 12.9 (s, H, NH), 7.6–7.1 (m, 8H, C_6H_4), 4.1 (s, 2H, SH), 3.2–3.0 (m, 8H, C_2H_4), 2.6 (s, 3H, CH_3). FD mass spectrum (CH$_2$Cl$_2$, m/z): 368 (['$N_{Me}S_4$'-H_3]$^+$).

[Fe('$N_{Me}S_4$')]$_x$ (6)

A suspension of [Fe(CO)('$N_{Me}S_4$')] (1) (900 mg, 2.0 mmol) in 50 ml of MeOH was refluxed with concentrated

hydrochloric acid (0.6 ml, 7.2 mmol) for 2 h. 390 mg (7.2 mmol) of NaOMe were added to the clear yellowish solution. The resulting greenish yellow precipitate was filtered off, washed with 60 ml of MeOH, and dried in vacuo. Yield 790 mg (93%).

Anal. Calc. for $C_{17}H_{19}FeNS_4$ (421.5) = [Fe('$N_{Me}S_4$')]: C, 48.45; H, 4.54; N, 3.32. Found: C, 48.73; H, 4.56; N, 3.05%.

FD mass spectrum (DMF, m/z): 842 ([Fe-('$N_{Me}S_4$')]$_2^+$), 421 ([Fe('$N_{Me}S_4$')]$^+$).

[Fe(N_2H_4)('$N_{Me}S_4$')] (8)

0.15 ml (4.5 mmol) of hydrazine was added to a green–yellow suspension of [Fe('$N_{Me}S_4$')]$_x$ (6) (420 mg, 1.0 mmol) in 50 ml of THF. The color of the suspension immediately turned light brown. The brown solid was filtered off, washed with 30 ml of THF and dried in vacuo. Yield 365 mg (80%).

Anal. Calc. for $C_{17}H_{23}FeN_3S_4$ (453.5) = [Fe(N_2H_4)-('$N_{Me}S_4$')]: C, 45.03; H, 5.11; N, 9.27. Found: C, 44.49; H, 5.20; N, 9.13%.

IR (KBr): ν(NH) = 3285, 3275, 3225, 3150 cm^{-1}; δ(NH) = 1608, 1596 cm^{-1}. FD mass spectrum (THF, m/z): 453 ([Fe(N_2H_4)('$N_{Me}S_4$')]$^+$).

[Fe(PMe$_3$)('$N_{Me}S_4$')] (10)

0.5 ml (4.74 mmol) of PMe$_3$ was added to a suspension of [Fe('$N_{Me}S_4$')]$_x$ (6) (665 mg, 1.58 mmol) in 50 ml of THF yielding a clear green solution. A green, microcrystalline precipitate formed slowly, was filtered off after 12 h, and dried in vacuo. Yield 535 mg (68%).

Anal. Calc. for $C_{20}H_{28}FeNPS_4$ (497.5) = [Fe(PMe$_3$)-('$N_{Me}S_4$')]: C, 48.28; H, 5.67; N, 2.82. Found: C, 48.49; H, 5.73; N, 2.85%.

IR (KBr): δ(PCH) = 949 cm^{-1}. NMR (CD$_2$Cl$_2$, δ(ppm)): ^1H NMR (270 MHz): 7.7–6.7 (m, 8H, C_6H_4), 2.85–2.1 (m, 8H, C_2H_4), 2.55 (s, 3H, N-CH_3), 0.85 (s, 9H, P-CH_3). $^{13}C\{^1H\}$ NMR (67.94 MHz): 161, 135, 131, 130, 128, 121 (C_6H_4), 61, 45 (C_2H_4), 51 (N-CH_3), 17 (d, P(CH_3)$_3$). FD mass spectrum (THF, m/z): 421 ([Fe(PMe$_3$)('$N_{Me}S_4$')]$^+$).

[Fe(NO)('$N_{Me}S_4$')](BF$_4$) (12)

(a) From [Fe(CO)('$N_{Me}S_4$')] 1 and NOBF$_4$. 140 mg (1.2 mmol) of NOBF$_4$ were added to a solution of [Fe(CO)('$N_{Me}S_4$')] (1) (510 mg, 1.13 mmol) in 40 ml of CH$_2$Cl$_2$ at 0 °C. Evolution of gas could be observed and the deep red solution changed its color over brown to dark green within a few minutes. The reaction mixture was filtered after 1 h and concentrated in vacuo to one half of its original volume. The solution was layered with Et$_2$O and cooled to −30 °C. The precipitated green–brown microcrystals were collected after 12 h and washed with Et$_2$O. When dried in vacuo, they weathered to give a powder. Yield 370 mg (61%).

(b) From [Fe('N$_{Me}$S$_4$')]$_x$ (6) and NOBF$_4$. 120 mg (1.0 mmol) of NOBF$_4$ were added at 0 °C to a suspension of [Fe('N$_{Me}$S$_4$')]$_x$ (6) (420 mg, 1.0 mmol) in 50 ml of CH$_2$Cl$_2$. Within a few minutes a deep green solution formed which was filtered after 1 h. The volume of the filtrate was reduced to one third *in vacuo*, layered with Et$_2$O, and cooled to −30 °C. The precipitating green–brown microcrystals were isolated as described above. Yield 350 mg (65%).

Anal. Calc. for C$_{17}$H$_{19}$BF$_4$FeN$_2$OS$_4$ (538.3) = [Fe(NO)('N$_{Me}$S$_4$')]BF$_4$: C, 37.94; H, 3.56; N, 5.20. Found: C, 38.08; H, 3.63; N, 5.01%.

IR (CH$_2$Cl$_2$): ν(NO) = 1892 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ (ppm), 270 MHz): 7.9–7.25 (m, 8H, C$_6$H$_4$), 3.7–3.4 (m, 8H, C$_2$H$_4$), 3.1 (s, 3H, N-CH$_3$). FD mass spectrum (THF, m/z): 421 ([Fe('N$_{Me}$S$_4$')]$^+$).

[Fe(NO)('N$_{Me}$S$_4$')] (13)

(a) From [Fe(NO)('N$_{Me}$S$_4$')](BF$_4$) (12) and NEt$_4$N$_3$. 280 mg (1.65 mmol) of NEt$_4$N$_3$ were added to a green solution of [Fe(NO)('N$_{Me}$S$_4$')](BF$_4$) (12) (440 mg, 0.82 mmol) in 30 ml of CH$_2$Cl$_2$ at 0 °C. The color of the reaction mixture immediately turned red–brown. The solvent was evaporated *in vacuo* and the remaining green–brown residue was stirred with 50 ml of MeOH for 12 h. The resulting green solid was filtered off, washed with MeOH, and dried *in vacuo*. Yield 175 mg (47%).

(b) From [Fe('N$_{Me}$S$_4$')]$_x$ (6) and NO. 24 ml of NO gas were injected via a septum into a suspension of [Fe('N$_{Me}$S$_4$')]$_x$ (6) (450 mg, 1.07 mmol) in 50 ml of CH$_2$Cl$_2$. The color of the suspension changed from yellow–green to dark green within 5 min. The green solid was filtered off after 12 h and dried *in vacuo*. Yield 245 mg (51%).

Anal. Calc. for C$_{17}$H$_{19}$FeN$_2$OS$_4$ (451.4) = [Fe(NO)-('N$_{Me}$S$_4$')]: C, 45.23; H, 4.24; N, 6.21. Found: C, 45.10; H, 4.32; N, 6.11%.

IR (KBr): ν(NO) = 1640 cm^{-1}. FD mass spectrum (CH$_2$Cl$_2$, m/z): 421 ([Fe('N$_{Me}$S$_4$')]$^+$).

'N$_E$S$_4$'-H$_2$·HCl (5) (E = CH$_2$CH$_2$CO$_2$CH$_3$)

0.98 ml (7.13 mmol) of concentrated hydrochloric acid was added to a red solution of [Fe(CO)('N$_E$S$_4$')] (2) (1.020 g, 1.96 mmol) in 60 ml of CH$_2$Cl$_2$. After 45 min the solution became a yellow suspension. After addition of anhydrous Na$_2$SO$_4$ and stirring for another 2 h, the suspension was filtered. The filtrate was evaporated to dryness and the oily residue was stirred with 20 ml of hexane for 3 h. The resulting colorless oil was collected and dried *in vacuo*. Yield 795 mg (85%).

Anal. Calc. for C$_{20}$H$_{26}$ClNO$_2$S$_4$ (476.2) = 'N$_E$S$_4$'-H$_2$·HCl: C, 50.25; H, 5.64; N, 2.67. Found: C, 50.45; H, 5.50; N, 2.94%.

IR (CH$_2$Cl$_2$): ν(SH) = 2539, ν(NH) = 2173, ν(CO) = 1737 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ (ppm), 270 MHz): 13.0 (s, 1H, NH), 7.4–7.1 (m, 8H, C$_6$H$_4$), 3.6 (s, 3H, CO$_2$CH$_3$), 3.2–3.1 (m, 10H, NCH$_2$CH$_2$S, NCH$_2$CH$_2$CO$_2$CH$_3$), 2.8 (t, 2H, NCH$_2$CH$_2$CO$_2$CH$_3$). FD mass spectrum (CH$_2$Cl$_2$, m/z): 440 (['N$_E$S$_4$'-H$_3$]$^+$).

[Fe('N$_E$S$_4$')]$_x$ (7) (E = CH$_2$CH$_2$CO$_2$CH$_3$)

(a) From 'N$_E$S$_4$'-H$_2$·HCl (5), FeCl$_2$·4H$_2$O and LiOMe. 1.3 ml of a 2 M solution of LiOMe in MeOH (2.6 mmol LiOMe) and 160 mg (0.81 mmol) of FeCl$_2$·4H$_2$O were added to a solution of 'N$_E$S$_4$'-H$_2$·HCl (5) (385 mg, 0.81 mmol) in 20 ml of MeOH. Immediately a red solution formed from which a yellow solid precipitated after 1 min. It was filtered off after 1 h, washed with 10 ml of MeOH and 10 ml of Et$_2$O, and dried *in vacuo*. Yield 270 mg (68%).

(b) From [Fe(CO)('N$_E$S$_4$')] (2). A bright red suspension of [Fe(CO)('N$_E$S$_4$')] (2) (495 mg, 0.95 mmol) and concentrated hydrochloric acid (0.28 ml, 3.38 mmol) in 20 ml of MeOH were refluxed for 30 min. The resulting colorless suspension was cooled to room temperature and 1.8 ml of a 2 M solution of LiOMe in MeOH (3.6 mmol LiOMe) was added. A red solution formed from which a yellow powder precipitated after 1 min. It was filtered off after 1 h, washed with 10 ml of MeOH and 10 ml of Et$_2$O, and dried *in vacuo*. Yield 395 mg (84%).

(c) From [Fe(CO)('N$_E$S$_4$')] (2) by thermal decarbonylation. A deep red solution of [Fe(CO)('N$_E$S$_4$')] (2) (245 mg, 0.47 mmol) in 40 ml of THF was refluxed for 1.5 h yielding a yellow suspension. After cooling to room temperature, the yellow solid was isolated, washed with 10 ml of THF, and dried *in vacuo*. Yield 170 mg (73%).

Anal. Calc. for C$_{20}$H$_{23}$FeNO$_2$S$_4$ (493.6) = [Fe('N$_E$S$_4$')]: C, 48.67; H, 4.70; N, 2.84. Found: C, 48.40; H, 4.79; N, 2.75%.

IR (KBr): ν(CO) = 1735 cm^{-1}. FD mass spectrum (CH$_2$Cl$_2$, m/z): 986 ([Fe('N$_E$S$_4$')]$_2^+$), 493 ([Fe-('N$_E$S$_4$')]$^+$).

[Fe(N$_2$H$_4$)('N$_E$S$_4$')] (9) (E = CH$_2$CH$_2$CO$_2$CH$_3$)

0.1 ml (3 mmol) of N$_2$H$_4$ was added to a suspension of [Fe('N$_E$S$_4$')]$_x$ (7) (650 mg, 0.66 mmol, x = 2) in 40 ml of THF. The color of the reaction mixture turned from yellow to light brown within 20 min. After 1 h, the light brown solid was filtered off, washed with 3 ml of MeOH and 10 ml of Et$_2$O, and dried *in vacuo*. Yield 340 mg (49%).

Anal. Calc. for C$_{20}$H$_{27}$FeN$_3$O$_2$S$_4$ (525.6) = [Fe-(N$_2$H$_4$)('N$_E$S$_4$')]: C, 45.71; H, 5.18; N, 8.00. Found: C, 46.08; H, 5.46; N, 6.76%.

IR (KBr): ν(NH) = 3318, 3292, 3225, ν(CO) = 1731, δ(NH) = 1595, 1584 cm^{-1}. FD mass spectrum (DMSO, m/z): 493 [Fe('N$_E$S$_4$')]$^+$.

[Fe(PMe$_3$)('N$_E$S$_4$')] (11) (E = CH$_2$CH$_2$CO$_2$CH$_3$)

0.13 ml (1.26 mmol) of PMe$_3$ was added to a yellow suspension of [Fe('N$_E$S$_4$')]$_x$ (7) (545 mg, 0.55 mmol, x = 2) in 30 ml of CH$_2$Cl$_2$. A green solution formed immediately which stirred for 1 h, filtered over filter pulp, and evaporated to dryness. The green residue was suspended in 40 ml of MeOH to which 0.05 ml (0.48 mmol) of PMe$_3$ had been added, stirred for 2 h, and recrystallized from CH$_2$Cl$_2$ (25 → −78 °C). Yield 440 mg (70%).

Anal. Calc. for C$_{23}$H$_{32}$FeNO$_2$PS$_4$ (569.6) = [Fe-(PMe$_3$)('N$_E$S$_4$')]: C, 48.50; H 5.66; N, 2.46. Found: C, 48.40; H, 5.78; N, 2.47%.

IR (KBr): ν(CO) = 1725 cm^{-1}, δ(PCH) = 932 cm^{-1}. NMR (CDCl$_3$, δ (ppm)): ^{1}H NMR (270 MHz): 7.5–6.5 (m, 8H, C$_6$H$_4$), 3.7 (m, 2H, NCH$_2$CH$_2$CO$_2$CH$_3$), 3.5 (s, 3H, CO$_2$CH$_3$), 2.9 (m, 2H, NCH$_2$CH$_2$S), 2.7 (m, 2H, NCH$_2$CH$_2$S), 2.3 (m, 4H, NCH$_2$CH$_2$S, NCH$_2$CH$_2$CO$_2$CH$_3$), 2.0 (m, 2H, NCH$_2$CH$_2$S), 0.8 (d, 9H, P(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (67.94 MHz): 173 (NCH$_2$CH$_2$CO$_2$CH$_3$), 157, 135, 131, 130, 127 (C$_6$H$_4$), 57 (NCH$_2$CH$_2$CO$_2$CH$_3$), 56 (NCH$_2$CH$_2$S), 52 (NCH$_2$CH$_2$CO$_2$CH$_3$), 47 (NCH$_2$CH$_2$S), 29 (NCH$_2$CH$_2$-CO$_2$CH$_3$), 15 (d, P(CH$_3$)$_3$). FD mass spectrum (CH$_2$Cl$_2$, m/z): 569 ([Fe(PMe$_3$)('N$_E$S$_4$')]$^+$), 493 ([Fe('N$_E$S$_4$')]$^+$).

Na$_3$-'N$_A$S$_4$' (14) (A = CH$_2$CH$_2$CO$_2^-$)

5.9 ml of a 1 M solution of NaOH in H$_2$O were added to a colorless solution of 700 mg (1.47 mmol) of 'N$_E$S$_4$'-H$_2$·HCl (5) in 4 ml of THF. The solution was evaporated to dryness after 2 h to yield a white mixture of Na$_3$-'N$_A$S$_4$' (14) and NaCl which was not separated.

IR (KBr): ν(CO) = 1562, 1421 cm^{-1}. NMR (D$_2$O, δ (ppm)): ^{1}H NMR (270 MHz): 7.4–6.9 (m, 8H, C$_6$H$_4$), 3.1 (t, 2H, NCH$_2$CH$_2$S), 2.9 (m, 4H, NCH$_2$CH$_2$CO$_2^-$, NCH$_2$CH$_2$S), 2.4 (t, 2H, NCH$_2$CH$_2$CO$_2^-$). ^{13}C{^{1}H} NMR (67.94 MHz): 182 (CO$_2^-$), 145, 138, 135, 125, 124, 123 (C$_6$H$_4$), 52.51, 35, 28 (CH$_2$).

[Na{Fe('N$_A$S$_4$')}]$_x$ (15)

A mixture of Na$_3$-'N$_A$S$_4$' (14) and NaCl (1.47 mmol of Na$_3$-'N$_A$S$_4$') was dissolved in 15 ml of MeOH. Addition of 295 mg (1.47 mmol) of FeCl$_2$·4H$_2$O yielded a red solution from which a yellow powder began precipitating after 10 min. The solid was filtered off after 1 h, washed with 5 ml of MeOH and 5 ml of Et$_2$O, and dried *in vacuo*. Yield 340 mg (48%).

Anal. Calc. for C$_{19}$H$_{23}$FeNNaO$_2$S$_4$ (485.4) = [Na{Fe-('N$_A$S$_4$')}]: C, 45.51; H, 4.02; N, 2.79. Found: C, 45.38; H, 4.21; N, 2.78%.

IR (KBr): ν(CO) = 1567, 1391 cm^{-1}.

Na[Fe(CO)('N$_A$S$_4$')] (16)

CO was bubbled through a yellow suspension of [Na{Fe('N$_A$S$_4$')}]$_x$ (15) (330 mg, 0.34 mmol, x = 2) in 20 ml of MeOH for 30 min. The resulting red solution was filtered, cooled to −20 °C and after 1 day a bright red solid precipitated. It was isolated and recrystallized from 10 ml of MeOH (+25 → −20 °C) yielding bright red, microcrystalline needles, which were washed with 5 ml of Et$_2$O, and dried *in vacuo*. Yield 320 mg (89%).
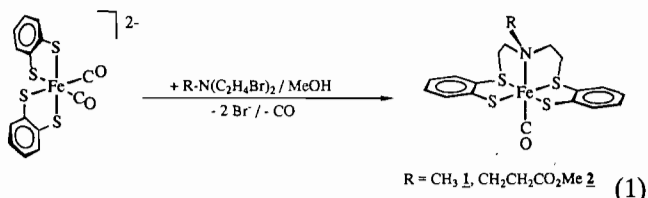
Anal. Calc. for C$_{20}$H$_{20}$FeNNaO$_3$S$_4$ (529.5) = Na[Fe-(CO)('N$_A$S$_4$')]: C, 45.37; H, 4.16; N; 2.34. Found: C, 44.38; H, 4.16; N, 2.34%.

IR (KBr): ν(CO) = 1951, 1568, 1419 cm^{-1}. ^{1}H NMR (CD$_3$OD, δ (ppm), 270 MHz): 7.6–6.9 (m, 8H, C$_6$H$_4$), 4.0–2.4 (m, 12H, CH$_2$).

Results and discussion

Syntheses and reactions

The target 'N$_R$S$_4$'$^{2-}$ ligands were formed by template syntheses according to eqn. (1).

$$R = CH_3 \; \underline{1}, \; CH_2CH_2CO_2Me \; \underline{2} \qquad (1)$$

Alkylation of [Fe(CO)$_2$('S$_2$')$_2$]$^{2-}$ by the respective N-substituted bis(β-bromoethyl)amine derivatives yielded [Fe(CO)('N$_{Me}$S$_4$')] (1) and [Fe(CO)('N$_E$S$_4$')] (2) (E = CH$_2$CH$_2$CO$_2$Me) [9] as red microcrystalline solids. 1 and 2 are well soluble in THF, CH$_2$Cl$_2$, acetone, DMF and DMSO. They show characteristic and strong ν(CO) bands in the IR (KBr) spectra (1: 1940 cm^{-1}, 2: 1965 cm^{-1}); the spectrum of 2 also reveals the characteristic absorption of the ester group at 1735 cm^{-1}. 1 and 2 are diamagnetic and accordingly contain low-spin Fe(II) centers. The ^{13}C NMR spectra of 1 and 2 display only six signals for the twelve aromatic C atoms. This indicates C_s symmetry, i.e. *cis*-coordinated thiolate donors for 1 and 2 as shown in Fig. 1(a). This coordination geometry was confirmed for 1 by X-ray structure analysis. Hence, 1 and 2 characteristically differ from the parent complex [Fe(CO)('N$_H$S$_4$')] (3) which has C_1 symmetry and *trans* thiolate sulfur atoms as shown in Fig. 1(b) [12].

The diamagnetism of 1 and 2, i.e. the presence of low-spin Fe(II) centers, is remarkable. The symmetry of 1 and 2 is remarkable too because the achiral *meso*
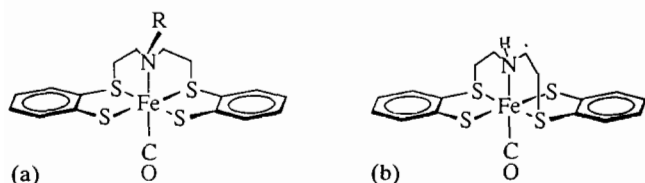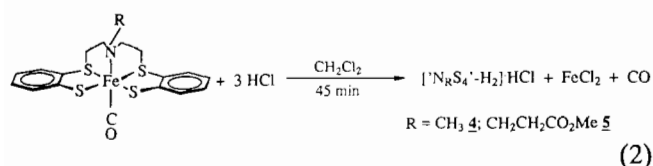
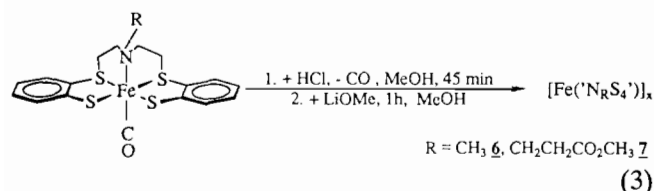Fig. 1. Schematic structures of: (a) **1** (R = Me) and **2** (R = CH₂CH₂CO₂Me); (b) [Fe(CO)('N_HS₄')] (**3**).

structure of the [Fe('NS₄')] core has so far only been observed in high-spin [Fe(L)('N_HS₄')] complexes with hard σ donors like MeOH or NH₃.

As well as the different structures, **1** and **2** also show higher reactivity than the parent complex **3**. While the acid hydrolysis of **3** requires 3 h in boiling CH₂Cl₂ [7a], **1** and **2** hydrolyze in the course of 45 min at room temperature according to eqn. (2).


$$\text{[Fe('NS}_4\text{')]} + 3\,HCl \xrightarrow[\text{45 min}]{CH_2Cl_2} \text{['N}_R S_4\text{'-H}_2] HCl + FeCl_2 + CO$$

R = CH₃ **4**; CH₂CH₂CO₂Me **5**

(2)

The 'N_RS₄'²⁻ ligands were isolated as their ammonium chlorides 'N_MeS₄'-H₂·HCl (**4**) and 'N_ES₄'-H₂·HCl (**5**). **4** and **5** are colorless oils and well soluble in CHCl₃, CH₂Cl₂, THF and acetone.

In order to obtain suitable educts for the synthesis of further [Fe(L)('N_RS₄')] complexes, the CO complexes **1** and **2** were decomposed by acid hydrolysis and the resulting mixtures were subsequently neutralized with equivalent amounts of NaOMe or LiOMe (eqn. (3)).
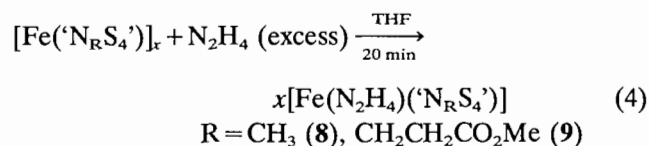

$$\text{[Fe('NS}_4\text{')]} \xrightarrow[\text{2. + LiOMe, 1h, MeOH}]{\text{1. + HCl, - CO , MeOH, 45 min}} \text{[Fe('N}_R S_4\text{')]}_x$$

R = CH₃ **6**, CH₂CH₂CO₂CH₃ **7**

(3)

[Fe('N_MeS₄')]_x (**6**) and [Fe('N_ES₄')]_x (**7**) were isolated as green–yellow solids and characterized by elemental analysis and IR spectroscopy. **6** and **7** are only slightly soluble in DMSO, DMF and CH₂Cl₂ and it could not be established whether they are mononuclear (A, $x = 1$) or dinuclear (B, $x = 2$).
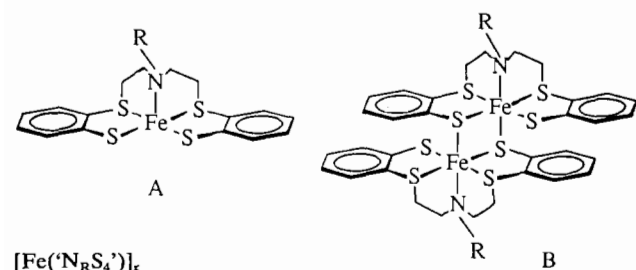
[Fe('N_RS₄')]_x

Low solubility, magnetism, and mass spectra indicate a dinuclear structure according to B. The magnetic moments (**6**: $\mu_{eff} = 4.65$ BM, **7**: $\mu_{eff} = 4.39$ BM, 293 K) are smaller than those which are observed for related mononuclear high-spin [Fe(L)('N_HS₄')] complexes. This could be due to spin coupling of the iron centers via thiolate bridges as, for example, in [Fe('S₂')₂]₂²⁻ [13]. Dinuclear structures are also indicated by mass spectra which always show the signals of [Fe('N_RS₄')]₂⁺ (**6**: $m/z = 841$, **7**: $m/z = 986$) in addition to the mononuclear ions [Fe('N_RS₄')]⁺ (**6**: $m/z = 421$, **7**: $m/z = 493$).
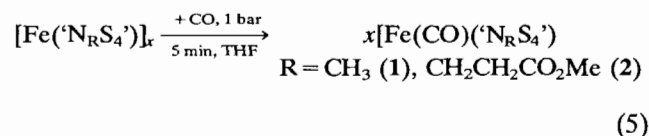
The solvent complexes [Fe(MeOH)('N_RS₄')] which are analogous to the parent complex [Fe(MeOH)-('N_HS₄')] [7a], could not be obtained, the stronger σ ligand N₂H₄, however, formed the hydrazine complexes [Fe(N₂H₄)('N_MeS₄')] (**8**) and [Fe(N₂H₄)('N_ES₄')] (**9**) according to eqn. (4).

$$\text{[Fe('N}_R S_4\text{')]}_x + N_2H_4 \text{ (excess)} \xrightarrow[\text{20 min}]{THF}$$

$$x\text{[Fe(N}_2H_4)\text{('N}_R S_4\text{')]}$$

R = CH₃ (**8**), CH₂CH₂CO₂Me (**9**)

(4)

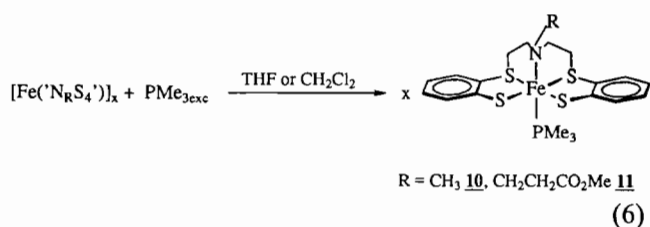**8** and **9** are light brown solids, paramagnetic, and only slightly soluble in DMF, DMSO and CH₂Cl₂. They show strong ν(NH) and δ(NH) bands in their IR (KBr) spectra and the magnetism of [Fe(N₂H₄)('N_ES₄')] (**9**) ($\mu_{eff} = 5.12$ BM, 293 K) corresponds to four unpaired electrons indicating a high-spin Fe(II) center.

8 and **9** were of interest for the syntheses of diazene or dinitrogen complexes [7b, 14]. However, while oxidation of the parent complex [Fe(N₂H₄)('N_HS₄')] yields the dinuclear diazene complex [μ-(N₂H₂){Fe-('N_HS₄')}₂][7b], all attempts to obtain corresponding N₂H₂ or N₂ complexes with [Fe('N_RS₄')] cores were unsuccessful.

Reaction of [Fe('N_MeS₄')]_x (**6**) and [Fe('N_ES₄')]_x (**7**) with CO and PMe₃ rapidly yielded the corresponding diamagnetic 18-electron low-spin complexes. When CO was bubbled through suspensions of **6** or **7** in CH₂Cl₂, deep red solutions of the carbonyl complexes **1** and **2** immediately formed according to eqn. (5).

$$\text{[Fe('N}_R S_4\text{')]}_x \xrightarrow[\text{5 min, THF}]{+ CO, 1 \text{ bar}} x\text{[Fe(CO)('N}_R S_4\text{')]}$$
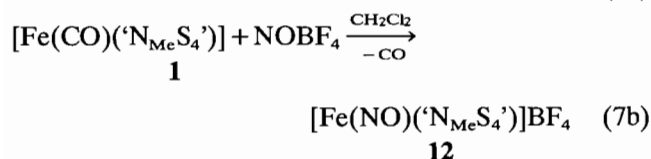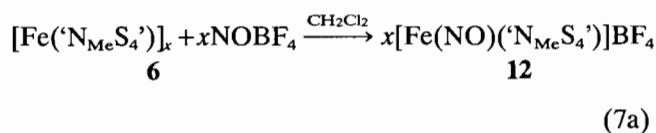
R = CH₃ (**1**), CH₂CH₂CO₂Me (**2**)

(5)

The corresponding PMe₃ complexes [Fe(PMe₃)-('N_MeS₄')] (**10**) and [Fe(PMe₃)('N_ES₄')] (**11**) were isolated as dark green solids with an excess of PMe₃ (eqn. (6)).
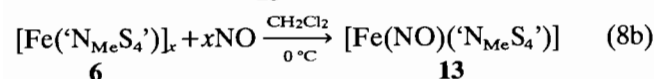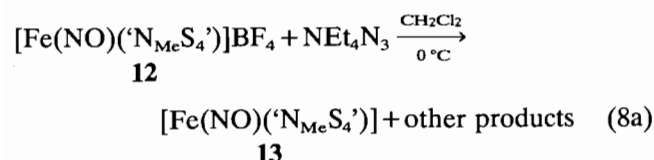
$$[Fe('N_RS_4')]_x + PMe_{3exc} \xrightarrow{\text{THF or } CH_2Cl_2} x \text{ [complex structure]}$$

$$R = CH_3 \; \underline{10}, \; CH_2CH_2CO_2Me \; \underline{11} \tag{6}$$

10 and **11** are well soluble in DMF, DMSO, acetone, THF, CH_2Cl_2 and $CHCl_3$. The IR (KBr) spectra of **10** and **11** show typical 'N_RS_4' bands and strong $\delta(PCH)$ absorptions at 950 cm^{-1}. While **10**, like the analogous parent complex $[Fe(PMe_3)('N_HS_4')]$ [12], is stable in solution, NMR spectra of **11** could only be obtained in the presence of additional PMe_3. Six signals for the twelve aromatic C atoms of **10** and **11** in the ^{13}C NMR spectra again indicate C_s symmetry and *cis* thiolate donors for the $[Fe('NS_4')]$ cores.

With regard to model compounds for nitrogenases, the coordination of the NO^+ cation, being isoelectronic to N_2, was of interest too. The cationic diamagnetic nitrosyl complex $[Fe(NO)('N_{Me}S_4')]BF_4$ (**12**) was formed by reaction of either $[Fe('N_{Me}S_4')]_x$ (**6**) or $[Fe(CO)('N_{Me}S_4')]$ (**1**) with $NOBF_4$ according to eqns. (7a) and (7b). The rapid substitution of CO in **1** by NO^+ under mild conditions might take place according to a previously discussed mechanism via thionitrosylation of a thiolate sulfur atom [15].

$$[Fe('N_{Me}S_4')]_x + xNOBF_4 \xrightarrow{CH_2Cl_2} x[Fe(NO)('N_{Me}S_4')]BF_4$$
$$\underset{\mathbf{6}}{} \qquad\qquad\qquad \underset{\mathbf{12}}{}$$

$$\tag{7a}$$

$$[Fe(CO)('N_{Me}S_4')] + NOBF_4 \xrightarrow[-CO]{CH_2Cl_2}$$
$$\underset{\mathbf{1}}{}$$

$$[Fe(NO)('N_{Me}S_4')]BF_4 \tag{7b}$$
$$\underset{\mathbf{12}}{}$$

The green–brown complex **12** is well soluble in CH_2Cl_2, THF, DMF and DMSO, and displays an intense $\nu(NO)$ absorption at 1890 cm^{-1} in its IR spectrum. Like the parent complex $[Fe(NO)('N_HS_4')]BF_4$ [15], **12** could also be reduced by NEt_4N_3 to the neutral 19-electron nitrosyl complex $[Fe(NO)('N_{Me}S_4')]$ (**13**) according to eqn. (8a). **13** was also formed in the direct reaction of $[Fe('N_{Me}S_4')]_x$ (**6**) with stoichiometric amounts of NO gas (eqn. (8b)).
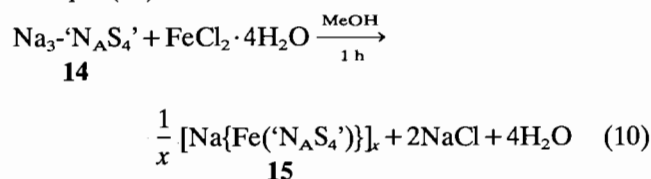
$$[Fe(NO)('N_{Me}S_4')]BF_4 + NEt_4N_3 \xrightarrow[0\,°C]{CH_2Cl_2}$$
$$\underset{\mathbf{12}}{}$$

$$[Fe(NO)('N_{Me}S_4')] + \text{other products} \tag{8a}$$
$$\underset{\mathbf{13}}{}$$

$$[Fe('N_{Me}S_4')]_x + xNO \xrightarrow[0\,°C]{CH_2Cl_2} [Fe(NO)('N_{Me}S_4')] \tag{8b}$$
$$\underset{\mathbf{6}}{} \qquad\qquad\qquad\qquad \underset{\mathbf{13}}{}$$

$[Fe(NO)('N_{Me}S_4')]$ (**13**) was isolated as a green powder and is well soluble in CH_2Cl_2, THF, DMF and DMSO. Its IR (KBr) spectrum shows an intense low frequent $\nu(NO)$ absorption at 1640 cm^{-1}. The magnetism of **13** ($\mu_{eff} = 1.92$ BM, 293 K), indicating one unpaired electron and a 19-electron low-spin configuration of the Fe(II) center, corresponds to the magnetism of the parent complex $[Fe(NO)('N_HS_4')]$ [15]. In contrast to $[Fc(NO)('N_HS_4')]$, however, no highly resolved ^{1}H NMR spectrum of **13** could be obtained in order to establish the achiral C_s or the chiral C_1 symmetry for the $[Fe('N_{Me}S_4')]$ core of **13**. **13** is one of the rare examples of isolable 19-electron complexes formed by one-electron reductions of 18-electron complexes.

Syntheses of complexes which are soluble in water and may potentially form micelles were attempted via saponification of the methyl ester of the 'N_ES_4' ligand in $[Fe(CO)('N_ES_4')]$ (**2**) (E = CH_2CH_2COOMe) with OH^- ions. These experiments, however, led to decomposition of the 'N_ES_4' ligand which might be due to a primary attack of the OH^- ions at the C_2H_4 bridges of the $[Fe('NS_4')]$ backbone. The desired Na_3-'N_AS_4' ligand (**14**) (A = $CH_2CH_2COO^-$) was finally obtained by saponification of the free ligand 'N_ES_4'-$H_2 \cdot HCl$ (**5**) according to eqn. (9).

$$5 + 4NaOH \xrightarrow[2\,h]{THF/H_2O} 14 + NaCl + MeOH \tag{9}$$
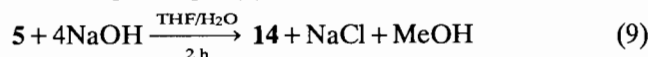
14 yielded the yellow $[Na\{Fe('N_AS_4')\}]_x$ (**15**) according to eqn. (10).

$$Na_3\text{-'}N_AS_4\text{'} + FeCl_2 \cdot 4H_2O \xrightarrow[1\,h]{MeOH}$$
$$\underset{\mathbf{14}}{}$$

$$\frac{1}{x}[Na\{Fe('N_AS_4')\}]_x + 2NaCl + 4H_2O \tag{10}$$
$$\underset{\mathbf{15}}{}$$

15 is only slightly soluble in DMSO, DMF and MeOH, and shows intense carbonyl absorptions at 1565 and 1390 cm^{-1} in its IR (KBr) spectrum. The magnetism of **15** ($\mu_{eff} = 4.32$ BM, 293 K) is consistent with a dinuclear species analogous to **6** and **7**.

15 reacted with CO in MeOH suspensions to form the red $Na[Fe(CO)('N_AS_4')]$ (**16**) immediately (eqn. (11)).

$$[Na\{Fe('N_AS_4')\}]_x \xrightarrow{CO, \; MeOH} x \text{ [complex structure]}$$
$$\underset{\underline{15}}{} \qquad\qquad\qquad\qquad\qquad \underset{\underline{16}}{}$$

$$\tag{11}$$
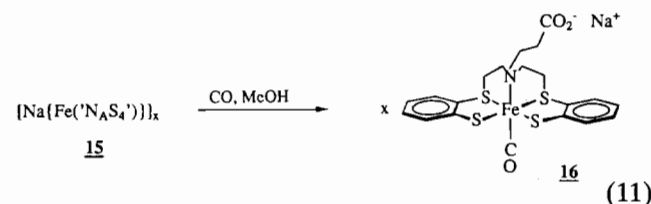
In addition to the $\nu(CO)$ band at 1951 cm^{-1}, **16** displays characteristic carboxylate absorptions at 1570 and 1420

cm^{-1} in its IR (KBr) spectrum. **16** is soluble not only in MeOH, DMSO and DMF, but also in H_2O. Thus it shows the desired water solubility which is due to the insertion of alkyl carboxylate substituents into the [Fe('NS$_4$')] core. However, the formation of micelles in water could not be observed. The separation of hydrophilic carboxylate groups and hydrophobic [Fe(CO)('N$_R$S$_4$')] cores by only two CH_2 groups is obviously insufficiently short.

X-ray structure analysis of [Fe(CO)('N$_{Me}$S$_4$')] (1)

[Fe(CO)('N$_{Me}$S$_4$')] (**1**) was characterized by X-ray structure analysis. Figure 2 shows the molecular structure, and Table 3 lists selected distances and angles. The iron center of **1** is pscudo-octahcdrally surrounded by the amine and sulfur donors of the pentadentate 'N$_{Me}$S$_4$' ligand and the C donor of the CO ligand. The four sulfur donors form a plane, the amine donor and CO occupy *trans* positions. The thiolate sulfur atoms coordinate in *cis* positions such that the [Fe('N$_{Me}$S$_4$')] fragment obtains the *meso* configuration and the complex approximates C_s symmetry.

The X-ray structure analysis confirmed the structure of **1** that had been concluded from the NMR data [12]. Nevertheless, this structure is remarkable in two regards. First, all diamagnetic complexes of the parent ligand 'N$_H$S$_4$'$^{2-}$ have chiral [Fe('N$_H$S$_4$')] fragments with C_1 symmetry, while the *meso* configuration of the

Fig. 2. Molecular structure of [Fe(CO)('N$_{Me}$S$_4$')] (**1**) (H atoms omitted).

TABLE 3. Selected distances (pm) and angles (°) of [Fe(CO)('N$_{Me}$S$_4$')] (**1**)

Fe(1)–C(1)	173.2(4)	C(1)–Fe(1)–S(2)	90.2(2)
Fe(1)–S(1)	228.5(2)	S(1)–Fe(1)–S(2)	89.8(1)
Fe(1)–S(2)	224.5(2)	S(1)–Fe(1)–S(3)	176.7(1)
Fe(1)–S(3)	224.7(2)	C(1)–Fe(1)–N(1)	176.8(2)
Fe(1)–S(4)	228.7(2)	S(1)–Fe(1)–N(1)	91.4(1)
Fe(1)–N(1)	218.7(4)	Fe(1)–C(1)–O(1)	178.1(4)
S(2)–C(15)	178.5(5)	C(17)–N(1)–C(2)	106.2(3)
S(1)–C(19)	174.4(5)	C(27)–N(1)–C(2)	106.4(3)
S(2)–C(16)	181.3(4)	C(17)–N(1)–C(27)	112.4(3)
N(1)–C(17)	149.2(6)	Fe(1)–N(1)–C(17)	109.1(2)

[Fe('NS$_4$')] backbone had so far only been observed in paramagnetic [Fe(L)('N$_H$S$_4$')] complexes. Thus, the substitution of the H atom by a CH_3 group at the amine donor has an unexpectedly strong influence on the configuration of the [Fe('NS$_4$')] core. Secondly, the iron donor distances in **1** show peculiarities in comparison to the distances in low-spin and high-spin [Fe(L)('N$_H$S$_4$')] complexes.

The average Fe–S distances in **1** ($\bar{d}$(Fe–thiolate) = 228.6 pm; $\bar{d}$(Fe–thioether) = 224.6 pm) and in the diamagnetic low-spin and chiral [Fe(CO)('N$_H$S$_4$')] (**3**) complex ($\bar{d}$(Fe–thiolate) = 229.5 pm; $\bar{d}$(Fe–thioether) = 224.4 pm) are approximately identical, but the Fe–N distance of **1** (218.7 pm) is much longer than in **3** (207.2 pm). Such long Fe–N distances of 218 pm were hitherto only found in paramagnetic high-spin [Fe(L)('N$_H$S$_4$')] complexes with *meso* configuration and hard σ ligands L = MeOH, N_2H_4, and NH_3 or in the paramagnetic low-spin complex [Fe(NO)('N$_H$S$_4$')]. This could be explained in terms of the molecular orbital theory by the fact that unpaired electrons occupy antibonding metal ligand σ^* bonds [7a]. Thus, **1** combines structural characteristics which were found in the [Fe(L)('N$_H$S$_4$')] system exclusively either in diamagnetic complexes (short Fe–N and Fe–S distances, chiral [Fe('NS$_4$')] cores) or in paramagnetic complexes (long Fe–N and Fe–S distances, *meso* [Fe('NS$_4$')] cores). This is summarized in Table 4.

Table 4 shows that, with respect to distances, in the two diamagnetic complexes **1** and **3** only the Fe–N distances change. The different configurations and Fe–N distances of **1** and **3** must obviously be due to the different amine donors. **3** has a secondary amine, **1**, however, a tertiary amine donor, which is expected to have different steric properties.

One way to estimate steric properties of ligands is to consider their cone angles which have been evaluated for many monodentate phosphines [16] and recently for amines [17]. Because the amine donors in 'N$_R$S$_4$' ligands are part of a multidentate chelate, however, we prefer the alternative method of discussing the angular sum of the RNR bonds around the amine donors (Table 5). As Table 5 shows, cone angles and angular sums increase with growing substitution of H atoms by alkyl groups. Inconsistencies are also shown: NH$_2$Me and NHMe$_2$ have almost identical angular sums, though their cone angles differ by 13°, N(i-prop)$_3$, however, is planar according to the angular sum, but has a cone angle of 220° which means that it must be pyramidal. According to Table 5, 329 and 333° can be expected for the angular sums and 119 and 132° for the cone angles for the free ligands 'N$_H$S$_4$'-H$_2$ and 'N$_{Me}$S$_4$'-H$_2$.

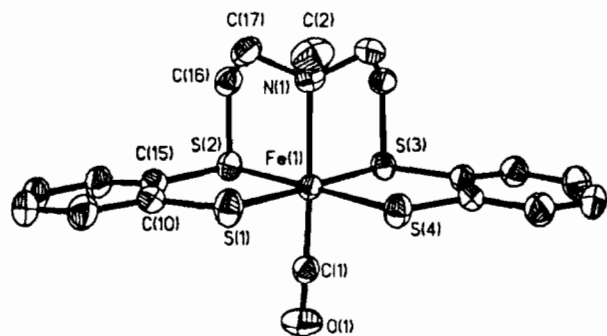The molecular structures of **1** and **3** show that the angular sums around the N donors are distinctly smaller

TABLE 4. Fe donor distances (pm) in [Fe(CO)('N$_H$S$_4$')] [12], [Fe(CO)('N$_{Me}$S$_4$')], [Fe(NO)('N$_H$S$_4$')] [15] and [Fe(MeOH)('N$_H$S$_4$')] [7a]

	d(Fe–N)	$\bar{d}$(Fe–thiolate)	$\bar{d}$(Fe–thioether)
[Fe(CO)('N$_H$S$_4$')] (3) 18 e$^-$, chiral, low-spin	207.2	229.5	224.4
[Fe(CO)('N$_{Me}$S$_4$')] (1) 18 e$^-$, meso, low-spin	218.7	228.4	224.6
[Fe(NO)('N$_H$S$_4$')] 19 e$^-$, meso, low-spin	225.8	228.4	232.3
[Fe(MeOH)('N$_H$S$_4$')] 18 e$^-$, meso, high-spin	220.3	238.5	258.0

TABLE 5. Angular sum (°) of RNR bonds and cone angles (°) of amines (R = H, alkyl)

Compound	Angular sum	Reference	Cone angle [17]
NH$_3$	320.4	18	94
NH$_2$Me	329.9	19	106
NHMe$_2$	329.2	20	119
NMe$_3$	332.7	21	132
N(i-prop)$_3$	357.6	22	220
'N$_H$S$_4$'-H$_2$	329		119^a
'N$_{Me}$S$_4$'-H$_2$	333		132^a
[Fe(CO)('N$_H$S$_4$')] (3)	318.5	12	
Fe(CO)('N$_{Me}$S$_4$') (1)	325.2	this paper	

^{a}Expected values.
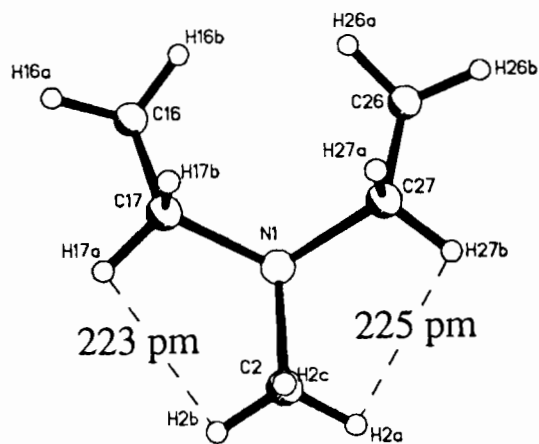
Fig. 3. Overlap of the van der Waals radii of the (CH$_3$)N(C$_2$H$_4$)$_2$ groups in [Fe(CO)('N$_{Me}$S$_4$')] (1).

than in the free ligands. Thus, coordination to the iron centers causes a deformation of the angles. Furthermore it can be noted that this decrease for 'N$_H$S$_4$'-H$_2$ and 3 (10.5°) is larger than for 'N$_{Me}$S$_4$'-H$_2$ and 1 (7.8°). Due to the small steric demand of an H atom in comparison to a CH$_3$ group, 'N$_H$S$_4$'$^{2-}$ is obviously more easily deformed than 'N$_{Me}$S$_4$'$^{2-}$. As a consequence the Fe–N bond in 3 can attain 207.2(8) pm which is close to the typical Fe–N distances in low-spin Fe(II) com-

plexes such as [μ-N$_2$H$_2${Fe('N$_H$S$_4$')}$_2$] (203.7 pm [7b]) or [Fe(TPTCN)](ClO$_4$)$_2$ (200.1 pm, TPTCN = tris(2-pyridylmethyl)-1,4,7-triazacyclononane [23]). In contrast, steric pressure of the three amine alkyl substituents and subsequently reduced capability of deformation prevent the amine donor from getting equally close to the iron center in 1. Thus, the long Fe–N distance in 1 is the result of contrary electronic and steric effects. The former ones favor short, the latter ones, due to the flat NC$_3$ pyramid, long Fe–N distances.

Comparison of 18-electron low-spin [Fe(CO)('N$_H$S$_4$')] (3), 19-electron low-spin [Fe(NO)('N$_H$S$_4$')] and 18-electron high-spin [Fe(MeOH)('N$_H$S$_4$')] furthermore shows that long iron ligand distances favor the meso configuration of the [Fe('NS$_4$')] core in comparison to the chiral configuration [7, 12, 15]. Even in this meso configuration, however, there must still be considerable steric strain in 1. This can be concluded from distances between the methyl and the α-methylene H atoms around the N donor (223 and 225 pm) which are smaller than the sum of the van der Waals radii (240 pm) [24] (Fig. 3).

Thus, [Fe(CO)('N$_{Me}$S$_4$')] (1) does not reach optimal conditions, neither from the electronic nor the steric point of view. As a consequence, it is more reactive than [Fe(CO)('N$_H$S$_4$')] (3).

Conclusions

In the search for model compounds for nitrogenase centers the complexes [Fe(L)('N$_R$S$_4$')] (R = Me, L = CO, NO$^+$, NO, PMe$_3$, N$_2$H$_4$; R = CH$_2$CH$_2$CO$_2$Me, L = CO, PMe$_3$, N$_2$H$_4$; R = CH$_2$CH$_2$CO$_2^-$, L = CO) were synthesized. The substituents R at the amine donor were expected to modify the electronic properties of the metal center and, in some instances, to cause water solubility of the resulting complexes.

[Fe(CO)('N$_{Me}$S$_4$')] (1) had previously been obtained by reaction of [Fe(CO)('N$_H$S$_4$')] (3) with LiN(SiMe$_3$)$_2$ and subsequent alkylation by MeI, but only in low yields [12]. After the unequivocal elucidation of the

molecular structure of **1**, this can now be understood easily. In the course of alkylation, the chiral [Fe('NS$_4$')] core of **3** has to isomerize into the achiral *meso* [Fe('NS$_4$')] core of **1**. This isomerization probably takes place via five-coordinated intermediates, leading to decomposition by side reactions. **3** was now obtained in a more efficient way. Furthermore, the X-ray structure analysis showed a strong elongation of the Fe–N distance in **1** in comparison to the parent complex [Fe(CO)('N$_H$S$_4$')] (**3**). This could be traced back to steric strain caused by the CH$_3$ substituent at the amine donor in the [Fe('NS$_4$')] core. This steric strain also enhances the reactivity of **1**, resulting in, for example, faster hydrolysis reactions and more labile coordination of the coligands L in [Fe(L)('N$_R$S$_4$')] complexes. Accordingly, ligands which are already labile bound in [Fe(L)('N$_H$S$_4$')] do not coordinate any more to [Fe('N$_R$S$_4$')] fragments. [Fe('N$_R$S$_4$')] complexes with alkyl carboxylate substituents at the amine donor show the desired solubility in water, but no tendency to form micelles so far.

In conclusion, substitution of the H atom by alkyl substituents at the amine donor in the 'N$_H$S$_4$'$^{2-}$ ligand changes structures and reactivities of [Fe('N$_R$S$_4$')] complexes in an unexpectedly strong way.

Supplementary material

Further details of the X-ray structure analysis have been deposited and can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-76344 Eggenstein-Leopoldshafen by citing the deposition No. CSD 400231, the authors and reference.

Acknowledgements

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